# Surface Science Division
# Fachverband Oberflächenphysik (O)

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## Overview of Invited Talks and Sessions

(Lecture rooms: MA 001, MA 004, MA 005, MA 041, MA 042, MA 043, MA 141, MA 144, and HE 101; Posters: A and B)

### Invited Talks

| | | | | |
|---|---|---|---|---|
| O 1.1 | Mon | 9:30–10:15 | HE 101 | **The Smallest Surface Adsorbed Magnets** — •Harald Brune |
| O 2.1 | Mon | 10:30–11:00 | MA 004 | **Unusual magnetic properties of Fe and Co atoms on MgO** — •Andreas Heinrich |
| O 2.9 | Mon | 12:45–13:15 | MA 004 | **Interface-induced magnetic skyrmions studied with spin-polarized STM** — •Kirsten von Bergmann |
| O 6.3 | Mon | 11:00–11:30 | MA 043 | **CO oxidation over a Pt/$Fe_3O_4$ model catalyst: Watching Mars van Krevelen at work** — •Gareth Parkinson |
| O 13.1 | Mon | 15:00–15:30 | MA 041 | **Advanced spin-resolved momentum microscopy** — •Christian Tusche |
| O 17.1 | Tue | 9:30–10:15 | HE 101 | **Angle-Resolved Photoemission Spectroscopy (ARPES) and its applications to novel 2D materials** — •Eli Rotenberg |
| O 19.1 | Tue | 10:30–11:00 | MA 004 | **Electronic structure in the vicinity of strong non-adiabatic couplings** — •Eberhard K.U. Gross |
| O 22.1 | Tue | 10:30–11:00 | MA 042 | **Electron dynamics at molecule-semiconductor interfaces** — •Katrin R. Siefermann |
| O 26.1 | Tue | 14:00–14:30 | MA 004 | **First-principles theories of electron-plasmon and electron-spin fluctuation interactions in nanomaterials** — •Johannes Lischner |
| O 42.1 | Wed | 9:30–10:15 | HE 101 | **Understanding organic/inorganic interfaces from first principles** — •Leeor Kronik |
| O 43.1 | Wed | 10:30–11:00 | MA 005 | **Electronic Interactions and Ultrafast Carrier Dynamics at Hybrid Organic / Inorganic Interfaces** — •Oliver L.A. Monti |
| O 47.1 | Wed | 10:30–11:00 | MA 004 | **Transport and excitations in biased nano-junctions: DFT-based simulations** — •Mads Brandbyge |
| O 48.8 | Wed | 12:15–12:45 | MA 041 | **Electronic structure and electron dynamics in two-dimensional materials** — •Philip Hofmann |
| O 54.1 | Wed | 13:15–13:45 | HE 101 | **Porphyrin molecules at interfaces** — •Willi Auwärter |
| O 55.1 | Wed | 15:00–15:30 | HE 101 | **Electronic structure of Organo-Metal Halide Perovskites Films and Interfaces** — •Antoine Kahn |
| O 56.1 | Wed | 15:00–15:30 | MA 004 | **Ultrafast coherent dynamics in photovoltaics** — •Carlo Andrea Rozzi, Sarah Maria Falke, Daniele Brida, Margherita Maiuri, Michele Amato, Ephraim Sommer, Antonietta De Sio, Angel Rubio, Giulio Cerullo, Elisa Molinari, Christoph Lienau |
| O 57.3 | Wed | 15:30–16:00 | MA 005 | **2D silcon materials: From single layer silicene to double-layer structures and multi-layer stacks** — •Patrick Vogt |
| O 76.1 | Thu | 9:30–10:15 | HE 101 | **1D Metal Wires at Surfaces: Preparation, Phase Transitions, and Ultrafast non-Equilibrium Dynamics** — •Michael Horn-von Hoegen |
| O 78.1 | Thu | 10:30–11:00 | MA 004 | **Interaction and Correlation Effects in Quasi Two-dimensional Materials** — •Steven G. Louie |
| O 79.5 | Thu | 11:30–12:00 | HE 101 | **Spin Excitations and Correlations in Individual Molecules on Surfaces** — •Markus Ternes |
| O 85.1 | Thu | 15:00–15:30 | MA 004 | **Natural orbital functional theory with higher-order occupation probabilities** — •Ralph Gebauer, Roberto Car, Morrel Cohen |

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| O 86.1 | Thu | 15:00–15:30 | HE 101 | **On-surface synthesis of molecular and polymeric nanostructures** — •J. Michael Gottfried |
| O 93.1 | Fri | 9:30–10:15 | HE 101 | **Ternary oxides: New surfaces structures and surprising interface properties** — •Wolf Widdra |
| O 96.1 | Fri | 10:30–11:00 | MA 004 | **Ultrafast electron dynamics at oxide surfaces: How metallic is a semiconductor?** — •Julia Stähler |
| O 102.1 | Fri | 13:15–14:00 | HE 101 | **Energiewende: Grenzgänge und Grenzflächen** — •Robert Schlögl |

## Topical Talks

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| O 18.1 | Tue | 10:30–11:00 | HE 101 | **Water adsorption on Ru(0001): A molecular perspective** — •Sabine Maier |
| O 18.4 | Tue | 11:30–12:00 | HE 101 | **Using resonant inelastic soft x-ray scattering maps to study liquids, gases, and their interfaces** — •Lothar Weinhardt |
| O 18.5 | Tue | 12:00–12:30 | HE 101 | **Effect of flow on water organization at solid interfaces** — •Mischa Bonn |
| O 25.1 | Tue | 14:00–14:30 | HE 101 | **First-Principles Microkinetic Modeling at Solid-Liquid Interfaces: First Steps** — •Karsten Reuter |
| O 25.2 | Tue | 14:30–15:00 | HE 101 | **Structure of metal electrode-electrolyte interfaces determined from first principles** — •Axel Gross |
| O 25.3 | Tue | 15:00–15:30 | HE 101 | **Synchrotron x-ray determination of ion distributions at liquid interfaces** — •Jean Daillant |
| O 25.4 | Tue | 15:30–16:00 | HE 101 | **Modelling of electrical double layers at metal oxide electrodes** — •Michiel Sprik, Jun Cheng |
| O 44.2 | Wed | 10:45–11:15 | HE 101 | **Electronic spectroscopy at the solid-liquid interface: a window to electrochemistry and solvation phenomena** — •Miquel Salmeron |
| O 46.1 | Wed | 10:30–11:00 | MA 001 | **Opportunities for THz-pump x-ray-probe experiments at free-electron lasers** — •Wilfried Wurth |
| O 46.2 | Wed | 11:00–11:30 | MA 001 | **Understanding the Ultrafast Insulator-Metal Tranisition in Vanadium Dioxide: An Ultrabroadband Terahertz Perspective** — •Alfred Leitenstorfer, Bernhard Mayer, Alexej Pashkin |
| O 46.3 | Wed | 11:30–12:00 | MA 001 | **Magnetization Dynamics seen via Pump-Probe Holographic X-ray Imaging** — •Stefan Eisebitt |
| O 46.4 | Wed | 12:00–12:30 | MA 001 | **THz induced spin motions probed by x-rays** — •Urs Staub |
| O 77.1 | Thu | 10:30–11:00 | MA 005 | **Photoinduced phase transitions in vanadium dioxide revealed by ultrafast electron diffraction and broadband spectroscopy** — •Bradley Siwick, Vance Morrison, Robert Chatelain, Kunal Tiwari, Ali Hendaoui, Andrew Bruhacs, Mohamed Chaker |
| O 77.2 | Thu | 11:00–11:30 | MA 005 | **Spatial and temporal resolution studies on a highly compact ultrafast electron diffractometer and lattice dynamics in few-layer graphene** — Christian Gerbig, Arne Senftleben, Silvio Morgenstern, Marlene Adrian, Cristian Sarpe, •Thomas Baumert |
| O 84.1 | Thu | 15:00–15:30 | MA 005 | **Femtosecond electron probes for the investigation of structural dynamics and ultrafast currents in nanomaterials** — •Ralph Ernstorfer, Melanie Müller, Lutz Waldecker, Roman Bertoni, Thomas Vasileiadis, Alexander Paarmann |
| O 84.6 | Thu | 16:30–17:00 | MA 005 | **Exploring the Spatial and Temporal Resolution Limits of Ultrafast Electron Microscopy** — •David J. Flannigan, Dayne A. Plemmons, Daniel R. Cremons, David T. Valley |
| O 84.8 | Thu | 17:15–17:45 | MA 005 | **Ultrafast single-electron diffraction and its perspectives** — •Peter Baum |

## Invited talks of the joint symposium SYOP

See SYOP for the full program of the symposium.

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| SYOP 1.1 | Mon | 15:00–15:30 | H 0105 | **Formation mechanisms of covalent nanostructures** — •Jonas Björk |
| SYOP 1.2 | Mon | 15:30–16:00 | H 0105 | **Selective C-H Activation and C-C coupling on Metal Surfaces** — •Lifeng Chi |
| SYOP 1.3 | Mon | 16:00–16:30 | H 0105 | **On-Surface Synthesis on Insulating Substrates** — •Angelika Kuehnle |

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| SYOP 1.4 | Mon | 16:45–17:15 | H 0105 | **On-surface polymerization - a synthetic route to 2D polymers** — •Markus Lackinger |
| SYOP 1.5 | Mon | 17:15–17:45 | H 0105 | **On-surface azide-alkyne click chemistry and a novel metal-organic network based on Cu adatom trimers** — •Trolle Linderoth |

## Invited talks of the joint symposium SYHM

See SYHM for the full program of the symposium.

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| SYHM 1.1 | Wed | 15:00–15:30 | H 0105 | **Amplitude or Higgs Modes in Condensed Matter** — •Chandra Varma |
| SYHM 1.2 | Wed | 15:30–16:00 | H 0105 | **Higgs Particles for Systems with U(1) Symmetry in Two Dimensions** — •Lode Pollet |
| SYHM 1.3 | Wed | 16:00–16:30 | H 0105 | **Massive Photons and the Anderson-Higgs Mechanism in Superconductors** — •Dirk van der Marel |
| SYHM 1.4 | Wed | 16:45–17:15 | H 0105 | **Amplitude Higgs Mode in $2H$-$NbSe_2$ Superconductor** — •Marie-Aude Méasson, Romain Grasset, Yann Gallais, Max Cazayous, Alain Sacuto, Pierre Rodière, Laurent Cario |
| SYHM 1.5 | Wed | 17:15–17:45 | H 0105 | **The Higgs Mode in Disordered Superconductors Close to a Quantum Phase Transition** — •Aviad Frydman, Daniel Sherman, Uwe S. Pracht, Boris Gorshunov, Martin Dressel |

## Invited talks of the joint symposium SYME

See SYME for the full program of the symposium.

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| SYME 1.1 | Fri | 9:30–10:00 | H 0105 | **Excitations and charge transfer phenomena in C based systems** — •Elisa Molinari |
| SYME 1.2 | Fri | 10:00–10:30 | H 0105 | **Towards optimal correlation factors for many-electron perturbation theories** — •Andreas Grüneis |
| SYME 1.3 | Fri | 10:30–11:00 | H 0105 | **Towards an ab-initio description of high temperature superconductivity** — •Garnet Chan |
| SYME 1.4 | Fri | 11:15–11:45 | H 0105 | **Correlation effects in unconventional superconductors: from micro- to nano- and macroscales.** — •Roser Valenti |
| SYME 1.5 | Fri | 11:45–12:15 | H 0105 | **Stochastic density functional and GW theories scaling linearly with system size** — •Roi Baer, Daniel Neuhauser, Eran Rabani |

## Sessions

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|---|---|---|---|---|
| O 1.1–1.1 | Mon | 9:30–10:15 | HE 101 | **Overview Talk (Harald Brune)** |
| O 2.1–2.9 | Mon | 10:30–13:15 | MA 004 | **Surface Magnetism and Spin Phenomena** |
| O 3.1–3.10 | Mon | 10:30–13:00 | MA 005 | **Inorganic/Organic Interfaces: Growth I** |
| O 4.1–4.11 | Mon | 10:30–13:15 | MA 041 | **Electronic Structure of Surfaces I** |
| O 5.1–5.10 | Mon | 10:30–13:00 | MA 042 | **Plasmonics: Nanoantennas, Nanoparticles** |
| O 6.1–6.10 | Mon | 10:30–13:15 | MA 043 | **Catalysis** |
| O 7.1–7.8 | Mon | 9:30–11:30 | ER 270 | **Graphene: THz, NIR and Transport Properties (HL with O/TT)** |
| O 8.1–8.6 | Mon | 9:30–11:00 | ER 164 | **Organic-Inorganic Perovskite Semiconductors (HL with CPP)** |
| O 9.1–9.5 | Mon | 11:45–13:00 | ER 270 | **Transition-Metal Dichalcogenides and Boron Nitride (HL with O/TT)** |
| O 10.1–10.14 | Mon | 15:00–18:30 | HE 101 | **Metal/Water Interfaces: Structure and Reactivity** |
| O 11.1–11.12 | Mon | 15:00–18:00 | MA 004 | **Ultrafast and Nonlinear Plasmonics** |
| O 12.1–12.13 | Mon | 15:00–18:15 | MA 005 | **Inorganic/Organic Interfaces: Growth II** |
| O 13.1–13.12 | Mon | 15:00–18:15 | MA 041 | **Electronic Structure of Surfaces II** |
| O 14.1–14.12 | Mon | 15:00–18:00 | MA 042 | **Oxide Surfaces: Adsorption and Reactivity** |
| O 15.1–15.13 | Mon | 15:00–18:15 | MA 043 | **Scanning Probe Techniques: STM/AFM** |
| O 16.1–16.9 | Mon | 15:00–17:15 | ER 164 | **Graphene: Theory (HL with O/TT)** |
| O 17.1–17.1 | Tue | 9:30–10:15 | HE 101 | **Overview Talk (Eli Rotenberg)** |
| O 18.1–18.5 | Tue | 10:30–12:30 | HE 101 | **Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces I** |

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| O 19.1–19.11 | Tue | 10:30–13:30 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale I** |
| O 20.1–20.11 | Tue | 10:30–13:15 | MA 005 | **Inorganic/Organic Interfaces: Growth III** |
| O 21.1–21.10 | Tue | 10:30–13:00 | MA 041 | **Graphene: Growth & Intercalation** |
| O 22.1–22.9 | Tue | 10:30–13:00 | MA 042 | **Ultrafast Surface Dynamics** |
| O 23.1–23.11 | Tue | 10:30–13:15 | MA 043 | **Plasmonics and Nanooptics: Structure, Fabrication and Characterization** |
| O 24.1–24.11 | Tue | 10:30–13:15 | MA 144 | **Catalysis: Structural Effects** |
| O 25.1–25.4 | Tue | 14:00–16:00 | HE 101 | **Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces II** |
| O 26.1–26.6 | Tue | 14:00–15:45 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale II** |
| O 27.1–27.9 | Tue | 14:00–16:15 | MA 005 | **Nanostructures: Low Dimensions** |
| O 28.1–28.8 | Tue | 14:00–16:00 | MA 041 | **Moire and Graphene Stacking** |
| O 29.1–29.8 | Tue | 14:00–16:00 | MA 042 | **Near-Field Microscopy** |
| O 30.1–30.8 | Tue | 14:00–16:00 | MA 043 | **Inorganic/Organic Interfaces: Towards Application** |
| O 31.1–31.7 | Tue | 14:00–15:45 | MA 144 | **Tribology** |
| O 32.1–32.8 | Tue | 18:15–21:00 | Poster A | **Surface Magnetism and Spin Phenomena** |
| O 33.1–33.20 | Tue | 18:15–21:00 | Poster A | **Graphene** |
| O 34.1–34.11 | Tue | 18:15–21:00 | Poster A | **Metal Substrates: Structure, Epitaxy and Growth** |
| O 35.1–35.18 | Tue | 18:15–21:00 | Poster A | **Nanostructures at Surfaces** |
| O 36.1–36.24 | Tue | 18:15–21:00 | Poster A | **Plasmonics and Nanooptics** |
| O 37.1–37.15 | Tue | 18:15–21:00 | Poster A | **Scanning Probe Techniques** |
| O 38.1–38.9 | Tue | 18:15–21:00 | Poster A | **Semiconductor Substrates** |
| O 39.1–39.7 | Tue | 18:15–21:00 | Poster A | **Heterogeneous Catalysis** |
| O 40.1–40.16 | Tue | 18:15–21:00 | Poster A | **Solid-Liquid Interfaces** |
| O 41.1–41.49 | Tue | 18:15–21:00 | Poster B | **Inorganic/Organic Interfaces** |
| O 42.1–42.1 | Wed | 9:30–10:15 | HE 101 | **Overview Talk (Leeor Kronik)** |
| O 43.1–43.10 | Wed | 10:30–13:15 | MA 005 | **Inorganic/Organic Interfaces: Electronic Properties I** |
| O 44.1–44.3 | Wed | 10:30–11:30 | HE 101 | **Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces III** |
| O 45.1–45.6 | Wed | 11:30–13:00 | HE 101 | **Nonaqueous Liquid/Solid Interfaces** |
| O 46.1–46.4 | Wed | 10:30–12:30 | MA 001 | **Focus Session: THz meets X-ray** |
| O 47.1–47.11 | Wed | 10:30–13:30 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale III** |
| O 48.1–48.9 | Wed | 10:30–13:00 | MA 041 | **Graphene: Dynamics** |
| O 49.1–49.9 | Wed | 10:30–12:45 | MA 042 | **Metal Substrates: Structure, Epitaxy and Growth** |
| O 50.1–50.10 | Wed | 10:30–13:00 | MA 043 | **Coupled Nanostructures and Light Localization** |
| O 51.1–51.8 | Wed | 9:30–11:30 | ER 270 | **Topological Insulators: Theory (HL with DS/MA/O/TT)** |
| O 52.1–52.6 | Wed | 11:00–13:00 | EW 201 | **Focus Session: Nanophotonic Concepts and Materials for Energy Harvesting - Plasmonics, Transformation Optics, Upconversion, and beyond** |
| O 53.1–53.5 | Wed | 11:45–13:00 | ER 270 | **Topological Insulators: Transport (HL with DS/MA/O/TT)** |
| O 54.1–54.1 | Wed | 13:15–13:45 | HE 101 | **Gaede Prize Talk** |
| O 55.1–55.12 | Wed | 15:00–18:15 | HE 101 | **Inorganic/Organic Interfaces: Electronic Properties II** |
| O 56.1–56.13 | Wed | 15:00–18:30 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale IV** |
| O 57.1–57.10 | Wed | 15:00–17:45 | MA 005 | **2D Materials beyond Graphene: TMDCs, Slicene and Relatives** |
| O 58.1–58.12 | Wed | 15:00–18:00 | MA 041 | **Electronic Structure of Surfaces II** |
| O 59.1–59.13 | Wed | 15:00–18:15 | MA 042 | **Oxide and Insulator Surfaces: Structure, Epitaxy and Growth** |
| O 60.1–60.12 | Wed | 15:00–18:00 | MA 043 | **Dielectric and Molecular/Water Interfaces** |
| O 61.1–61.6 | Wed | 15:00–16:30 | ER 270 | **Topological Insulators: Structure and Electronic Structure (HL with DS/MA/O/TT)** |
| O 62.1–62.8 | Wed | 16:45–18:45 | ER 270 | **Graphene: Applications, Luminescence and Spin Relaxation (HL with O/TT)** |
| O 63.1–63.5 | Wed | 18:15–21:00 | Poster A | **2D Materials beyond Graphene** |
| O 64.1–64.7 | Wed | 18:15–21:00 | Poster A | **New Methods** |
| O 65.1–65.10 | Wed | 18:15–21:00 | Poster A | **Oxides and Insulators** |
| O 66.1–66.17 | Wed | 18:15–21:00 | Poster A | **Electronic Structure of Surfaces** |
| O 67.1–67.7 | Wed | 18:15–21:00 | Poster A | **Electronic Structure Theory: General, Method Development** |

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| O 68.1–68.10 | Wed | 18:15–21:00 | Poster A | **Electronic Structure Theory: Many-Body Effects** |
| O 69.1–69.10 | Wed | 18:15–21:00 | Poster A | **Ultrafast Electron and Spin Dynamics** |
| O 70.1–70.18 | Wed | 18:15–21:00 | Poster A | **Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses** |
| O 71.1–71.5 | Wed | 18:15–21:00 | Poster A | **Surface Dynamics** |
| O 72.1–72.7 | Wed | 18:15–21:00 | Poster A | **Graphene: Adsorption, Intercalation and Doping** |
| O 73.1–73.10 | Wed | 18:15–21:00 | Poster A | **Nanostructures at Surfaces: 1D and 2D Structures** |
| O 74.1–74.6 | Wed | 18:15–21:00 | Poster A | **Oxide and Insulator Surfaces** |
| O 75.1–75.15 | Wed | 18:15–21:00 | Poster A | **Plasmonics and Nanooptics** |
| O 76.1–76.1 | Thu | 9:30–10:15 | HE 101 | **Overview Talk (Michael Horn-von Hoegen)** |
| O 77.1–77.8 | Thu | 10:30–13:15 | MA 005 | **Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses** |
| O 78.1–78.10 | Thu | 10:30–13:15 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale V** |
| O 79.1–79.9 | Thu | 10:30–13:00 | HE 101 | **Scanning Probe Techniques: STM** |
| O 80.1–80.10 | Thu | 10:30–13:00 | MA 041 | **Graphene: Structure** |
| O 81.1–81.5 | Thu | 10:30–13:00 | MA 042 | **Gerhard Ertl Young Investigator Award** |
| O 82.1–82.12 | Thu | 10:30–13:30 | MA 043 | **Nanostructure at Surfaces: Dots and Clusters** |
| O 83.1–83.12 | Thu | 10:30–13:30 | MA 144 | **Surface Chemistry and Growth** |
| O 84.1–84.10 | Thu | 15:00–18:15 | MA 005 | **Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses** |
| O 85.1–85.13 | Thu | 15:00–18:30 | MA 004 | **Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale VI** |
| O 86.1–86.10 | Thu | 15:00–17:45 | HE 101 | **Nanostructure at Surfaces: Molecular Assembly** |
| O 87.1–87.13 | Thu | 15:00–18:15 | MA 041 | **Graphene: Electronic Structure** |
| O 88.1–88.13 | Thu | 15:00–18:15 | MA 042 | **Electronic Structure: Surface Magnetism and Spin Phenomena** |
| O 89.1–89.14 | Thu | 15:00–18:30 | MA 043 | **Inorganic/Organic Interfaces: Molecular Switches** |
| O 90.1–90.14 | Thu | 15:00–18:30 | MA 144 | **Sensing, Active Structures and other Applications** |
| O 91 | Thu | 19:00–19:30 | HE 101 | **Annual General Meeting of the Surface Science Division** |
| O 92 | Thu | 19:30–20:30 | HE 101 | **Post-Deadline Session** |
| O 93.1–93.1 | Fri | 9:30–10:15 | HE 101 | **Overview Talk (Wolf Widdra)** |
| O 94.1–94.5 | Fri | 9:30–12:15 | H 0105 | **Frontiers of Electronic Structure Theory: Many-body Effects on the Nano-scale** |
| O 95.1–95.13 | Fri | 9:30–13:15 | H 2032 | **Metallic nanowires on the atomic scale (DS with O)** |
| O 96.1–96.8 | Fri | 10:30–12:45 | MA 004 | **Ultrafast Electron Dynamics at Surfaces and Interfaces** |
| O 97.1–97.9 | Fri | 10:30–12:45 | MA 005 | **Nanostructure at Surfaces: Structures and Properties** |
| O 98.1–98.9 | Fri | 10:30–12:45 | MA 041 | **Graphene: Intercalation** |
| O 99.1–99.9 | Fri | 10:30–12:45 | MA 042 | **Semiconductor Substrates: Structure, Epitaxy and Growth** |
| O 100.1–100.10 | Fri | 10:30–13:00 | MA 043 | **Metal Substrates: Adsorption and Reactivity** |
| O 101.1–101.9 | Fri | 10:30–12:45 | MA 144 | **Scanning Probe Techniques: AFM** |
| O 102.1–102.1 | Fri | 13:15–14:00 | HE 101 | **Overview Talk (Robert Schlögl)** |

## Annual General Meeting of the Surface Science Division

Thursday 19:00–19:30 HE 101

- Report of the Chairman
- Presentation of the Gerhard Ertl Young Investigator Award
- Miscellaneous

# O 1: Overview Talk (Harald Brune)

Time: Monday 9:30–10:15 Location: HE 101

**Invited Talk** O 1.1 Mon 9:30 HE 101

**The Smallest Surface Adsorbed Magnets** — •Harald Brune — Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Making magnets smaller increases thermal fluctuations of the magnetization direction, magnetization reversal by tunneling and by electron scattering. For magnetic storage, the spin relaxation time has to be high, and for quantum computing the spin coherence time. We review the state-of-the art in small surface adsorbed magnets. The ultimate question is, can a single atom be a magnet in the sense that it exhibits remanence or a significant spin coherence time ?

The currently smallest anti-ferromagnets are composed of 12 Fe atoms adsorbed on $Cu_2N$/Cu(100) [1], and the smallest ferromagnets consist of only 5 Fe atoms on Cu(111) [2]. We find exceptionally large magnetic anisotropy energies for single surface adsorbed atoms of $3d$ elements, with Co on MgO(100) being the record [3]. Nevertheless, these atoms are paramagnetic. $4f$ elements have higher spin-orbit coupling and the potential of magnetic stability. Using X-ray magnetic circular dichroism, we find for Ho and Er on close-packed Pt and Cu surfaces magnetic ground states that are not compatible with long spin coherence times [4]. We show other systems that are more promising for the realization of single atom magnets.

[1] S. Loth *et al.*, Science **335**, 196 (2012); [2] A. A. Khajetoorians *et al.*, Science **339**, 55 (2013); I. G. Rau *et al.*, Science **344**, 988 (2014); F. Donati *et al.*, PRL **113**, 237201 (2014).

# O 2: Surface Magnetism and Spin Phenomena

Time: Monday 10:30–13:15 Location: MA 004

**Invited Talk** O 2.1 Mon 10:30 MA 004

**Unusual magnetic properties of Fe and Co atoms on MgO** — •Andreas Heinrich — IBM Research, San Jose, USA

The ability to control the magnetic properties of nanoscale systems will open novel avenues for spintronics, magnetic memory devices, and quantum computation. Key among those properties is the magnetic anisotropy, which governs the stability and directionality of their magnetization.

I will present scanning tunneling and x-ray absorption spectroscopy measurements of Co and Fe atoms deposited on thin MgO layers. Both species retain most of their free atom orbital moment and interact strongly with the crystal field of their binding site. In the case of Co, the almost cylindrical symmetry of the binding site preserves the full orbital angular momentum around the surface normal and leads to the maximum magnetic anisotropy for 3d transition metal atoms. On the other hand, Fe responds to the four-fold perturbation of the binding site and hence has much smaller magnetic anisotropy.

Spin-polarized tunneling measurements reveal relatively stable magnetic ground states for Fe and Co with long spin relaxation times (ms range) for the excited state with opposite magnetic moment.

These results offer a strategy, based on symmetry arguments and careful tailoring of the interaction with the environment, for the rational design of nanoscopic permanent magnets and single atom magnets.

O 2.2 Mon 11:00 MA 004

**Chiral magnetism in nanostructures of adatoms on Au(111) surface** — •Juba Bouaziz, Stefan Blügel, and Samir Lounis — Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

We investigate possible chiral magnetic textures in superstructures made of $3d$ adatoms interacting via the Rashba spin-splitted surface state of Au(111) surface. We utilize multiple-scattering theory based on the Rashba model [1] to describe the related electronic structure and perform a mapping to an extended Heisenberg model and extract the tensor of magnetic exchange interactions among the adatoms. We find different type of interactions that can be of the same order of magnitude: a two-ion anisotropy term besides the usual isotropic exchange interaction and the Dzyaloshinskii-Moriya interaction. The inter-adatom distance controls the strength of these terms, which we exploit to design chiral magnetism for large nanostructures containing up to 169 adatoms deposited on Au(111) surface. Depending on the rim-decoration of the nanostructures, different chiral structures of skyrmionic type are obtained. Also different applied magnetic fields are considered while the evolution of the total energy and the topological charge of the nanoclusters are scrutinized.

[1] S. Lounis *et al.* Phys. Rev. Lett. **108**, 207202 (2012)

This work is supported by the HGF-YIG Programme VH-NG-717 (Functional Nanoscale Structure and Probe Simulation Laboratory – Funsilab).

O 2.3 Mon 11:15 MA 004

**Conduction-electron mediated Dzyaloshinskii-Moriya interactions between adatoms revealed by ISTS** — Alexander A. Khajetoorians[1,2], Manuel Steinbrecher[1], Mohammed Bouhassoune[3], Manuel dos Santos Dias[3], Samir Lounis[3], Markus Ternes[4], •Jens Wiebe[1], and Roland Wiesendanger[1] — [1]Institut für Nanostruktur- und Festkörperphysik, Universität Hamburg, 20355 Hamburg, Germany — [2]Institute for Molecules and Materials, Radboud University, 6525 AJ Nijmegen, The Netherlands — [3]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — [4]Max-Planck Institut für Festkörperphysik, 70569 Stuttgart, Germany

It is known since more than three decades that anisotropic exchange between magnetic impurities mediated via strong spin-orbit scattering of conduction electrons by nonmagnetic host atoms leads to a term in the RKKY interaction which is of the Dzyaloshinskii-Moriya (DM) type [1,2]. We report the first direct experimental distance-dependency study of this interaction in pairs of an Fe-$H_2$ Kondo-complex and an Fe atom adsorbed on Pt(111) by inelastic scanning tunneling spectroscopy (ISTS) showing that the DM exchange is of similar strength as the isotropic exchange. The data is analysed by a model including the coupling to the substrate electrons in third order perturbation theory [3] and is affirmed by our first-principles calculations using the KKR method [4]. [1] A. Fert *et al.*, PRL **44**, 1538 (1980); [2] S. Lounis *et al.*, PRL **108**, 207202 (2012); [3] Y.-H. Zhang *et al.*, Nat. Comm. **4**, 127203 (2013); [4] L. Zhou *et al.*, Nat. Phys. **6**, 187 (2010).

O 2.4 Mon 11:30 MA 004

**Magnetotransport at surfaces of epitaxially grown Bi and BiSb thin films** — •Philipp Kröger[1], Julian Koch[1], Sergii Sologub[2], Herbert Pfnür[1], and Christoph Tegenkamp[1] — [1]Leibniz Universität Hannover, Festkörperphysik, 30167 Hannover — [2]Inst. of Physics, Nat. Acad. of Sc., Nauky Av. 46, 03028 Kyiv, Ukraine

Bi has unique electronic properties such as low carrier concentrations, large mobilities and pronounced Rashba splitting of the surface states. We investigated the manipulation of spin-polarized transport properties in Bi(111) films by controlled adsorption of magnetic adatoms (Fe,Co,Tb,Cr). Besides pronounced effects of charge carrier doping and surface diffusion the spin-orbit scattering rate ($1/\tau_{SO}$) can be tuned by the amount and type of the adsorbate giving rise to weak anti- / weak- localization transitions. To enhance the spin polarization, $Bi_{1-x}Sb_x$ alloys were grown which exhibit a topological non-trivial phase for certain concentrations x. Magnetotransport measurements of a 30 BL $Bi_{0.82}Sb_{0.18}$ film on Si(111) reveals weak anti localization behavior. Compared to Bi(111) films the $\tau_{SO}$ is increased by one order of magnitude reflecting the strong spin-orbit coupling in this system with carrier concentrations of $n = 1 \cdot 10^{13} cm^{-2}$ and $p = 2 \cdot 10^{13} cm^{-2}$. The corresponding mobilities amounts to $\mu_n = 260\ cm^2(Vs)^{-1}$ and $\mu_p = 190\ cm^2(Vs)^{-1}$. By adsorption of Cr (4,8 $\mu_B$) we got a first insight into the spin dependent scattering processes in this class of material.

O 2.5 Mon 11:45 MA 004

**Ballistic Anisotropic Magnetoresistance of Single-Atom Contacts** — •Johannes Schöneberg[1], Fabian Otte[2], Nicolas Néel[3], Alexander Weismann[1], Yuriy Mokrousov[4], Jörg Kröger[3], Richard Berndt[1], and Stefan Heinze[2] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — [2]Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — [3]Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany — [4]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

Junctions involving a non-magnetic and a single ferromagnetic layer may exhibit anisotropic magnetoresistance (AMR), i. e., their resistances depend on the magnetization direction relative to the crystallographic axes via spin-orbit coupling. Large AMR effects were predicted for the ballistic transport range but their experimental verification is challenging. We deposited single Co and Ir atoms on domains and domain walls of ferromagnetic Fe layers on W(110) to control their magnetization directions. At a temperature of 5 K they are contacted with nonmagnetic tips in a scanning tunneling microscope to measure the junction conductances. AMR is observed and changes drastically between tunneling and the ballistic regime. First-principles calculations demonstrate that this change is due to a competition of delocalized and localized d states of different orbital symmetry.

O 2.6 Mon 12:00 MA 004

**ISTS of Ho atoms and Ho-Fe atom pairs on Pt(111) in the RKKY-coupling regime** — •Manuel Steinbrecher[1], Andreas Sonntag[1], Manuel dos Santos Dias[2], Mohammed Bouhassoune[2], Samir Lounis[2], Jens Wiebe[1], Roland Wiesendanger[1], and Alexander Ako Khajetoorians[1,3] — [1]INF, Hamburg University, 20355 Hamburg, Germany — [2]PGI-1 and IAS-1, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — [3]IMM, Radboud University, 6525 AJ Nijmegen, The Netherlands

Rare-earth atoms which are adsorbed on surfaces [1] or introduced as metal centers into molecules [2] are regarded as promising quantum-bit candidates due to the strong localization of their $4f$-electrons. For the same reason, an electrical read-out of the rare-earth bit's magnetic state and the coupling of two bits is more challenging than for $3d$ atoms, where a read-out via inelastic scanning tunneling spectroscopy (ISTS) and coupling via RKKY-interaction has been unambiguously demonstrated [3, 4]. Here, we show magnetic field dependent ISTS at 300 mK on individual Ho adatoms and Ho-Fe pairs on Pt(111) with distances in the RKKY regime. In conflict with [1] there are no signatures of spin-excitations on Ho in the tunneling regime, and the RKKY-coupling strength is below our thermal energy resolution. These results are supported by our *ab-initio* calculations which show that RKKY interaction of Ho via the Pt(111) conduction electrons is very weak. [1] Miyamachi *et al.*, Nature **503**, 242 (2013); [2] Fahrendorf *et al.*, Nat. Comm. **4**, 2425 (2014); [3] Khajetoorians *et al.*, PRL **106**, 037205 (2012); [4] Khajetoorians *et al.*, Nat. Phys. **8**, 497 (2012).

O 2.7 Mon 12:15 MA 004

**Room-temperature magnetic ordering of an Eu monolayer under graphene on Ni and Co thin films** — •Felix Huttmann[1], David Klar[2], Carolin Schmitz-Antoniak[2], Antonio J. Martínez-Galera[1], Alevtina Smekhova[2], Nicolae Atodiresei[3], Vasile Caciuc[3], Stefan Blügel[3], Heiko Wende[2], and Thomas Michely[1] — [1]II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany — [2]Fakultät für Physik and Center for Nanointegration (CENIDE), Universität Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany — [3]Peter Grünberg Institut (PGI) and Institute for Advanced Simulation (IAS), Forschungszentrum Jülich, 52425 Jülich, Germany

We expose epitaxial graphene on ferromagnetic thin films of Co and Ni to vapor of the rare earth metal Eu at elevated temperatures, resulting in the intercalation of an Eu monolayer in between graphene and its substrate. The Eu monolayer forms a $(\sqrt{3}\times\sqrt{3})\mathrm{R}30^\circ$ superstructure with respect to the graphene lattice irrespective of any epitaxial rotation of graphene with respect to its Co or Ni substrate. We use X-ray magnetic circular dichroism at the Co and Ni $\mathrm{L}_{2,3}$, Eu $\mathrm{M}_{4,5}$, and C K edges as an element-specific technique to investigate magnetism in these systems. We find an antiferromagnetic alignment between Eu and Co/Ni moments, while for C, a dichroic signal is not unambiguously identified. Density functional theory calculations confirm the antiferromagnetic coupling and provide an insight into the coupling mechanism.

O 2.8 Mon 12:30 MA 004

**ISTS of Fe adatoms in contact to superconducting Ta** — •Anand Kamlapure[1], Lasse Cornils[1], Lihui Zhou[1,2], Alexander A. Khajetoorians[1,3], Jens Wiebe[1], and Roland Wiesendanger[1] — [1]Department of Physics, Hamburg University, Hamburg, Germany — [2]Max-Planck Institute for Solid State-Research, Stuttgart, Germany — [3]Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Recent local scale investigations of the competition of superconductivity and magnetism in molecular systems revealed rich physics associated with a quantum phase transition [1]. Here, we experimentally study individual Fe atoms adsorbed on a reconstructed surface of superconducting Ta by inelastic scanning tunneling spectroscopy (ISTS) at a temperature of 1 K and as a function of magnetic field of strength up to 3 T perpendicular to the surface. We observe strong inelastic excitations at three different adsorption sites of the Fe adatoms. The majority site shows a sharp step around 2 meV which is almost independent of the magnetic field. The other two sites exhibit excitations around 1 meV and 4 meV which have a weak magnetic field dependence indicating the magnetic origin of this excitation. In all three cases the superconducting energy gap and coherence peaks are preserved at zero magnetic field indicating very weak coupling between the magnetic moment and the cooper pairs. [1] K. J. Franke *et al.*, Science **332**, 940 (2011).

**Invited Talk** O 2.9 Mon 12:45 MA 004

**Interface-induced magnetic skyrmions studied with spin-polarized STM** — •Kirsten von Bergmann — Department of Physics, University of Hamburg, Germany

The spin textures of ultra-thin magnetic layers exhibit surprising variety. The loss of inversion symmetry at the interface of magnetic layer and substrate gives rise to the so-called Dzyaloshinsky-Moriya interaction which favors non-collinear spin arrangements with unique rotational sense [1]. An ideal tool to investigate such systems down to the atomic scale is spin-polarized scanning tunneling microscopy, which has enabled the discovery of spin spirals with unique rotational sense at surfaces [2]. Recently, different interface-driven skyrmion lattices have been found [3,4], which can be viewed as a two-dimensional analogon to spin spirals. Depending on the involved magnetic interactions single particle-like skyrmions can be realized and their writing as well as the deletion based on local spin-polarized current injection has been demonstrated [4]. Such interface-induced non-collinear magnetic states enable the study of fundamental magnetic interactions and are promising candidates for future spintronic applications.

[1] K. von Bergmann et al., J. Phys.: Cond. Mat. 26, 394002 (2014).
[2] M. Bode et al., Nature 447, 190 (2007).
[3] S. Heinze et al., Nature Phys. 7, 713 (2011).
[4] N. Romming et al., Science 341, 636 (2013).

# O 3: Inorganic/Organic Interfaces: Growth I

Time: Monday 10:30–13:00 Location: MA 005

O 3.1 Mon 10:30 MA 005

**Tracking and Removing Br during the Bottom-Up Synthesis of a Graphene Nanoribbon** — •Christopher Bronner[1,2], Jonas Björk[3], and Petra Tegeder[1] — [1]Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut — [2]Freie Universität Berlin, Fachbereich Physik — [3]Linköping University, Department of Physics

Thermally induced, two-step bottom-up synthesis from halogen-substituted molecular precursors adsorbed at metal surfaces is an intriguing concept for obtaining graphene nanoribbons with well-defined edge structure and widths on the nanometer scale. The reaction pathways of the dissociated Br atoms have so far not been in the focus of research although they may very well interfere with the on-surface synthesis. Using temperature-programmed desorption we show that Br leaves the surface as HBr in an associative desorption process during the second reaction step, the cyclodehydrogenation. Density functional theory is employed to compare this process to the competing desorption of molecular hydrogen and furthermore shows that prior to desorption, Br is submerged under the three-dimensional intermediate reaction product, polyanthrylene. Upon exposure of this intermediate co-adsorbate to an atmosphere of molecular hydrogen, Br is removed from the surface but the cyclodehydrogenation step is still feasible which demonstrates that Br does not influence the on-surface synthesis. Generally, the ability to remove Br by providing molecular hydrogen opens an effective way to exclude unfavorable influences of the halogen (e.g. side-products, steric effects) in on-surface coupling reactions.

O 3.2 Mon 10:45 MA 005

**Schiff base formation on metal surfaces: towards low dimensional conjugated nanomaterials** — •Li Jiang[1], Anthoula C. Papageorgiou[1], Seung Cheol Oh[1], Özge Sağlam[1], David D. Duncan[1], Yi-Qi Zhang[1], Florian Klappenberger[1], Sandeep More[2], Rajesh Bhosale[2], Aurelio Mateo-Alonso[2,3], Joachim Reichert[1], and Johannes V. Barth[1] — [1]TU München, DE — [2]Albert-Ludwigs-Universität Freiburg, DE — [3]Ikerbasqu, ES

Recently, graphene nanoribbons, especially doped with heteroatoms have spurred extensive attention and exploration [1] and covalent organic frameworks (COF) have been successfully synthesized based on Schiff base formation [2]. Inspired by these findings, we systematically investigated the condensation reaction of a tetraamine molecule with a tetraketone molecule on the three coinage close packed metal surfaces Au, Ag and Cu under ultrahigh vacuum conditions by scanning tunneling microscopy. On all three substrates the reactants readily intermix at room temperature forming two-dimensional bi-component networks. We demonstrated the feasibility to form Schiff base conjugated oligomers on the Ag(111) surface by thermal treatment and further investigated the X-ray photoelectron spectroscopy signatures of the reactants and products as a function of the annealing temperature. In contrast to the behavior on Ag(111), the monomers desorb from the Au(111) surface before they react, whereas on the Cu(111) surface undesired thermal decomposition is observed after annealing at temperatures too low for imine formation.

1) Science 2011, 333, 999; 2) Chem. Sci. 2014, 5, 2789.

O 3.3 Mon 11:00 MA 005

**Potassium doping of ultrathin layers of coronene on Ag(111)** — •Tobias Huempfner, Falko Sojka, Roman Forker, and Torsten Fritz — Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany

We report on the influence of potassium doping on ultrathin coronene layers in the (sub-) monolayer regime on Ag(111). The film growth and doping are successively traced in situ via differential reflectance spectroscopy (DRS) [1,2]. During the doping process the formation of a primary phase and, subsequently, of monoanions and dianions was observed by comparing the measured data to solution spectra [3]. After stopping the potassium deposition the dianions decay into monoanions and into molecules in the primary phase. The two latter species are stable and could be further investigated structurally and electronically via low energy electron diffraction (LEED) and scanning tunneling microscopy / spectroscopy (STM, STS). Besides the already known structure for one monolayer (ML) of undoped coronene on Ag(111) a new epitaxial structure is found for a coverage below 1 ML. Although the doped molecules do not show any highly ordered structure, they could be identified via STM measurements. While the potassium atoms are not resolved in the STM images, the doping process is evidenced by characteristic features in the related STS data.

References: [1] R. Forker *et al.*, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **108**, 34-68 (2012). [2] R. Forker and T. Fritz, Phys. Chem. Chem. Phys. **11**, 2142-2155 (2009). [3] G. J. Hoijtink, Mol. Phys. **2**, 85-95 (1959).

O 3.4 Mon 11:15 MA 005

**STM study of molecular n-dopants for organic electronics** — •Justus Krüger[1,2], Frank Eisenhut[1,2], Jörg Meyer[1,2], Anja Nickel[1,2], Gianaurelio Cuniberti[1,2] und Francesca Moresco[1,2] — [1]Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — [2]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

Controllable doping of organic semiconductors is of paramount importance for future application of organic electronics; however, effective air-stable and solution-processable n-type dopants are still rare. A new class of molecular materials based on 1H-benzoimidazole derivates has recently been identified [1] as promising candidate for strong n-type doping. Whereas the experimental results look encouraging, there is still a lack of knowledge on the detailed doping mechanism. Therefore, we have investigated the properties of one particular dopant on a single molecular level by scanning tunneling microscopy (STM) at low temperatures. By depositing dopant and C60 molecules on the same Au(111) surface, the electronic and structural interactions of the host-guest system can be addressed. In particular, spectroscopic measurements of dopant molecules resting on C60 clusters will help to understand the working mechanism of the doping effect. [1] P. Wei et al., J. Am. Chem. Soc. 2010 132 (26), 8852-8853

O 3.5 Mon 11:30 MA 005

**Single photon emission in STM-induced luminescence from fullerene excitons** — •Pablo Merino[1], Christoph Grosse[1], Klaus Kuhnke[1], and Klaus Kern[1,2] — [1]Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany — [2]Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Quantum systems like molecules or quantum dots cannot emit two photons at the same time which results in an antibunching of the emitted photon train and a dip in the photon-photon correlation function. Such single photon emitters are key elements for quantum cryptography and their miniaturization to the nanoscale would be desirable. This requires reproducible emitter separations typically below the optical diffraction limit and has imposed strong limitations on suitable structures and materials. In this contribution we demonstrate single photon emission excited locally by a low temperature (4 K) Scanning Tunneling Microscope (STM) and characterized with sub-molecular resolution. Using a Hanbury Brown-Twiss interferometer scheme in STM-induced electroluminescence we discovered that localized trap states in fullerene multilayers form single photon emitters. The emission spectrum is a line spectrum attributable to exciton recombination and from the correlation data, exciton life times as short as 0.25 ns are determined. With increasing tunnel current a saturation of the emission and a change of the correlation function are observed. We will discuss these observations within the frame of a three state kinetic model.

O 3.6 Mon 11:45 MA 005

**2D-Nanopatterns of molecular polygons and spoked wheels** — •Stefan-Sven Jester, A. Vikas Aggarwal, Robert May, and Sigurd Höger — Rheinische Friedrich-Wilhelms-Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Shape-persistent macrocycles self-assemble at the solid/liquid interface of graphite (HOPG) into two-dimensional monolayer patterns that can be imaged by scanning tunneling microscopy (STM). We recently investigated monolayers of arylene-alkynylene macrocycles that can be viewed as molecular polygons consisting of $n$ corners and $n$ sides ($n = 3 - 6$) and form supramolecular Archimedean tiling patterns. Thereby, two conformers of the hexamer were observed: an equilateral and a collapsed hexagon. Stimulated by these observations, we studied the mono- and multilayer formation of molecular spoked wheels, in which the hexagonal macrocycle rim is stiffened by an intraannular spoke/hub system. In addition, the importance and informative value of STM techniques for the compound characterization of large organic molecules is highlighted. [1] S.-S. Jester, E. Sigmund, S. Höger *J. Am. Chem. Soc.* **2011**, *133*, 11062. [2] S.-S. Jester, A. V. Aggarwal, D. Kalle, S. Höger *Beilstein J. Org. Chem.* **2014**, *10*, 2783. [3] R. May, S.-S. Jester, S. Höger *J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja5096705.

O 3.7 Mon 12:00 MA 005

**Polymer statistics of single P3HT molecules on Au(001) determined by STM** — •Erik Kohl[1], Stefan Förster[1], and Wolf Widdra[1,2] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — [2]Max-Planck-Institute für Mikrostrukturphysik, Halle, Germany

Using in-situ UHV electrospray deposition (ESD), isolated poly(3-hexylthiophene) (P3HT) molecules have been deposited on a Au(001) surface. Scanning tunneling microscopy (STM) reveals two different adsorption states of P3HT in the low coverage limit at room temperature: Strongly adsorbed polymer chains show fully stretched conformations, which result from a reorganization of the surface atoms in the presence of the polymer chain [1]. Additionally, weakly adsorbed molecules are present, which show two-dimensional random-coil like conformations.

For the weakly adsorbed P3HT species, the full statistical information is extracted from STM measurements. By tracing the experimentally observed chain configurations, the radius of gyration and the end-to-end distance of about 700 molecules of different polymer lengths have been extracted in the single chain limit [2].

[1] S. Förster and W. Widdra, J. Chem. Phys. 141, 054713 (2014)
[2] S. Förster, E. Kohl, M. Ivanov, J. Gross, W. Widdra and W. Janke, J. Chem. Phys. 141, 164701 (2014)

O 3.8 Mon 12:15 MA 005

**Thermally and photoinduced polymerization of ultrathin sexithiophene films** — •Anke Sander[1,3], Rene Hammer[1], Klaus Duncker[1], Stefan Förster[1], and Wolf Widdra[1,2] — [1]Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — [2]Max Planck Institute of Microstructure Physics, Halle, Germany — [3]present address: Unite Mixte de Physique CNRS/Thales, Palaiseau, France

Due to their semiconducting properties, polythiophenes are highly promising for use in organic electronics. Apart from their direct deposition onto a substrate, one could also deposit smaller thiophene compounds and form covalent bonds between them by further processing which additionally enables a manipulation of the morphology. This study addresses the polymerization of ultrathin sexithiophene (6T) films on Ag(001) and Au(001). Annealing of initially well-ordered films leads to local reactions between neighboring molecules. Depending on the surface temperature and the annealing time, long unbranched polythiophene polymers or branched polymer networks are formed. In general, the onset temperature and the complexity of structure formation depend on the strength of interaction with the underlying substrate. Here, on both substrates the polymerization occurs at temperatures significantly lower than found for crystalline powder. Similar structural changes and 6T polymerization are found upon exposure to UV radiation in the range from 3.0 to 4.2 eV. The observed reactions induced by thermal annealing as well as by UV excitation are explained by a polymerization via formation of cation radicals that necessitates the interplay with metallic substrate states.

O 3.9 Mon 12:30 MA 005

**Layer resolved evolution of $\alpha$-sexithiophene films: Correlation between PEEM and optical reflectance** — •Ebrahim Ghanbari, Thorsten Wagner, and Peter Zeppenfeld — ebrahim.ghanbari@jku.at

$\alpha$-sexithiophene ($\alpha$-6T) is a well-known organic dye pigment which represents a model system to study the photo-physical properties of $\pi$-conjugated molecules. We apply a combination of Differential Reflectance Spectroscopy (DRS) and Photo Electron Emission Microscopy (PEEM) to follow the growth of $\alpha$-6T on Ag(111) surfaces in real time. The deposition of the molecules modifies the density of states at the surface as well as the actual photoelectron emission barrier. Therefore, the lateral variation of the electron yield can be used to follow the growth of layers and 3D crystallites. Initially, the PEEM intensity rises uniformly across the entire field of view (145 $\mu$m) until the first layer is closed. The following drop of the electron yield is terminated when the wetting layer is completed and the nucleation of 3D islands sets in. The initial rise of the electron yield can be attributed to the formation of an interface dipole. The DRS and the PEEM measurements are synchronized and both signals are recorded simultaneously. The evolution of different features in the normalized differential optical reflectance can be attributed to the formation of the first layer, the second layer, as well as the nucleation and growth of 3D crystallites. Thus, we obtain a direct correlation between the PEEM and the transients of the spectral reflectance which provides a deeper insight into the nature of the adsorbate-metal system.

O 3.10 Mon 12:45 MA 005

**Structural, optical, and electronic properties of mono- and multilayers of tetraphenyldibenzoperiflanthene (DBP)** — •Tino Kirchhuebel[1], Tino Morgenroth[1], Marco Gruenewald[1], Roman Forker[1], Takashi Yamada[2], Toshiaki Munakata[2], Fabio Bussolotti[3], Satoshi Kera[3], Nobuo Ueno[3], and Torsten Fritz[1] — [1]Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany — [2]Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan — [3]Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

The dye molecule tetraphenyldibenzoperiflanthene (DBP, $C_{64}H_{36}$) [1] is a promising candidate for usage in opto-electronic devices . It consists of an aromatic backbone and four additional phenyl rings perpendicular to the molecular plane. In order to investigate the growth and the optical properties of DBP on various substrates from submonolayers to 10 monolayers, in situ differential reflectance spectroscopy (DRS) [2,3] measurements were performed. A strong interaction between molecules and single crystalline metal surfaces was found, where structural characterization by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) at cryogenic temperatures revealed a well-ordered flat-lying thin film growth in a herringbone arrangement in the first monolayer. Depending on the coverage two distinct spectral fingerprints of DBP molecules could be identified for multilayer films. To elucidate their origin, complementary photoelectron spectroscopies as well as (time dependent) density functional theory ((TD-)DFT) calculations were performed.

# O 4: Electronic Structure of Surfaces I

Time: Monday 10:30–13:15 Location: MA 041

O 4.1 Mon 10:30 MA 041

**Phonon-Mediated Electron Transport through CaO Thin Films** — •Niklas Nilius[1], Yi Cui[2], and Hans-Joachim Freund[2] — [1]Institut für Physik, Carl von Ossietzky Universität, D-26111 Oldenburg, Germany — [2]Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

Scanning tunneling microscopy has developed into a powerful tool for the characterization of conductive surfaces, for which the overlap of tip and sample wavefunctions determines the image contrast. On insulating layers, as the CaO thin-film grown on Mo(001) investigated here, direct overlap between initial and final states is not possible anymore and electrons are transported via hopping through the conduction-band states of the oxide. In this case, carrier transport is accompanied by strong phonon excitations, imprinting an oscillatory behavior onto the differential conductance of the system. The phonons show a characteristic spatial dependence and become softer around lattice irregularities in the oxide film, such as dislocation lines.

O 4.2 Mon 10:45 MA 041

**Orientational Tuning Of The Two-Dimensional Electron Gases At The Low-Index Surfaces of SrTiO3** — •Tobias C. Rödel[1,2], Cédric Bareille[1], Franck Fortuna[1], François Bertran[2], Patrick Le Fèvre[2], Thomas Maroutian[3], Philippe Lecoeur[3], Marc Gabay[4], Marcelo J. Rozenberg[4], and Andres F. Santander-Syro[1] — [1]CSNSM, Orsay, France — [2]Synchrotron SOLEIL, Gif-sur-Yvette, France — [3]IEF, Orsay, France — [4]LPS, Orsay, France

Two-dimensional electron gases (2DEGs) in SrTiO3 have been studied extensively in the last decade after its discovery at the LaAlO3/SrTiO3 interface by Ohtomo & Hwang. This heterostructure displays many fundamentally interesting properties, such as field-effect induced insulator-to-superconductor transitions and the coexistence of magnetism and superconductivity.

To clarify the microcopic electronic structure of the 2DEG, we conducted angle resolved-photoemission spectroscopy (ARPES) experiments of a closely related system: the 2DEG at the surface of SrTiO3. Our group studied the 2DEGs at various different surface orientations of SrTiO3 (as well as KTaO3) at different synchrotron facilities.

Recent results demonstrate that the electronic structure of the 2DEG at the surface of SrTiO3 (Fermi surfaces, subband masses and orbital ordering) can be tuned by confining the electrons at different surface orientations. This occurs due to the different crystallographic symmetries of the surface and subsurface planes as well as the different effective electron masses along the confinement direction.

O 4.3 Mon 11:00 MA 041

**Angle-resolved ultraviolet photoemission spectroscopy of quasicrystalline $BaTiO_3$ films on Pt(111)** — •Richard Kraska[1], Konrad Gillmeister[1], Stefan Förster[1], Eva Maria Zollner[1], Klaus Meinel[1], Cheng-Tien Chiang[2,1], and Wolf Widdra[1,2] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Bulk $BaTiO_3$ is a widely investigated perovskite. As recently discovered, thin films of this material can form a long-range ordered, quasicrystalline structure on the hexagonal Pt(111) surface with 12-fold rotational symmetry. Although the two-dimensional structure has been investigated by STM, LEED and XPS [1], no information on the electronic valence band structure has been reported so far. Here we present angle-resolved photoelectron spectroscopy data along the $[1\bar{2}1]$ and $[1\bar{1}0]$ directions of the substrate for a well-ordered quasicrystalline $BaTiO_3$-derived film using a photon energy of 21.22 eV. Comparing the data from the quasicrystalline film and from the clean platinum substrate, we can identify a weakly dispersive feature at 6 eV below the Fermi level that is assigned to the aperiodic structure.

[1] S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, 215 (2013)

O 4.4 Mon 11:15 MA 041

**Employing Infrared Reflection Absorption Spectroscopy to Probe Polarons in Photoactive Oxides: $TiO_2$ and ZnO** — •Fabian Bebensee, Hikmet Sezen, Alexei Nefedov, and Christof Wöll — Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

$TiO_2$ and ZnO are wide-band gap metal oxides exhibiting various desirable physico-chemical properties, e.g. high photocatalytic activity. In the context of photoexcitations, primarily excitons have been studied including their very recently reported ultrafast formation dynamics.[1] It is important to note that charge carriers generated from dissociation of excitons may be trapped in polaronic states. Consequently, the polaron binding energy becomes crucial for the photocatalytic activity, as this energy is not available to drive the desired reaction. Yet, only very little work has been devoted to these trap states. Here, we report a novel approach to study polarons in metal oxide single crystals by populating these trap states via UV-light irradiation and probe them using infrared reflection absorption spectroscopy (IRRAS). We will present results for $TiO_2$ (cf. [2]) and ZnO, where a number of previously unobserved bands ascribed to polaronic states appear in the IR-spectra upon irradiation and compare them to theoretical work. Exploiting time-resolved IRRAS, we were able to deduce lifetimes and binding energies of these states experimentally for ZnO.

[1] Deinert, et al., PRL 2014, 113, 057602.

[2] Sezen, et al., Sci Rep 2014, 4, 3808.

O 4.5 Mon 11:30 MA 041

**High Resolution Electron Energy Loss Study of Pd and Pt Phthalocyanine on Ag(111)** — •Jessica Sforzini, Francois Bocquet, and Stefan Tautz — Peter Gruenberg Institute 3, Forschungszentrum Juelich, 52428 Juelich, Germany

We have investigated the geometrical and the vibrational properties of Pd and Pt Phthalocyanine on Ag(111) by Low Energy Electron Diffraction (LEED) and by High Resolution Electron Energy Loss Spectroscopy (HREELS). The LEED patterns show that the molecules grow highly ordered on the surface. The HREELS spectrum is dominated by vibrational modes with symmetry A2u that produce an out-of-plane variation in the dipole moment. This indicates a flat adsorption geometry. The asymmetric vibrational losses, between 1000 and 1500 $cm^{-1}$, indicate the presence of an interfacial dynamical charge transfer that is more pronounced in the case of Pd molecules. We also studied both systems after exposure to molecular hydrogen, but observe no drastical changes in the behavior with the central metal type.

O 4.6 Mon 11:45 MA 041

**One- and many-electron computational scheme for XES and NEXAFS spectra calculation within DFT and pseudopotential approach** — •Roman Ovcharenko[1], Elena Voloshina[1], Alexander Shulakov[2], and Yuriy Dedkov[3] — [1]Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany — [2]V. A. Fock Institute of Physics, Saint-Petersburg State University, 198504 Saint-Petersburg, Russia — [3]SPECS Surface Nano Analysis GmbH, Voltasraße 5, 13555 Berlin, Germany

In this work we present the density functional method using the PAW pseudopotential and the plane wave basis set for X-ray emission and absorption spectra calculation of simple metals and graphene-like systems. As it is well known, smoothed pseudo wave functions differ from the standard all-electron crystal orbitals in the atomic core region which is particularly important for X-ray matrix elements calculation. Therefore, to calculate the probabilities of X-ray spectra, we have reconstructed all-electron orbitals in the core region leaving wave function outside core sphere unchanged.

Moreover, even after such reconstruction many materials demonstrate spectral features which cannot be described by one-electron treating. The problem is in originally many particle nature of the dynamical core-hole screening during X-ray transition, which partially can be overcome by adopting Mahan-Nozieres-De Dominicis theory. The results of numerical application of such one- and many-electron approaches to a number of simple metals as well as graphene-like systems is the topic of present talk.

O 4.7 Mon 12:00 MA 041

**First principles exploration of noble metal lanthanide sur-**

**face alloys** — •Matthieu Verstraete[1], Bin Xu[1], Lucia Vitali[2], Laura Fernandez[2], Frederik Michael Schiller[2], Maider Ormaza[2], and Enrique Ortega[2] — [1]University of Liège, Liège, Belgium — [2]Universidad del Pais Vasco, San Sebastian, Spain

The electronic and magnetic structure of $X_2L$ alloys of noble metals (X = Ag Au Cu) with lanthanides (L = La Gd Ce...) is investigated by first principles calculations, to explain and complement a series of surface science techniques (ARPES, XRD, STM, STS, MOKE). The complex interplay of magnetic, strain, and chemical variables produces a variety of different electronic states for very similar geometric structures. STM profile inversions, relativistic and spin polarized band splittings, and a series of hole and electron like surface states all result from varying the noble metal or lanthanide. The common point in these systems is the existence of an experimental "sweet spot" in the synthesis, generating a homogeneous surface alloy showing a hexagonal motif and a long range moiré pattern. Density functional theory band and structure calculations shed light on the nature of the states and their magnetism.

Xu, B. et al. in preparation (2015)
Ormaza, M. et al. in preparation (2015)
Ormaza, M., et al. Phys. Rev. B 88, 125405 (2013)
Corso, M., et al. Phys Rev Lett 105, 016101 (2010)

O 4.8 Mon 12:15 MA 041

**Interface electronic structure and charge transfer processes in layered ferecrystalline [(SnSe)1.15]5(TaSe2)5 compound: Photoemission study** — •Pavel Shukrynau[1], Lars Smykalla[1], Matthias Falmbigl[2], David Johnson[2], and Michael Hietschold[1] — [1]Institute of Physics, Technische Universität Chemnitz, Reichenhainer Straße 70, D-09107 Chemnitz, Germany — [2]Materials Science Institute and Chemistry Department, University of Oregon, Eugene, Oregon 97403, USA

In situ synchrotron radiation photoelectron spectroscopy was used to characterize electronic structure at the cleaved interface of the layered ferecrystalline [(SnSe)1.15]5(TaSe2)5 material. Detailed analysis of the Sn 3d, Ta 5d and Se 4p core levels spectra obtained at various incident angles revealed significant differences in chemical bonding of atoms in surfaces with divers terminating layers. On the basis of energy positions and widths of the Sn-derived features of the valence band spectra, a weak coupling between SnSe and TaSe2 layers is suggested. However, the Ta 5d signal reveals different electronic structures depending on the terminating layer. The observed changes can be attributed to stronger interaction between TaSe2-TaSe2 layers and a large charge transfer between Se 4p and Ta 5d orbitals. Comparisons were made with classical misfit compounds.

O 4.9 Mon 12:30 MA 041

**Orbital signatures of Fano-Kondo lineshapes in STM adatom spectroscopy** — •Sebastian Frank and David Jacob — MPI of Microstructure Physics, Halle, Germany

Scanning tunnel spectroscopy has become a routine tool for probing the Kondo effect of magnetic atoms deposited on conducting surfaces [1]. The Kondo effect manifests itself as so-called Fano line shape in the measured conductance spectrum. However, it is often unclear which of the d-orbitals causes the observed Kondo signature in the conductance. Here we fill this gap by finding the Kondo signatures of individual d-orbitals. To this end, we perform DFT calculations augmented by local dynamic correlations. We add correlations to specific d-orbitals only, instead of the entire d-shell, and compute the corresponding conductance curves. The Fano line shapes strongly depend on the type of the correlated orbital, the effective interaction parameter U and the d-level position. Furthermore, we laterally displace our model STM tip to find the spatial evolution of the Fano signature. Hence it is possible to identify the d-orbital responsible for the observed Fano line shape.

[1] Madhavan et al., Science 280, 567 (1998); Li et al., PRL 80, 2893 (1998); Knorr et al., PRL 88, 096804 (2002)

O 4.10 Mon 12:45 MA 041

**A new setup for investigation of advanced materials by means of dynamic-XPS** — •Sergey Babenkov[1], Olga Molodtsova[1], Victor Aristov[1,2,3], Frank Scholz[1], Joern Seltmann[1], Ivan Shevchuk[1], Leif Glaser[1], and Jens Viefhaus[1] — [1]DESY Hamburg, Germany — [2]Uni Hamburg, Germany — [3]ISSP RAS, Russia

Using dynamic-XPS method is a big step toward understanding of fast processes on the solid surfaces and subsurfaces of advanced materials, which are taking place during changing of different conditions. The experimental setup for such experiments, based on a hemispherical electron spectrometer Argus (Omicron NanoTechnology GmbH), has been built up, commissioned and currently is available for regular users of beamline P04 (PETRA III, DESY). Such combination allows to acquire both traditional scanning and extremely fast snapshot (down to 0.1 sec/spectrum) XPS spectra of several core levels (CL). It opens new possibilities to real time characterization of the fast processes both from quantitative and qualitative point of view by dynamical measuring of XPS. The concept was verified by real time XPS characterization of thermally induced process of graphene formation on model cubic-SiC(001)/Si(001) wafer. We were able to control time/temperature/rare-gas pressure parameters and follow the changes in C 1s CL spectra. Moreover, we present the dynamic-XPS study of controllable metal-organic interface formation (Indium/CuPcF4) at room temperature conditions. This work was supported by grants of RFBR No 13-02-00818, 14-02-00949, BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211.

O 4.11 Mon 13:00 MA 041

**Elektronische Eigenschaften von Au(111) mittels Dichtefunktionaltheorierechnungen** — •Ari Paavo Seitsonen — Institut für Chemie, Universität Zürich, Schweiz — Département de Chimie, École Normale Supérieure, Paris, Frankreich

Die Fischgräten-Rekonstruktion (engl. Herringbone) von der Au(111) Oberfläche hat Forscher besonders seit der Rastertunnelmikroskopieuntersuchung [1] inspiriert. Die elektronischen Eigenschaften sind unter anderem durch winkelabhängige Photoelektronenspektroskopie gemessen worden [2].

In den letzten Jahren sind zwei Dichtefunktionaltheorierechnungen zu der Geometrie und elektronische Reaktivität der rekonstruktuierten Au(111) erschienen [3,4]. Wir haben diese Untersuchungen weitergeführt, da wir die elektronische Struktur, darunter den Oberflächenzustand in der Näher von der Fermi-Energie, analysiert haben. Wir diskutieren sowohl die Bandstruktur wie die Spin-Bahnspaltung des Zustandes.

[1] Johannes V Barth, Harald Brune, Gerhard Ertl and Rolf Jürgen Behm, *Physical Review B* **42**, 9307 (2010)

[2] S. LaShell, B. A. McDougall and E. Jensen, *Physical Review Letters* **77**, 3419 (1996)

[3] Yun Wang, Noel S Hush and Jeffrey R Reimers, *Physical Review B* **75**, 233416 (2006)

[4] Felix Hanke and Jonas Björk, *Physical Review B* **87**, 235422 (2013)

## O 5: Plasmonics: Nanoantennas, Nanoparticles

Time: Monday 10:30–13:00 Location: MA 042

O 5.1 Mon 10:30 MA 042

**Antenna-mediated single molecule FRET** — •Janning Herrmann, Katharina Ditte, and Christiane Höppener — Physikalisches Institut, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Förster Resonance Energy Transfer (FRET) is a wide-spread tool for quantitative evaluation of interaction ranges of molecular systems in single molecule studies. As the FRET efficiency is inversely proportional to the 6th power of the separation distance of donor and acceptor, it serves as a precise nanometer-ruler. Because of the high distance sensitivity, FRET is limited to the sub-8 nm range.

Optical antennas can be utilized to enhance the light-matter interactions, namely the electric field enhancement associated with the irradiated antenna, the modification of the radiative transition rate and the redirection of light [1].

In this contribution, we demonstrate in a single molecule FRET study that a single spherical AuNP antenna opens up the possibility to tune the transition rates of the donor and the acceptor ambivalently in order to boost the energy transfer rate significantly. In addition the FRET efficiency benefits also from the improved photon counting statistics in the presence of an antenna.

[1] C. Höppener and L. Novotny; Quart. Rev. Biophys. 45 (2012), 209-255

O 5.2 Mon 10:45 MA 042

**Electrically-driven optical antennas** — •René Kullock[1], Johannes Kern[1,2], Jord Prangsma[3], and Bert Hecht[1] — [1]Experimental Physics 5, University of Würzburg, Germany — [2]Physikalisches Institut, University of Münster, Germany — [3]MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Antennas play a key role in today's wireless communication networks as they efficiently link localized electrical signals and electromagnetic waves. Driven by the demand for higher bandwidth, antenna carrier frequencies are ever increasing, however, electrically driven nanoantennas at optical frequencies seemed beyond reach. Although fabrication of optical antennas is already possible, unlike radiowave antennas they are not fed by a generator. Instead they are driven by light directly or via optically active materials in their proximity.

Here, we demonstrate direct electrical driving of an optical nanoantenna featuring an atomic-scale feed gap. Upon applying a voltage, quantum tunneling of electrons across the feed gap creates a broadband quantum shot noise. The optical frequency components of this fluctuating current are efficiently converted into photons by the antenna. We demonstrate that the properties of the emitted photons can be fully controlled by the antenna architecture, and that the antenna improves the quantum efficiency by up to two orders of magnitude with respect to a non-resonant reference system. Our work represents a new paradigm for interfacing electrons and photons at the nanometer scale, e.g. for on-chip wireless data communication.

O 5.3 Mon 11:00 MA 042

**Gold Nanoantennas with Reduced Substrate Contact for Plasmonic Enhancement in the Infrared** — •Christian Huck[1], Andrea Toma[2], Frank Neubrech[1,3], Manohar Chirumamilla[2], Jochen Vogt[1], Francesco De Angelis[2], and Annemarie Pucci[1] — [1]Kirchhoff Institute for Physics, University of Heidelberg, Germany — [2]Istituto Italiano di Tecnologia, Genova, Italy — [3]4th Physics Institute and Research Center SCoPE, Stuttgart, Germany

Plasmon-polariton excitations of metal nanoparticles can couple to other excitations of similar energy, which enables strong vibrational signal enhancement in the infrared. Commonly used substrates for surface enhanced infrared absorption (SEIRA) consist of meal nanoparticles located on a dielectric substrate. However, this planar arrangement substantially weakens plasmonic resonances because of the substrate polarizability and, furthermore, a great part of the electromagnetic near-field is located inside the substrate and thus not accessible for enhanced vibrational spectroscopy of an analyte. In this contribution we present one way to reduce the undesirable influences of the substrate by fabricating gold nanowires situated on a silicon pedestal and therefore in a reduced contact with the substrate. The influence of the pedestal height is studied by finite-difference time-domain simulation and plays a crucial role for the optimization of near-field intensities. Furthermore we show a comparison of the plasmonic response as well as the SEIRA activity between rods prepared by standard electron beam lithography and rods which were additionally treated with reactive ion etching to remove the silicon substrate around the hot-spots of the rods.

O 5.4 Mon 11:15 MA 042

**Photoelectron imaging of resonant modes of plasmonic antennas** — •Anna-Katharina Mahro, Deirdre Kilbane, Pascal Melchior, Stefan Mathias, and Martin Aeschlimann — Physics Department and Research Centre OPTIMAS, University of Kaiserslautern, Germany

Knowledge of fundamental light-matter interactions such as the local response of nanostructures to incident light is necessary for designing plasmonic devices such as biosensors. This response is determined on the nanometer scale (below the diffraction limit of light). To achieve high spatial resolution we use a photoemission electron microscope (PEEM) in combination with different laser sources for excitation.

To gain information about the spectral properties of the nanoantennas we apply two approaches in the time and frequency domain. The time domain experiment involves phase-resolved interferometric PEEM using a broadband ultrashort pulse laser. The frequency domain experiment is wavelength dependent PEEM using a narrow bandwidth highly tuneable laser source, in our case an optical parametric oscillator (OPO). Comparing spectra from both techniques gives us insight into the local response of our nanoantennas.

O 5.5 Mon 11:30 MA 042

**Fano resonances and near-field coupling efficiency in plasmonic nanostructures based on nanorods** — •Manuel Gonçalves[1], Madeleine Nilsen[1], Ines Martin[1], Taron Makaryan[2], Armen Melikyan[3], Hayk Minassian[4], and Othmar Marti[1] — [1]Ulm University - Inst. of Experimental Physics, Ulm, Germany — [2]Yerevan State University - Radiophysics Department, Yerevan Armenia — [3]Russian-Armenian (Slavonic) University, Yerevan, Armenia — [4]Yerevan Physics Institute, Yerevan, Armenia

Nanorods present well separated dipolar and higher order multipolar plasmon resonances. These resonances scale up approximately with the aspect ratio. Several configurations of rods of non-identical size can be used to produce Fano resonances, by coupling one radiant mode (dipole) with one sub-radiant mode (quadrupole). The near-field coupling between rods arranged in T- and H-like configurations is very efficient and leads to well pronounced Fano resonances in the absorption and scattering spectra. On the other hand, these structures are among the most simple to fabricate.

We have investigated several structures by varying the geometrical and optical parameters and their influence in the Fano resonance. The near-field coupling between rods can be quantitatively characterized, using the ratio between absorption cross sections calculated separately for each part of the resonant system. At the Fano resonance this ratio achieves a maximum. It can also be generalized for other structures presenting Fano resonances, like heptamers and pentamers of coupled disks.

O 5.6 Mon 11:45 MA 042

**The influence of porphyrin adsorption on the LSP resonances of individual silver clusters investigated with multi-photon photoemission electron microscopy** — •Klaus Stallberg and Winfried Daum — Institut für Energieforschung und physikalische Technologien, TU Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld

Photoemission electron microscopy (PEEM) in combination with short-pulse laser excitation is a valuable probe for the investigation of plasmonic excitations, as it allows for direct imaging of the electric field enhancement with a lateral resolution down to 50 nm. In this talk we adress the application of energy-resolved multi-photon PEEM for the investigation of localized surface plasmons (LSPs) of silver clusters in contact with zinc-tetraphenyl-porphyrin (ZnTPP) molecules. ZnTPP is a metal-organic dye with a strong absorption band at 422 nm, which is close to the LSP resonances of selected silver nanoparticles on Si(100). Recording PEEM images for incrementally increased laser wavelengths enables us to derive spatially resolved excitation spectra. We observe the electronic $S_0 \rightarrow S_2$ Soret transition of porphyrin molecules as a strong resonance in the excitation spectra of thin porphyrin films. Similarly LSP resonances of individual silver clusters are obtained. Deposition of zinc-tetraphenyl-porphyrin (ZnTPP) molecules results in a shift of the LSP resonance towards shorter wavelengths while the porphyrins' Soret resonance appears to be shifted to lower wavelengths indicating a coupling of the silver clusters' LSP with the molecular Soret excitation.

O 5.7 Mon 12:00 MA 042

**Plasmon spectroscopy of metal nanoparticles** — •Viktor Myroshnychenko[1], Naoki Yamamoto[2], Javier Garcia de Abajo[3], and Jens Förstner[1] — [1]University of Paderborn, Paderborn, Germany — [2]Physics Department, Tokyo Institute of Technology, Tokyo, Japan — [3]ICFO-Institut de Ciencies Fotoniques, Castelldefels (Barcelona), Spain

The current interest in the optical properties of metal nanoparticles is due to their ability to host localized surface plasmon excitations in the visible and near-infrared parts of the spectrum [1]. The study of the electromagnetic field distributions associated to localized plasmon excitations in metal nanoparticles are of critical importance for applications. In this work, we use optical spectroscopy (which records light scattering exerted by the particles on externally incoming light) and cathodoluminescence (based on electron-induced radiation emission produced by interaction with an electron beam) to study plasmon excitations in sub-wavelength noble-metal nanoparticles [2]. We provide a theoretical description of these techniques and numerical modeling of the spectral features and spatially resolved maps of nanoparticle plasmon modes.

[1] N. J. Halas et al., Plasmons in strongly coupled metallic nanostructures, Chem. Rev. 111, 3913-3961, 2011.

[2] V. Myroshnychenko et al., Plasmon spectroscopy and imaging of individual gold nanodecahedra: A combined optical microscopy, cathodoluminescence, and electron energy-loss spectroscopy study, Nano Letters 12, 4172-4180, 2012.

O 5.8 Mon 12:15 MA 042

**A novel dielectric unidirectional antenna** — •Andre Hildebrandt, Matthias Reichelt, Torsten Meier, and Jens Förstner — University of Paderborn, Germany

Optical and infrared antennas provide a promising way to couple photons in and out of nanoscale structures. As counterpart to conventional radio antennas, they are able to increase optical fields in subwavelength volumes [1], to enhance excitation and emission of quantum emitters or to direct light, radiated by quantum emitters [2]. The directed emission of these antennas has been mainly pursued by surface plasmon based devices, e.g. Yagi-Uda like antennas, which are rather complicated due to the coupling of several metallic particles. Also, like all metallic structures in optical or infrared regime, these devices are very sensitive to fabrication tolerances and are affected by strong losses.

In this paper we present a design idea and numerical simulations for a dielectric antenna, which performs better than plasmonic counterpart, due to the lack of losses by an appropriate choice of the dielectric material. These antennas are robust concerning fabrication tolerances and can be realized with different materials for both the antenna and the substrate, without using high index materials.

[1] A. Hildebrandt et al., "Optimization of the intensity enhancement in plasmonic nanoantennas," AIP Conference Proceedings 1475, pp. 59-61 (2012)

[2] A. G. Curto et al., "Unidirectional Emission of a Quantum Dot Coupled to a Nanoantenna," Science 329, 930 (2010)

O 5.9 Mon 12:30 MA 042

**Near-field trapping of nanoparticles on plasmonic nanoantenna arrays** — •Anastasia Babynina[1,2,3] and Theobald Lohmüller[1,2,3] — [1]Photonics and Optoelectronics Group, Ludwig Maximilian University of Munich, Munich, Germany — [2]Nanosystems Initiative Munich (NIM), Munich, Germany — [3]The Center for NanoScience (CeNS), Munich, Germany

Optical trapping of nano-sized particles is challenging. In general, high laser powers are required to generate sufficient gradient forces for keeping such small objects confined in a trap. This is particularly problematic for biological samples. Plasmonically coupled nanostructures, such as bowtie nanoantennas, on the other hand, can be used to focus far-field propagating light down to a nanoscale volume in the optical near-field. The strong and localized field in such a plasmonic "hot-spot" results in strong gradient forces that can be harnessed for trapping of nano-sized objects.

We have fabricated and characterized large-scale arrays of plasmonic nanoantennas for optical near-field trapping of nanoparticles. Merely bottom-up nanofabrication methods are employed to control the size and the spacing of billions of gold triangles on one single substrate with nanometer precision. We show that such nanoantenna arrays can be applied for parallel near-field trapping and for releasing nanoobjects with a size and refractive index similar to that of a virus. The laser powers used here are orders of magnitude lower compared to a conventional far-field trapping experiment.

O 5.10 Mon 12:45 MA 042

**Nanoscale noble metal clusters: First principles atomistic time-dependent density functional calculations** — •Mikael Kuisma and Paul Erhart — Applied Physics, Chalmers University of Technology, Sweden

Nanoscale plasmonics has a variety of potential applications from cancer treatment to renewable energy. At these length scales a quantum mechanical treatment is required in order to obtain a reliable representation of the plasmonic response.

We have developed and implemented an efficient basis set based real-time propagation method in the GPAW code. The method is used together with the time-dependent GLLB-SC potential and applied to nanoscale noble metal clusters. For the first time, systems with over 10,000 valence electrons are available in *ab initio* all-electron time-dependent density functional (TDDFT) calculations with moderate computational effort. Using this approach we simulate the optical spectra of icosahedral silver clusters Ag ranging from 55 to 561 atoms (1.06–2.68 nm). We observe that localized surface plasmon resonances enter the asymptotic region already at diameters between 1-2 nm, converging to the classical quasistatic limit of 3.4 eV. We show that proper description of both *d*-band position and bandwidth is crucial.

As a further demonstration of the practicality of our method, we establish the nature of plasmonic response in palladium hydride nanoclusters. To this end, we combine the absorption spectra of hundreds of large palladium clusters with varying hydrogen content.

# O 6: Catalysis

Time: Monday 10:30–13:15 Location: MA 043

O 6.1 Mon 10:30 MA 043

**Support Effect in Oxide Catalysis: Methanol Oxidation on Vanadia/Ceria** — Thomas Kropp, •Joachim Paier, and Joachim Sauer — Institut für Chemie, Humboldt-Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany

We present a detailed mechanistic description of the methanol oxidation to formaldehyde at the $VO_x/CeO_2(111)$ catalytic system employing the DFT+$U$ approach as well as hybrid functionals to assess selected results. Compared to clean ceria (and depending on the pathway), depositing $VO_2$ on the surface does not affect significantly intrinsic barriers (1.3 eV) in the rate-determining H-transfer. It rather substantially increases the adsorption energy, which in turn leads to negative apparent barriers. The previously discussed pseudo vacancy, a structural feature of $VO_x$-decorated ceria, appears to be a favorable adsorption site for the methanol. Its dissociative adsorption at this very site, which is created by a oxygen spillover process from the support to the catalyst, was found to be as exothermic (-1.9 eV) as its adsorption at vanadium, i.e. insertion into the V-$O_{surf}$ bond, since both processes heal the aforementioned pseudo vacancy. Besides the above mentioned ease in transferring electrons from V $3d$ states to Ce $4f$ states, the pseudo vacancy is inherently related to surface morphology and represents another cooperative effect between catalyst and surface. Both, a highly exothermic adsorption step as well as a lowering of the activation energy in the rate-determining step explain the higher activity of $VO_x/CeO_2(111)$ compared to an inert $SiO_2$ support.

O 6.2 Mon 10:45 MA 043

**Travelling Vanadium Oxide Islands in a Catalytic Reaction** — •Bernhard von Boehn, Martin Hesse, and Ronald Imbihl — Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3 – 3a, D-30167 Hannover, Germany

Upon evaporation of a submonolayer coverage of vanadium in $O_2$ onto a Rh(111) surface one obtains well ordered two-dimensional V-oxide islands which we use as model catalysts for the partial oxidation of methanol to formaldehyde [1]. With photoemission electron microscopy we observe that under reaction conditions in the $10^{-4}$ mbar range the initially homogeneous $VO_x$ film ($\theta_V = 0.2$) transforms upon heating at 560 °C into a quasi-stationary macroscopic concentration pattern. This pattern consists of equidistant parallel stripes of $VO_x$ surrounded by nearly bare metal surface. Above 700 °C the stripe pattern changes into a spot pattern of circular $VO_x$ islands with 20 – 200 $\mu$m diameter. Due to attractive interactions the islands approach each other with a velocity up to a few $\mu$m/s depending on distance. The islands coalesce, afterwards their shape becomes rapidly circular again indicating a high line tension at the island boundaries. The islands only move under reaction conditions. A mechanism is proposed which is based on the chemical equilibrium of polymerization of individual $VO_x$ clusters into macroscopic VOx islands. Since the poly-/depolymerisation equilibrium is controlled by oxygen coverage, oxygen gradients surrounding the $VO_x$ islands under reaction conditions can cause the movement.

[1] J. Schoiswohl, S. Surnev, and F. P. Netzer, Topics in Catalysis **36** (2005) 91.

**Invited Talk** O 6.3 Mon 11:00 MA 043

**CO oxidation over a Pt/$Fe_3O_4$ model catalyst: Watching Mars van Krevelen at work** — •Gareth Parkinson — Institute of Applied Physics, TU Vienna, Vienna Austria

The nature of the active oxygen species during CO oxidation over supported metal catalysts is a long-standing and controversial issue. When metal oxides are utilized as the support, lattice O ions provide an additional pathway to $CO_2$ formation via the so-called Mars-van Krevelen (MvK) mechanism. Here, we provide direct evidence of an active MvK process during CO oxidation over a Pt/$Fe_3O_4$ model catalyst. Atomically resolved scanning tunneling microscopy images reveal etching of the $Fe_3O_4$ support in the vicinity of Pt clusters following exposure to CO at 280 °C, with subsequent re-growth upon exposure to $O_2$. The experimental data suggest CO oxidation is autocatalytic; extraction of the first O atom is most difficult energetically. The addition of $H_2$ to the gas mixture accelerates the reaction because a similar, more efficient, MvK process roughens the surface through the formation of water.

O 6.4 Mon 11:30 MA 043

**Spectromicroscopy of Dynamic Redistribution Patterns of V-Oxide on Rh(111) in Catalytic Methanol Oxidation** — •Martin Hesse[1], Bernhard von Boehn[1], Tevfik Onur Mentes[2], Andrea Locatelli[2], and Ronald Imbihl[1] — [1]Institut für Physikalische Chemie und Elektrochemie, 30167 Hannover, Germany — [2]Sincrotrone Trieste, 34012 Basovizza, Italy

Upon partial oxidation of methanol to formaldehyde onto a Rh(111) surface with a submonolayer coverage of vanadium one observes a redistribution of the supported vanadium oxide catalyst. Under reaction conditions ($10^{-6}$ mbar, >560°C) the initially homogeneous $VO_x$ film transforms into a quasi-stationary concentration pattern[1]. Depending on the temperature we find two kinds of patterns, stripes and circular islands. These patterns are investigated with LEEM (low energy electron microscopy), microprobe-LEED (low energy electron diffraction) and microprobe-XPS (X-ray photoelectron spectroscopy). The interior of the $VO_x$ islands contains a substructure with an inner boundary separating two regions. Remarkably, the highest V-concentration ($\theta_V$=0.8MLE) connected with a Moire pattern in LEED is located at the inner boundary whereas left and right of the boundary the V concentration reaches only about half of this value. Transport processes of the reactants that feedback on the V distribution are apparently responsible for this substructure.

[1] F. Lovis and R. Imbihl, J. Phys. Chem. C 115 (2011) 19149-19157

O 6.5 Mon 11:45 MA 043

**Surface oxide on Pt(111) as the active phase for NO and CO oxidation** — •Matthijs A. van Spronsen, Joost W.M. Frenken, and Irene M.N. Groot — Huygens-Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Platinum finds its main application as a car catalyst to control the emission of exhaust gases. When the catalyst operates in excess oxygen, platinum catalyzes the oxidation of CO, NO, and remnant hydrocarbons. Despite platinum's wide use for catalytic oxidation, the active surface phase under oxygen-rich reaction conditions is still highly debated. Traditionally, it was believed that the bare metallic surface was the most reactive. But the recent development of new in situ surface science tools led to the discovery of phase transitions to states of higher activity for CO oxidation. The explaining models are ranging from a hyperactive oxygen-covered surface, surface oxide, or bulk oxide.

For the Pt(111) surface, the facet lowest in energy, it is also not clear what the relevant structure is under oxygen-rich reaction conditions. Both a surface oxide and a bulk $\alpha$-PtO2 were found to be stable in different experiments. With the high-pressure, high-temperature ReactorSTM, we studied the oxidation of Pt(111) and found a stable surface oxide which assembles in a 'spoke wheel' superstructure at 1 bar O2 at 430 K. This surface oxide was also studied in both NO and CO oxidation under reaction conditions.

O 6.6 Mon 12:00 MA 043

**First-principles based modeling of the transport reactivity coupling: Catalytic explosion and non-chemical oscillations** — •Sandra Döpking[1,2], Karsten Reuter[1,3], and Sebastian Matera[1,2] — [1]Technische Universität München, Germany — [2]Freie Universität Berlin, Germany — [3]Stanford University, USA

Bridging the gap between ultra-high vacuum and realistic operation conditions is the goal of in-situ studies of defined model catalysts. In these near ambient environments a further level of complexity arises by the coupling of surface chemical reactions with macro-scale heat and mass transport. To investigate such effects, we revisit the CO oxidation on the $RuO_2(110)$ in a stagnation flow reactor [1]. Differently to the previous studies, we now perform fully spatially and temporally resolved simulation employing our a first-principles based multi-scale modeling approach, which integrates kinetic Monte Carlo simulations into the Computational Fluid Dynamics code catalyticFOAM [2]. We find that, after changing the inlet composition, the surface experiences a rapid explosion-like heat up by several hundred Kelvin. Furthermore, depending on the diameter of the single crystal, the system may end up in an oscillating state. However, these oscillations are non-chemical, i. e. they originate from the thermo-convection driven by the temperature difference between inlet and surface. [1] S. Matera and K. Reuter, Catal. Lett. 133, 156 (2009); Phys. Rev. B 82, 085446 (2010); J. Catal. 295,261 (2012). [2] S. Matera, M. Maestri, A. Cuoci, and K. Reuter, ACS Catal. 4, 4081 (2014).

O 6.7 Mon 12:15 MA 043

**A perturbative approach for quantifying mass transfer limitations in in-situ model catalyst studies** — •Sebastian Matera[1,2], Sara Blomberg[3], Max J. Hoffmann[1], Johan Zetterberg[3], Johan Gustafson[3], Edvin Lundgren[3], and Karsten Reuter[1,4] — [1]Technische Universität München, Germany — [2]Freie Universität Berlin, Germany — [3]Lund University, Sweden — [4]Stanford University, USA

Reaction chambers in in-situ studies of defined model catalysts often prohibit the disentangling of surface chemistry and gas phase transport by idealized reactor models. A full Computational Fluid Dynamics (CFD) treatment, however, is computationally extremely costly due to the stiff surface kinetics requiring very small times steps. We present a perturbative approach which decomposes the problem, such that the CFD can be performed with a low reactivity, non-stiff surface chemistry. The actual solution to the targeted problem, is then approximated in a post processing phase. In order to analyze recent Planar Laser Induced Fluorescence experiments [2] on the CO oxidation at Pd(100), we combine the perturbative approach with our first-principles based multi-scale modelling methodology integrating kinetic Monte Carlo simulations into CFD [1]. We find that a mixture of two different surface terminations explains the experiment the best, where the observed the reactivity stems from the minority termination. [1] S. Matera, M. Maestri, A. Cuoci, and K. Reuter, ACS Catal. 4, 4081 (2014). [2] J. Zetterberg et al., Rev. Sci. Instrum. 83, 053104 (2012)

O 6.8 Mon 12:30 MA 043

**CO oxidation on TiO$_2$ nanotube-supported Pt particles at near ambient pressures** — •Sandra Krick Calderon[1], Mathias Grabau[1], Jeong Eun Yoo[2], Patrik Schmuki[2], Hans-Peter Steinrück[1], and Christian Papp[1] — [1]Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3 — [2]Lehrstuhl für Korrosion und Oberflächentechnik, University of Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany

The CO oxidation reaction on two types of TiO$_2$ nanotube-supported Pt particle samples was examined by near-ambient pressure (NAP)-XPS and simultaneous online gas analyses. Both samples consist of vertical nanotubes (d=80, l=100 nm) decorated with platinum particles of different size. Temperature-programmed reaction experiments in continuous flow mode at a total pressure of 1 mbar and a CO:O$_2$ ratio of 1:4 were performed in the temperature range of 300 to 600 K. We compare these experiments to results obtained for the CO oxidation on a Pt(111) single crystal. The reaction onset temperatures were obtained by online gas analyses while the surface chemistry was investigated by XPS: we find a lower onset temperature on the nanoparticles with decreasing size and overall compared to Pt(111). Isothermal reactions were performed in-situ before at and above the onset temperatures, showing no adsorbed CO after reaction onset. Strong ageing of the samples with reaction time was observed resulting in changes of the reaction onset and CO conversion.

O 6.9 Mon 12:45 MA 043

**Comparing facets: First-principles kinetic Monte Carlo simulations of CO oxidation at RuO$_2$(111)** — •Tongyu Wang and Karsten Reuter — Technische Universität München, Germany

Systematic studies on polycrystalline powders are an appealing link between detailed surface science work on single crystals and the supported nanoparticles in real catalysis. Recent such work on RuO$_2$ powders points at a prominent role of the hitherto little studied apical facets for the long-term catalytic activity [1]. At near-ambient reaction conditions, particularly the {111} facet establishes a super-O-rich termination that features a singly-coordinated O$_{\mathrm{cus}}$ species, similar to the exhaustively studied (110) facet. In this context we establish a first-principles kinetic Monte Carlo model for CO oxidation at RuO$_2$(111), rigorously using rate constants derived from density-functional theory. For stoichiometric and net-oxidizing feed our simulations predict a catalytic activity of this facet that is comparable to the one of RuO$_2$(110). This indeed supports the relevance of this facet in understanding the catalytic activity of RuO$_2$ nanoparticles. [1] D. Rosenthal *et al.*, Z. Phys. Chem. (Muenchen Ger.) **57**, 225 (2001); T. Wang, J. Jelic, D. Rosenthal, and K. Reuter, Chem. Cat. Chem. **5**, 3398 (2013).

O 6.10 Mon 13:00 MA 043

**First Principles kinetic Monte Carlo simulations of competitive CO and NO Oxidation on Pd(100)** — •Juan Manuel Lorenzi[1], Sebastian Matera[1,2], and Karsten Reuter[1] — [1]Technische Universität München — [2]Freie Universität Berlin

Lean-burn automotive emissions are characterized by an increased NO$_x$ content. A crucial step for the effective operation of NO$_x$ storage reduction (NSR) catalysts is to oxidize excess NO into NO$_2$. In this context, interest shifts to understanding the oxidation properties of typically employed Pt-group catalysts under the simultaneous exposure to CO, NO and O$_2$. We assess this for the Pd(100) model catalyst surface with first-principles kinetic Monte Carlo (1p-kMC) simulations that are based on an extensive set of density-functional theory derived rate constants. For gas-phase conditions representative for the oxidative mode of NSR (600 K, 1 atm O$_2$, $10^{-3}$ atm NO) we obtain a NO oxidation activity of Pd(100) that is comparable to the one obtained previously for the $(\sqrt{5}\times\sqrt{5})R27^\circ$ surface oxide on Pd(100) [1]. Intriguingly, already corresponding small amounts of NO in the gas-mixture lead to qualitative changes in the CO oxidation properties. Particularly for oxygen-rich feeds the O coverage is substantially reduced, suggesting an increased resistance against oxide formation. [1] J. Jelic, K. Reuter, and R. Meyer, Chem. Cat. Chem. 2, 658 (2010).

## O 7: Graphene: THz, NIR and Transport Properties (HL with O/TT)

Time: Monday 9:30–11:30 Location: ER 270

O 7.1 Mon 9:30 ER 270

**Ratchet effects in graphene with a lateral periodic potential** — •P. Olbrich[1], J. Kamann[1], J. Munzert[1], M. König[1], L.E. Golub[2], L. Tutsch[1], J. Eroms[1], F. Fromm[3], Th. Seyller[3], D. Weiss[1], and S.D. Ganichev[1] — [1]University of Regensburg, Regensburg, Germany — [2]Ioffe Institute, St. Petersburg, Russia — [3]Technical University of Chemnitz, Germany

We report on the observation of terahertz (THz) radiation induced photocurrents in (a) epitaxially grown and (b) exfoliated graphene with a lateral periodic potential. The samples were covered with an insolating layer and a sequence of asymmetrically spaced thin/thick metallic stripes. While in the reference of sample (a) under normal incidence of THz radiation no photosignal was observed, the illumination of the lateral periodic potential resulted in pronounced photosignals, consisting of polarization dependent and independent contributions. In case of sample (b) the thin/thick metallic stripes act as a dual top gate structure to vary the potential profile and a back gate allows to change the carrier type and density of the sample. Here, the photocurrent reflects the degree of asymmetry induced by different top gate potentials and even vanished for a symmetric profile. Moreover, around the Dirac point the photocurrent shows strong oscillation. We discuss the experimental data, taking into account the calculated potential profile, near field effects of light scattering and the theoretical model [1, 2].

[1] E. L. Ivchenko and S. D. Ganichev, JETP Lett. 93, 673 (2011).

[2] P. Olbrich et al., Phys. Rev. B 83, 165320 (2011).

O 7.2 Mon 9:45 ER 270

**Mechanically Modulated Graphene for THz-Nanoelectronics.** — •Jonas Sichau[1], Timothy Lyon[1], August Dorn[1], Amaia Zurutuza[2], Amaia Pesquera[2], Alba Centeno[2], and Robert Blick[1] — [1]Center for Hybrid Nanostructures, Institutes of Nanostructure and Solid State Physics, University of Hamburg, Jungiusstrasse 11c, 20355 Hamburg, Germany. — [2]Graphenea S.A., 76 Tolosa Hiribidea, Donostia-San Sebastian, E-20018, Spain.

Graphene offers very high charge carrier mobility and a mean free path of several microns at room temperature. Consequently, it is a promising material for THz electronics [1]. For flat monolayer graphene, studies on microwave-photo excited transport have found spin resonance and zero-field pseudo-spin splitting [2]. The aim of our work is to investigate spatially modulated graphene under microwave excitation. Once carriers are propagating ballistically through the undulated graphene sheet, it is predicted that THz-radiation should be emitted [1].

We fabricated extremely large graphene membranes of up to 1 mm side lengths and transferred these onto a $SiO_2$-substrate. The pitch and height of the mechanical modulation are of the order of 200 nm and 50 nm, respectively. The measurements are performed with a variable temperature insert (VTI) at magnetic fields up to 12T. The microwave signal is coupled to the sample via a micro inductor forming a resonator with the graphene sheet. With this configuration we are able to probe magnetotransport and the interaction with electromagnetic radiation.

[1] Tantiwanichapan et al., Nanotechnology 24, 375205 (2013)

[2] Mani, R.G. et al., Nat. Commun., 3:996 (2012)

O 7.3 Mon 10:00 ER 270

**Investigations on the polarization dependent carrier excitation in graphene with low energetic photons** — •Jacob Otto[1,2], Martin Mittendorff[1,2], Torben Winzer[3], Ermin Malic[3], Andreas Knorr[3], Harald Schneider[1], Manfred Helm[1,2], and Stephan Winnerl[1] — [1]Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany — [2]Technische Universität Dresden, 01062 Dresden, Germany — [3]Technische Universität Berlin, 10623 Berlin, Germany

We demonstrate that in graphene a nonequelibrium charge carrier distribution retains its anisotropic nature on a 10 ps timescale if the photon energy is below the optical phonon energy. Recently evidence for an anisotropic carrier distribution has been found in near-infrared pump-probe experiments with varied angle between the orientation of pump and probe polarization [1]. This anisotropy vanishes after 150 fs due to electron optical-phonon scattering. Extending this study to the mid-infrared range ($E_{Photon} = 74\,\text{meV}$), i.e. to energies below the optical phonon energy, allows to strongly suppress this scattering mechanism. In accord with microscopic theory, traces of an anisotropic distribution on a 10 ps timescale are found. Note that carrier-carrier scattering, acting on a 10 fs timescale, is mainly colinear and therefor preserves the anisotropic distribution on rather long timsecales.

[1] M. Mittendorff, T. Winzer, E. Malic, A. Knorr, C. Berger, W. A. de Heer, H. Schneider, M. Helm and S. Winnerl *Nano Lett.* 2014, 14, 1504-1507

O 7.4 Mon 10:15 ER 270

**Magnetotransport in small angle twisted bilayers of folded graphene** — •Johannes Rode[1], Hennrik Schmidt[1,2], Dmitri Smirnov[1], and Rolf J. Haug[1] — [1]Institut für Festkörperphysik, Leibniz Universität Hannover — [2]Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore

Naturally occurring double-layer graphene consists of two hexagonal lattices in Bernal-stacking, described by a translational displacement between layers. While this type of bilayer is most commonly studied, the introduction of a rotational mismatch opens up a whole new field of rich physics, especially at small interlayer twist[1,2]. We investigate magnetotransport measurements on twisted graphene bilayers, prepared by folding of single layers. These reveal a strong dependence on the twist angle, which can be estimated by means of sample geometry. At small rotation, superlattices with a wavelength in the order of 10 nm arise and are observed by friction atomic force microscopy. Magnetotransport measurements in this small-angle regime show the formation of satellite Landau fans, which are attributed to additional Dirac singularities in the band structure[3].

[1] Lopes dos Santos, J. M. B., Peres, N. M. R. & Castro Neto, A. H. *Phys. Rev. Lett.* **99**, 256802.

[2] Mele, E. J. *Phys. Rev. B* **84**, 235439.

[3] Schmidt, H., Rode, J. C., Smirnov, D. & Haug, R. J. *Nat. Commun.* (accepted, Nov. 2014).

O 7.5 Mon 10:30 ER 270

**Carrier dynamics in Landau-quantized graphene** — •Florian Wendler[1], Martin Mittendorff[2], Stephan Winnerl[2], Manfred Helm[2], Andreas Knorr[1], and Ermin Malic[1] — [1]Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Germany — [2]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

We investigate the carrier dynamics in Landau-quantized graphene after an optical excitation using microscopic time-resolved calculations as well as differential transmission measurements. The calculations are performed within the density matrix theory accounting for the carrier-light, carrier-carrier, and carrier-phonon interaction which allows for a microscopic explanation of the experimental spectra.

The energy spectrum of Landau-quantized graphene is characterized by non-equidistant Landau levels where the optical selection rules enable a selective excitation of specific transitions. This is exploited to investigate the carrier dynamics in the energetically lowest Landau levels where an unexpected sign reversal in pump-probe spectra, observed in experiment and theory, provides an evidence for strong Auger scattering [1]. Based on our calculations we predict a substantial carrier multiplication [2]. Furthermore, the theory reveals the occurrence of population inversion in Landau-quantized graphene, suggesting its application as gain medium for a widely tunable Landau level laser[3].

[1] M. Mittendorff et al., Nat. Phys., DOI:10.1038/nphys3164.

[2] F. Wendler et al., Nat. Commun. 5:3703 (2014).

[3] F. Wendler, and E. Malic, arXiv:1410.2080v1.

O 7.6 Mon 10:45 ER 270

**Giant magnetophotoelectric effect in suspended graphene** — •Jens Sonntag, Annika Kurzmann, Martin Geller, Ralf Schützhold, and Axel Lorke — Faculty of Physics and CeNIDE, University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

Due to the broad absorption bandwidth and the possibility for carrier multiplication, graphene is a promising candidate for optoelectric applications.

In this context, we performed photocurrent measurements on a suspended graphene field-effect transistor structure in a magnetic field in the quantum Hall regime. Using an illumination power of only 3 $\mu$W, our device generates a current of up to 400 nA without an applied bias, which corresponds to a photoresponsivity of 0.14 A/W. To the best of our knowledge, this is one of the highest values ever measured for single layer graphene. Furthermore, the high current suggests that every absorbed photon creates more than 8 charge carriers, so that carrier multiplication is apparent.

We discuss these photocurrents in the framework of magnetothermoelectric effects and recent calculations of photocurrent generation in edge channels [1]. Taking into account the observed gate voltage, magnetic field and polarization dependence, we develop a quasi-ballistic model for the measured photocurrent. It includes edge channel transport and charge carrier multiplication and is in good agreement with the experimental results.

[1] Queisser et al. Phys. Rev. Let. **111**, 046601 (2013)

O 7.7 Mon 11:00 ER 270

**Ballistic transport in graphene antidot arrays** — •Andreas Sandner[1], Tobias Preis[1], Christian Schell[1], Paula Giudici[1], Kenji Watanabe[2], Takashi Taniguchi[2], Dieter Weiss[1], and Jonathan Eroms[1] — [1]Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Germany — [2]National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan

We report on the observation of antidot peaks in $\rho_{xx}$ in monolayer-graphene (MLG), encapsulated between hexagonal boron nitride (hBN). The hBN-MLG-hBN heterostructures were fabricated with a dry transfer pick-up technique; subsequently mesas were etched in Hall bar geometry and contacted with 1-dimensional side contacts. The periodic antidot lattice was defined in a following step by additional electron-beam lithography and reactive ion etching.

We performed measurements on stacks with different antidot lattice periods down to 100 nm. Several peaks in magnetoresistance can be identified and assigned to orbits around one and several antidots. This proves ballistic transport in our graphene heterostructures, in spite of the critical etching step for small lattice periods. We show measurements at different temperatures and can study antidots peaks down to very low carrier densities ($n = 2 \cdot 10^{11}\ \text{cm}^{-2}$) and magnetic fields ($B = 0.5$ T). At higher magnetic fields, well defined quantum Hall plateaus with filling factors down to $\nu = 1$ are observed, even at an antidot period of 100 nm.

O 7.8 Mon 11:15 ER 270

**Ballistic supercurrents in suspended graphene** — •Markus Weiss and Christian Schönenberger — Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel

Since the discovery of graphene there have been numerous efforts to use this material as a Josephson weak link between two superconductors. Devices based on oxidized silicon substrates have been produced a few years ago, and have shown bipolar, gate-tuneable supercurrents. The observation of effects are that unique to the Dirac semimetal graphene however has been prevented up to now by the large disorder modulation of the electric potential in graphene on silicon based substrates. For the direct observation of e. g. specular Andreev reflection, the disorder modulation of the Dirac point would have to be smaller that the proximity induced superconducting gap, a regime that cannot be reached in conventional devices. The road to cleaner graphene might go via deposition onto commensurate substrates like hexagonal boron nitride, or the removal of the silicon oxide substrate and suspension of graphene. The latter technique has been perfected in the recent years for devices with normal metal contacts, but turned out to be difficult to realize for superconducting contacts due to incompatibilities of superconducting materials with the fabrication process.

We have developed a device architecture that allows the realization of suspended graphene devices with superconducting contacts, and will show first experimental results, like the ballistic Josephson current through a graphene weak link.

## O 8: Organic-Inorganic Perovskite Semiconductors (HL with CPP)

Time: Monday 9:30–11:00 Location: ER 164

O 8.1 Mon 9:30 ER 164

**Tunable ferroelectric polarization and its interplay with spin-orbit coupling in tin iodide perovskites** — •Silvia Picozzi[1], Alessandro Stroppa[1], Domenico Di sante[1], Paolo Barone[1], Menno Bodkam[2], Georg Kresse[2], Cesare Franchini[2], and Myung-hwan Whangbo[3] — [1]CNR SPIN L'Aquila (IT) — [2]Univ. Vienna, Fac. Physics Wien (AT) — [3]North Carolina State Univ. Raleigh (USA)

Ferroelectricity is a potentially crucial issue in halide perovskites, breakthrough materials in photovoltaic research. Using density functional theory simulations and symmetry analysis, we show [1] that the lead-free perovskite iodide (FA)SnI3, containing the planar formamidinium cation FA, (NH2CHNH2)+, is ferroelectric (FE). In fact, the perpendicular arrangement of FA planes, leading to a "weak" polarization, is energetically more stable than parallel arrangements of FA planes. Moreover, we show that the "weak" and "strong" FE states with polar axis along different crystallographic directions are energetically competing. Therefore, at least at low temperatures, an electric field could stabilize different states with the polarization rotated by 45 degrees, resulting in a highly tunable ferroelectricity appealing for multi-state logic. Intriguingly, the relatively strong spin-orbit coupling in non-centrosymmetric (FA)SnI3 gives rise to a coexistence of Rashba and Dresselhaus effects and to a spin-texture that can be induced, tuned and switched by an electric field.

[1] A.Stroppa, D.Di Sante, P.Barone, M.Bodkam, G.Kresse, C.Franchini and S.Picozzi, Nature Comms. (in press)

O 8.2 Mon 9:45 ER 164

**In situ XRD monitoring of phases formed during growth of co-evaporated perovskite thin films** — •Juliane Borchert[1], Paul Pistor[1], Wolfgang Fränzel[1], René Csuk[2], and Roland Scheer[1] — [1]Martin-Luther-University Halle-Wittenberg, Physics Department, Halle, Germany — [2]Martin-Luther-University Halle-Wittenberg, Organic Chemistry Department, Halle, Germany

Currently, information on the phases and crystal structures, which form during the growth and annealing of $(CH_3NH_3)Pb(I,Cl)_3$ perovskite films is scarce. To gain an insight into these, we studied thin films during their growth. Films were grown through co-evaporation of $(CH_3NH_3)I$ and $PbCl_2$ or $PbI_2$. In situ x-ray diffraction (XRD) was utilized to study phase formation in real time. Films grown by evaporation of $PbCl_2$ and MAI exhibited a cubic crystal structure and two different $(CH_3NH_3)Pb(I_xCl_{(1-x)})_3$ phases could be distinguished for varying $(CH_3NH_3)I$ to $PbCl_2$ flux ratios. They differed in their crystal structure observed by XRD, optical absorption properties and I/I+Cl ratio (either above 0.95 or below 0.5). For films grown with $PbI_2$ and MAI a tetragonal structure was observed. To monitor thermally induced changes and decomposition, we studied the films during heating. Below $200°C$, recrystallization was observed. The chlorine free films additionally showed a transition from tetragonal to cubic structure. Above $200°C$ decomposition was observed. These results show the strong dependence of the phase formation on varying growth conditions. The formed structures can be monitored and adjusted in real time with the help of in situ XRD.

O 8.3 Mon 10:00 ER 164

**Electroabsorption spectroscopy investigation and hysteresis study of perovskite solar cells** — •Cheng Li[1], Steffen Tscheuschner[2], Tanaji Gujar[1], Johannes Kiessling[1], Anna Köhler[2], Mukundan Thelakkat[1], and Sven Hüttner[1] — [1]Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany — [2]Experimental Physics II, University of Bayreuth, 95440 Bayreuth, Germany

Solution-processed organic-inorganic perovskite solar cells (e.g. $CH_3NH_3PbI_{3-x}Cl_x$ and $CH_3NH_3PbI_3$ ) currently show the highest and most promising performances. However, the hysteresis in the J-V curve, i.e. the history dependence of the applied voltage, is still not sufficiently understood. This hysteresis is related to the way how perovskite solar cells are processed. This process exhibits significant influence on the electronic properties of these photovoltaic devices. In this respect, we study the temperature dependent dynamic processes in these pervoskite solar cells by characterizing their current-voltage behaviour. Through this method, we can elucidate the migration of ions and the origin of the hysteresis behaviour. Furthermore, we also use electroabsorption (EA) spectroscopy, a unique non-invasive characterization approach, to investigate the built-in potential in the working device. In this way, we can understand the interaction at the interface between the perovskite active layer and electrodes, providing guideline to optimize the device architecture.

O 8.4 Mon 10:15 ER 164

**Rutherford Backscattering Spectroscopy of Mass Transport by Transformation of $PbI_2$ into $CH_3NH_3PbI_3$ within np-$TiO_2$** — •Felix Lang[1], Albert Juma[1,2], Voranuch Somsongkul[1,3], Thomas Dittrich[1], and Marisa Arunchaiya[3] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — [2]Tallinn University of Technology, Department of Materials Science, Ehitajate tee 5, Tallinn 19086, Estonia — [3]Department of Materials Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

A key technique in methylammonium lead iodide ($CH_3NH_3PbI_3$) thin film preparation is the sequential transformation of an inorganic precursor layer such as $PbI_2$, infiltrated in nanoporous $TiO_2$ to the final $CH_3NH_3PbI_3$ by dipping into an organic precursor solution containing $CH_3NH_3I$. Here, we present an investigation on the mass transport during transformation by Rutherford backscattering spectroscopy (RBS). Energy dispersive X-Ray (EDX) spectroscopy mapping of cross sections first, revealed a homogenious $PbI_2$ infiltration in nanoporous $TiO_2$ before transformation and second, an accumulation of Pb and I at the surface after transformation. Quantitative depth profiles of Pb and I were obtained from RBS analysis. An instant degradation of $CH_3NH_3PbI_3$ upon $^4He^+$ ion radiation was found. The concentration profiles of Pb could be simulated with a one dimensional diffusion model taking into account an effective diffusion coefficient of Pb in the nanocomposite (about $1.5 \cdot 10^{-11}$ $cm^2/s$) as well as a parameter considering frazzling at the surface due to formation of crystallites.

O 8.5 Mon 10:30 ER 164

**Fluorescence studies on organometal halide perovskite nanoparticles** — •Niklas Mutz[1,2], Carlos Cárdenas-Daw[1,2], Ming Fu[1,2], Verena Hintermayr[1,2], Mathias Vollmer[1,2], Jacek Stolarczyk[1,2], Alexander Urban[1,2], and Jochen Feldmann[1,2] — [1]Photonics and Optoelectronics Group, Ludwig-Maximilians-Universität München, Amalienstr. 54 80799 München, Germany — [2]Nanosystems Initiative Munich Schellingstraße 4 80799 München, Germany

During recent years organometal halide perovskite based solar cells have shown a significant rise in power conversion efficiency. Despite this improvement in fabricating efficient perovskite solar cells, the underlying photophysical properties are not yet fully understood. An important insight into processes such as charge generation and separation can be obtained by studying single particles instead of disordered films. In this project we investigate the morphology and photoluminescence properties of individual lead halide perovskite particles by varying the chemical synthesis procedure. In particular we investigate their temperature dependent photoluminescence signal and in addition have performed electric field-dependent studies to get insight into the charge separation process.

O 8.6 Mon 10:45 ER 164

**Band structure and optical absorption of halide organometal perovskites from first principles** — •Menno Bokdam, Tobias Sander, Cesare Franchini, and Georg Kresse — University of Vienna, Faculty of Physics, Sensengasse 8, A-1090 Vienna, Austria

The high efficiency of lead halide organic perovskite solar cells has raised many questions on the mechanisms at work here. An accurate description of the macroscopic dielectric properties is essential for understanding the origin of the materials ability to convert light to electricity. In this talk, we present an accurate account of the electronic, optical and excitonic properties of twelve halide organometal perovskites $\mathrm{ABX_3}$ $(\mathrm{A = CH_3NH_3^+, HC(NH_2)_2^+; B = Pb, Sn; X = Cl, Br, I})$ by means of many-body first principles methods. We use optimized structures obtained at room temperature using parallel tempering molecular dynamics. Quasi particle band structures and absorption spectra are calculated at the $\mathrm{GW_0}$ level. Electron-hole interactions have been included in the dielectric function by solving a Bethe-Salpeter equation for the polarizability. We demonstrate that a description beyond independent particles is necessary to describe the onset of the optical absorption. The calculated degree of localization of the excitons in k-space indicates Wannier-Mott type excitons with binding energies ranging from 30 meV ($\mathrm{ABI_3}$) and 100-200 meV ($\mathrm{ABCl_3}$). To validate our predictions, we compare the results with available experimental data (band gap and optical absorption).

## O 9: Transition-Metal Dichalcogenides and Boron Nitride (HL with O/TT)

Time: Monday 11:45–13:00 Location: ER 270

O 9.1 Mon 11:45 ER 270

**k· p theory for two-dimensional transition metal dichalcogenide semiconductors** — •Andor Kormanyos and Guido Burkard — University of Konstanz

We present **k· p** Hamiltonians (for a review see [1]) parametrised by ab initio density functional theory calculations to describe the dispersion of the valence and conduction bands at their extrema (the $K$, $Q$, $\Gamma$, and $M$ points of the hexagonal Brillouin zone) in atomic crystals of semiconducting monolayer transition metal dichalcogenides. We review the parametrisation of the essential parts of the **k· p** Hamiltonians for $\mathrm{MoS_2}$, $\mathrm{MoSe_2}$, $\mathrm{WS_2}$, and $\mathrm{WSe_2}$, including the spin-splitting and spin-polarisation of the bands We use **k· p** theory to analyse:

i) optical transitions in two-dimensional transition metal dichalcogenides over a broad spectral range;

ii) to discuss magnetotransport properties of the charge carriers in the $K$ and $-K$ valleys.

[1] A. Kormányos, G. Burkard et al, arXiv:1410.6666

O 9.2 Mon 12:00 ER 270

**Coulomb-Induced Valley Coupling in Transition Metal Dichalcogenides** — •Gunnar Berghäuser, Andreas Knorr, and Ermin Malic — Institut für Theoretische Physik, Nichtlineare Optic und Quantenelektronik, Technische Universität Berlin, Germany

Within a microscopic model we investigate the impact of Coulomb-induced intervalley coupling on the optical properties of transition metal dichalcogenides (TMDs). Our approach is based on the density matrix formalism and allows an analytical treatment of the excitonic absorption under the influence of intervalley coupling. We find that the strong Coulomb interaction in these atomically thin 2-dimensional materials couples resonant excitonic states in K and K' valleys [1]. This coupling leads to a splitting of excitonic absorption peaks in the range of the trion binding energy. We further investigate the impact of experimentally accessible parameters, such as doping, dielectric environment, and the detuning of resonant states in the K and K' valley, on the intervalley coupling. The gained insights are of crucial importance for the application of TMDs in valleytronics.

[1] Gunnar Berghäuser and Ermin Malic, "Analytical approach to excitonic properties of $\mathrm{MoS_2}$", Phys. Rev. B 89, 125309 (2014)

O 9.3 Mon 12:15 ER 270

**Coupled spin-valley-dynamics in singlelayer transition metal dichalcogenides** — •Gerd Plechinger, Nicola Paradiso, Philipp Nagler, Sven Gelfert, Christoph Strunk, Christian Schüller, and Tobias Korn — Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93040 Regensburg, Germany

Single layers of transition metal dichalcogenides (TMDCs) like $\mathrm{MoS_2}$ and $\mathrm{WS_2}$ can be produced by simple mechanical exfoliation. Offering a direct bandgap at the K-points in the Brillouin zone, they represent a promising semiconductor material for flexible and transparent optoelectronic applications. Due to inversion symmetry breaking together with strong spin-orbit-interaction, the valley and spin degrees of freedom are coupled in singlelayer TMDCs. Via circularly polarized optical excitation, an efficient polarization of the $K^+$ or the $K^-$ valley can be generated. Here, we optically investigate the dynamics of these coupled spin-valley polarizations in singlelayer $\mathrm{MoS_2}$ and singlelayer $\mathrm{WS_2}$ by means of time-resolved Kerr rotation (TRKR) and display the dependence of the spin lifetime on the temperature and the excitation energy. Moreover, we probe the influence of mild annealing on the lifetimes.

O 9.4 Mon 12:30 ER 270

**Low-temperature photoluminescence of 2D Dichalcogenides and indirect excitons in their heterostructures** — •Philipp Nagler[1], Gerd Plechinger[1], Philipp Tonndorf[2], Steffen Michaelis de Vasconcellos[2], Rudolf Bratschitsch[2], Christian Schüller[1], and Tobias Korn[1] — [1]Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93040, Regensburg, Germany — [2]Physikalisches Institut, Westphälische Wilhelms-Universität Münster, 48149, Münster, Germany

Two-dimensional transition-metal dichalcogenides (TMD) have recently emerged as a promising class of direct-gap semiconductors. Here, we present low-temperature photoluminescence (PL) measurements of four different monolayer TMDs, namely $\mathrm{MoS_2}$, $\mathrm{MoSe_2}$, $\mathrm{WS_2}$ and $\mathrm{WSe_2}$. The diselenides show a clear splitting of neutral exciton and trion which enables us to deduce the binding energy of the trion. Furthermore, by using a deterministic transfer technique we are able to fabricate van-der-Waals heterostructures consisting of different 2D TMDs. At room temperature, we observe indirect excitons at the interface which probably stem from a spatial separation of electrons and holes. Power-dependent PL measurements on the heterostructures allow us to alter the excitonic regime and to probe saturation effects of the system.

O 9.5 Mon 12:45 ER 270

**Synthesis of atomically thin hexagonal boron nitride films on polycrystalline nickel substrates using MBE** — •Siamak Nakhaie, Joseph M. Wofford, Timo Schumann, Uwe Jahn, João Marcelo Lopes, and Henning Riechert — Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany

Hexagonal boron nitride (h-BN) has recently been the subject of an intense research effort. This has in large part been driven by the suitability of h-BN for integration into heterostructures with other 2-dimensional materials, such as graphene [1]. We report the synthesis of h-BN on polycrystalline Ni foils by molecular beam epitaxy (MBE) from elemental B and N. The presence of a well-ordered, crystalline h-BN film on the Ni foil substrate was confirmed using Raman spectroscopy, which revealed a sharp peak at 1365 $\mathrm{cm^{-1}}$. The ubiquity of wrinkle structures in numerous atomic force microscopy scans, together with the uninterrupted observation of the h-BN Raman signal, offer strong evidence of a continuous h-BN film. Using shorter duration depositions we were able to gain insight into the nucleation and growth behavior of h-BN before forming a closed film. According to scanning electron microscopy (SEM) images, we observed the morphology of sub-monolayer h-BN islands to evolve from star-shaped to much larger compact triangles with increasing growth temperature. SEM micrographs also clearly showed points of increased contrast at the approximate geometric centers of the islands, suggesting that the h-BN nucleated heterogeneously. [1] C.R. Dean et al., Nat. Nanotechnol. 5 (2010) 722

# O 10: Metal/Water Interfaces: Structure and Reactivity

Time: Monday 15:00–18:30 Location: HE 101

O 10.1 Mon 15:00 HE 101

**Adsorption of water and anions on noble metal electrodes: a surface vibrational spectroscopy study** — •Yujin Tong, Martin Wolf, and R. Kramer Campen — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

Reactions at noble metal electrode / electrolyte solution interfaces play a key role in electrochemistry. Despite their importance, our understanding of the mechanisms underlying this chemistry is still surprisingly limited. For example, the interpretation of the features of cyclic voltamograms for platinum single crystals in contact with various electrolyte solutions is still essentially speculative (*e.g.* see Catalysis Today, 202 (2013) 105). In these and similar systems the principle obstacle towards insight is a lack of an *in-situ* experimental probe of the population and structure of adsorbed hydrogen, hydroxyl groups, water and anions. Here we overcome this challenge by employing surface specific vibrational spectroscopy, Sum Frequency Generation (SFG), within a flow thin layer electrochemical cell, to concurrently characterize the potential dependent population and structure of surface hydroxyl, water, anions and reactive intermediates at Au and Pt surfaces during the electrochemical oxidation of formic acid. This approach allows the clear identification of bridge-bonded formate, interfacial hydroxyl and water and the evolution of each of these species as a function of potential.

O 10.2 Mon 15:15 HE 101

**On-line Detection of Different Concentrations of Organic Molecules Using a SERS Microfluidic Device** — •Oana M. Buja[1,2], Ovidiu D. Gordan[1], Nicolae Leopold[2], Andreas Morschhauser[3], Jörg Nestler[3], and Dietrich R.T. Zahn[1] — [1]Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz, Germany — [2]Faculty of Physics, Babes-Bolyai University, Kogalniceanu 1, 400084 Cluj-Napoca, Romania — [3]Fraunhofer Institute for Electronic Nano Systems, Technologie Campus 3, 09126 Chemnitz, Germany

In recent years the integration of microfluidic technology with powerful spectroscopic techniques such as surface-enhanced Raman scattering (SERS), has become important for analytical studies of hazardous chemicals. Here, we propose a SERS microfluidic device used for online detection and monitoring of different concentrations of two model organic molecules (caffeine and malachite green). The SERS active silver spot was synthesized on the bottom of the capillary when the laser beam ($\lambda = 514.7$ nm) was focused on a continuous flow of silver nitrate and sodium citrate[1]. Afterwards, different concentrations of selected analytes were injected and sequential SERS spectra were acquired. The adsorption of the molecules was investigated by monitoring the specific bands of caffeine (648 cm$^{-1}$) and malachite green (1617 cm$^{-1}$), respectively. By combining SERS and microfluidic technology a fast and reproducible on-line detection of organic molecules was achieved.

References: [1]N. Leopold, B. Lendl, Anal. Bioanal. Chem., 2010, 396, 2341-2348.

O 10.3 Mon 15:30 HE 101

**Hydrogen Bonding Within Water/Hydroxyl Overlayers on Rh(111)** — •Christine McMahon, Alan Massey, Andrew Hodgson, and George Darling — Surface Science Research Centre, Department of Chemistry, University of Liverpool, Liverpool, L69 3BX

At metal surfaces, water ice structures are determined by a competition between optimizing the bonding of molecules to the surface and optimizing the hydrogen bonding within the layer. On some metals the water overlayer is partially dissociated, this can be induced by preadsorbing oxygen, leading to a mixed OH+H2O overlayer on metals where dissociation is not spontaneous. We have used Density Functional Theory calculations to examine partially dissociated overlayers produced on Rh(111). Specifically we are looking to address questions that cannot be definitively answered by experiment: what is the optimum ratio of OH to H2O, and do the resultant structures favour Bjerrum defects (defects where H atoms point to each other rather than participating in hydrogen bonding or pointing into/away from the surface), as found on Cu surfaces.

O 10.4 Mon 15:45 HE 101

**Free energy assessment of water structures and their dissociation on Ru(0001)** — •Guillem Revilla-López, Piotr Błoński, and Núria López — Institute of Chemical Research of Catalonia, ICIQ, Av. Països Catalans 16, 43007 Tarragona, Spain

The structure and dissociation degree of the first water and heavy water adlayers on hexagonal close-packed metals is a keystone in disciplines such as catalysis, and surface science. Ru(0001) is considered as a model for such interactions since hexagonal Ice patterning and variable water dissociation are present on it. We have assessed the free energy landscape of the adsorption of different water motifs experimentally reported on Ru(0001). Our work provides computational results rationalizing the driving forces of Ice-like bilayer formation on Ru(0001) by describing thermodynamically feasible pathways. The key role of both electrostatics as a driving force and the recently discovered Chains-4a motif as a key intermediate structure have been revealed in the formation of molecular and dissociative Ice-like bilayers and other complex patterns. Thus, new routes for bilayer formation are proposed based on non-cluster structures like Rosette and Island. Further on, the isotopic and temperature dependent balance of dissociation degrees for the Ice-like bilayer and their troubled experimental determination are rationalized by configurational entropy contributions.

O 10.5 Mon 16:00 HE 101

**Water adsorption structures on the step edge of Pt(533) and Pt(553)** — •Manuel Kolb[1], Jasper Wermink[1], Jon Derouin[2], Rachel Farber[2], Dan Killelea[2], Ludo Juurlink[1], and Marc Koper[1] — [1]University Leiden, Leiden, The Netherlands — [2]Loyola University Chicago, Chicago, USA

The water-metal interface is being studied intensively today, due to its importance for electrochemistry and fuel cell applications. Many fundamental studies in the past have targeted the Pt(111)-Water system, however this model has clear deficits, namely the absence of step edges, corners and kinks, when comparing it to nano-particles which are important for industrial applications.

In this study we present DFT (density functional theory) calculations of water adsorption structures on the Pt(533) and Pt(553) surfaces at coverages significantly beyond the ones studied previously for these systems.

We compare the adsorption geometries and energies on the Pt(533) and Pt(553) surface to elucidate the influence of the type of step edge on the preferred adsorption geometries. We furthermore report the clear tendency of water to adsorb in an H-down configuration similar to the situation on Pt(111), however with significantly increased driving force towards this configuration. To verify the approach taken, we plan to compare our results to STM measurements performed on stepped single-crystal surfaces of the same orientation.

O 10.6 Mon 16:15 HE 101

**Neural Network-Based Molecular Dynamics Simulations of the Water-Copper Interface** — •Suresh Kondati Natarajan, Tobias Morawietz, and Joerg Beher — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

The interaction of water with metal surfaces is an important research topic in electrochemistry and surface science. However, realistic structural models of solid-liquid interfaces including surface defects like adatoms and steps are notoriously difficult to describe by efficient atomistic potentials. High-dimensional neural network (NN) potentials [1-2] have been demonstrated to provide an efficient and accurate way to construct interatomic potentials with close to first-principles quality. Here, we present an application of NN potentials to study the water-copper interface. preliminary results are discussed and compared to density functional theory data.

O 10.7 Mon 16:30 HE 101

**Comparing density functionals in modeling electrode-electrolyte interfaces** — •Sung Sakong and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Atomistic modeling of electrode-electrolyte interfaces requires an accurate description of electrode-water interactions in which dispersion interactions play a crucial role. Because of the lack of van der Waals interactions in conventional density functionals, pair-wise semi-empirical corrections or non-local functionals with an approximated dispersion interactions are necessary to improve the descriptions of the interfaces. Tonigold and Groß [1,2] demonstrated that the RPBE+D3 [3] method reproduces adsorption properties of water layers and structural properties of liquid water correctly. We extend these studies to address electrode-electrolyte interfaces using both explicit and implicit water models. The implicit water model in which water is described by a polarizable dielectric continuum is assumed to act as a thermodynamic reservoir. This allows to quantify the contribution of the electrode potential and solvation effects on the water-electrode interaction. Formation enthalpies of simple adsorbates such as H, O or OH on Pt in the presence of an electrolyte are derived using a combination of explicit and implicit water models. Here, several density functionals with/without dispersion corrections will be compared.

[1] K. Tonigold and A. Groß, J. Comput. Chem. **33**, 695 (2012)
[2] K. Forster-Tonigold and A. Groß, JCP **141**, 064501 (2014)
[3] S. Grimme *et al.*, J. Chem. Phys. **132**, 154104 (2010)

O 10.8 Mon 16:45 HE 101

**Equilibrium coverage of halides on metals electrodes** — •Florian Gossenberger, Tanglaw Roman, and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Under acidic conditions, the specific adsorption of anions is an integral part of the formation of the electric double layer at electrochemical metal/electrolyte interfaces. We studied the adsorption of the halides $Cl^-$, $Br^-$ and $I^-$ on Pt(111) and Cu(111) using density functional theory calculations [1]. Based on a thermodynamic approach, the stable equilibrium coverage is linked to the electrode potential without taking the electrochemical environment explicitly into account. Although there are still some quantitative discrepancies with experiment, the qualitative trends derived from the calculations are consistent with experimental observations, in particular as far as the stability of high-coverage halide structures is concerned.

However, under more realistic conditions and low electrode potentials, platinum is always covered with hydrogen, which is always available in an aqueous electrochemical environment. Therefore, mixed coverages of the halides with co-adsorbed hydrogen are considered in the next step to simulate the double layer and the solid-liquid interface at the electrode surface.

[1] Florian Gossenberger, Tanglaw Roman, and Axel Groß, Surf. Sci. **631** (2015), doi: 10.1016/j.susc.2014.01.021 .

O 10.9 Mon 17:00 HE 101

**$H_2O$ adsorption on bimetallic Pt-Ru(0001) surfaces - a low-temperature UHV-STM investigation** — •Martin Schilling, Albert K. Engstfeld, Sylvain Brimaud, and R. Jürgen Behm — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Profound knowledge of the elementary electrochemical/-catalytic processes on catalytically relevant electrode materials requires a detailed understanding of the solid | liquid interface, including the water | metal interaction. The latter has been investigated in detail in earlier studies, using model systems consisting of ice layers adsorbed on monometallic single crystal surfaces.[1,2] Where in former studies only $H_2O$ adsorption on monometallic surfaces were subject of investigation, we present results on the interaction of $H_2O$ with 2D bimetallic PtRu model electrodes. $H_2O$ was deposited under well defined conditions in ultra high vacuum (UHV) at low sample temperatures (100 K - 130 K) on Pt modified Ru(0001) single crystal surfaces. The structures have been investigated with scanning tunnelling microscopy (STM) in a temperature range of 100 K to RT. Depending on the Pt layer thickness on Ru(0001) and the dosing conditions of $H_2O$, a variety of molecular arrangements are observed, which vary from total disorder to well-ordered domains. The influence of substrate | molecule and molecule | molecule interactions are discussed based on the Pt modified Ru(0001) substrate.

[1] P.A. Thiel and T.E. Madey, *Surf. Sci. Rep.* **7** (1987) 211-385.
[2] M.A. Henderson, *Surf. Sci. Rep.* **46** (2002) 1-308.

O 10.10 Mon 17:15 HE 101

**Two-dimensional bimetallic molecular networks as electrocatalyst for oxygen reduction and evolution** — •Benjamin Wurster[1], Doris Grumelli[1,2], Diana Hötger[1], Rico Gutzler[1], and Klaus Kern[1,3] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]Instituto Nacional de Investigaciones Fisicoquímicas, teóricas y aplicadas, La Plata, Argentina — [3]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Inspired by catalytically active bimetallic centers commonly found in biology we prepared bimetallic coordination networks and studied their electrocatalytic properties. Two different functional groups for metal coordiniation of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were used to selectively incoporate different metals in the structures. The samples were prepared under ultra-high vacuum (UHV) conditions by evaporating TPyP containing the first metal (Cu, Fe, or Co) in the pyrollic macrocycle. The second metal (Fe or Co) was sublimed in an additional step and is coordinated by the pyridyl groups. The metal-organic networks were characterized by scanning tunneling microscopy in UHV prior to studying their electrocatalytic activity towards oxygen reduction and evolution in alkaline media. Linear voltammetry experiments show that the electrocatalytic response in the oxygen reduction can be altered by choosing different combinations of metals. The incoporation of the second metal led to a higher oxygen evolution, while the stability of the electrochemical signal was influenced by the central metal within TPyP.

O 10.11 Mon 17:30 HE 101

**Solvent Effects in Co-Catalyzed Oxygen Evolution: Efficient First-Principles Treatment** — •Markus Sinstein[1], Harald Oberhofer[1], Volker Blum[2], and Karsten Reuter[1] — [1]Technische Universität München, Germany — [2]Duke University, USA

Photoelectrochemically driven redox reactions like water splitting or $CO_2$ reduction are prominent examples for energy-conversion from abundant sunlight into solar-fuel type chemical compounds. A detailed analysis of the involved elementary processes via first-principles calculations requires to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte. Beyond traditionally assumed proton-coupled electron transfer (PCET) mechanisms the latter is particularly important in order to address charged reaction intermediates that are likely stabilized by the polar liquid environment. Aiming for a computationally efficient approach that allows for catalyst screening, we implement an implicit solvation scheme based on the Multipole Expansion (MPE) method into the all-electron DFT package FHI-aims. We define the cavity within the dielectric continuum from an iso-density surface which is sampled in a constraint dynamics scheme. As a first step towards modelling the full water splitting reaction, we apply this scheme to the oxygen evolution reaction on gold co-catalysts. These calculations indicate non-negligible solvent effects already for neutral intermediates in PCET mechanisms.

O 10.12 Mon 17:45 HE 101

**Electrocatalytic activity and stability of structurally well defined AgPt/Pt(111) surface alloys-correlation between structure and reactivity** — •Stephan Beckord, Albert K. Engstfeld, Sylvain Brimaud, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, 89069 Ulm, Germany

Bimetallic surface often show electrochemical and catalytic properties different from those of the individual metals. This is evident, e.g., in the oxygen reduction reaction (ORR), where Pt is known to be the most active single metal catalyst. However, in previous studies it was shown that this high activity can be enhanced by modifying Pt with transition or noble metals, such as Ni, Co or Cu.[1] We show results on the electrochemical and electrocatalytic properties of well defined $Ag_xPt_{1-x}$ surface alloys on Pt(111) with increasing Ag content (0%-100% Ag). The surface alloys were prepared under ultra high vacuum (UHV) conditions by physical vapor deposition of Ag on Pt(111), followed by an annealing step to 900 K. Via scanning tunneling microscopy (STM) the atomic distribution in the topmost layer, as well as the abundance of catalytic relevant ensembles (e.g. $Pt_1Ag_2$, $Pt_2Ag_1$) is determined. Subsequently the surfaces are characterized in an electrochemical flow cell attached to the main UHV system with respect to their stability and their ORR activity in $H_2SO_4$. To validate the stability of the surface alloys, they are re-analyzed by STM after the electrochemical measurements. Finally, the experimental results are compared to simulated activities based on DFT calculations.

[1] J. Greeley and J.K. Nørskov, *J. Phys. Chem.* **113** (2009) 4932.

O 10.13 Mon 18:00 HE 101

**First-principles reaction barriers for the splitting of water on Au nanocatalysts** — •Thomas Stecher, Harald Oberhofer, and Karsten Reuter — Technische Universität München

First-principles modeling of electrocatalytic surface reactions is still largely defined by the computational hydrogen approach. This approach evaluates free energy differences between consecutive reaction steps and therewith accounts only for possibly existing thermodynamic barriers. In order to access additional kinetic barriers in the photocatalytic oxidation of water we present an approach based on *ab initio* molecular dynamics (AIMD) simulations and umbrella sampling. For the proton transfer steps we hereby specifically use path-integral AIMD to also capture nuclear quantum effects. As a first showcase system we consider water splitting at a $Au_3$ co-catalyst, which was previously studied within the computational hydrogen electrode approach [1]. This allows to disentangle thermodynamic and kinetic contributions to the individual reaction barriers, as well as to assess the relevance of quantum effects by comparing classically and quantum-mechanically calculated barriers. [1] H. Oberhofer and K. Reuter, J. Chem. Phys. **139**, 044710 (2013).

O 10.14 Mon 18:15 HE 101

**Size dependent electrocatalytic activity of Pt nanoparticles on Ru(0001) supported graphene - hydrogen evolution reaction** — •Jens Klein, Albert K. Engstfeld, Sylvain Brimaud, and R. Jürgen Behm — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

In water electrolysers and fuel cell technology, carbon supported Platinum nanoparticles are the state-of-the-art catalyst for the hydrogen evolution reaction. The performance of this catalyst depends sensitively on the size, density, shape and stability of the Pt nanoparticles.[1] To get a more detailed understanding on the structure | activity relationship of this particular system, we present results of a model catalyst study on Pt nanoparticles on Ru(0001) supported graphene, investigated in a combined ultra high vacuum (UHV) - electrochemical flow cell setup. The graphene layer was prepared under UHV by ethylene decomposition on Ru(0001) at 1050 K. Lateral Pt nanoparticle arrays with well defined size distributions were grown by physical vapor deposition and characterized by scanning tunneling microscopy (STM). The sizes of the Pt nanoparticles are below 3 nm and they consist of 10-80 atoms in average. After structural analysis, the model electrodes were transferred to an electrochemical flow cell, attached to the UHV system, to investigate their electrocatalytic activity during the hydrogen evolution reaction (HER) by cyclic voltammetry. Finally, to assure that the particles are stable in the electrocatalytic environment, the model electrodes were again characterized by STM in UHV afterwards. [1] M.T.M. Koper, *Nanoscale* **3** (2011) 2054.

## O 11: Ultrafast and Nonlinear Plasmonics

Time: Monday 15:00–18:00 Location: MA 004

O 11.1 Mon 15:00 MA 004

**Surface plasmon polariton induced shortening of the optical response in perforated gold films** — •Felix Spitzer[1], Martin Pohl[1], Boris A. Glavin[2], Vladimir Belotelov[3], Ilya Akimov[1], Sachin Kasture[4], Arvind S. Vengurlekar[4], Achanta V. Gopal[4], and Manfred Bayer[1] — [1]Technische Universität Dortmund, Dortmund, Germany — [2]V.E. Lashkaryov Institute of Semiconductor Physics, Kiev, Ukraine — [3]Lomonosov Moscow State University, Moscow, Russia — [4]Tata Institute of Fundamental Research, Mumbai, India

Ultrafast relaxation dynamics of a laser-heated periodically perforated gold film are investigated using a femtosecond pump-probe technique with 30 fs pulses far from intrinsic gold resonances. The grating period is 595 nm with a thickness of 120 nm and 110 nm slit width. Changes of differential transmission are measured time- and angular-resolved and fitted afterwards using the nonequilibrium electron model to obtain the characteristic relaxation times. We observe, that the pump induced optical response becomes significantly shorter when the electrons in metal are excited with surface plasmon polaritons. These results uncover the role of thermal conductivity of electrons which becomes important in case of strongly inhomogeneous spatial distribution of hot carriers.

O 11.2 Mon 15:15 MA 004

**Probing electron relaxation in single metal nanotips with terahertz-induced field emission** — •Lara Wimmer, Georg Herink, Sergey V. Yalunin, and Claus Ropers — 4. Physical Institute - University of Göttingen, Göttingen, Germany

We implemented a streaking-type photoemission experiment at individual metal nanotips [1], employing single-cycle terahertz (THz) transients and femtosecond near-infrared (NIR) pulses. In a first scenario, the photoelectrons are generated by the NIR pulses and subsequently accelerated in the local THz electric field. Due to the high confinement of the THz-induced near-field at the tip apex, the photoelectrons leave the electric field in much less than one optical half-cycle [2]. This allows for a phase-resolved characterization of the THz near-field and for a control of the photoelectron kinetic energy spectra.

In a second set of measurements, we increase the local THz field strength to above 3 V/nm, inducing THz field emission [3]. Slightly below the threshold for cold field emission, the THz transient triggers the emission of NIR-excited hot electrons in the metal. The electron relaxation is quantitatively characterized by varying the relative time delay between the two pulses, and we find direct evidence for a confinement-induced prolongation of cooling times as compared with planar surfaces.

[1] Wimmer et al., Nature Physics 10, 432-436 (2014).
[2] Herink et al., Nature 483, 190-193 (2012).
[3] Herink et al., New Journal of Physics, in press (2014).

O 11.3 Mon 15:30 MA 004

**Transient absorption spectroscopy on gold nanorods coated with molecular J-aggregates** — •Thomas Simon[1,2], Dzimitry Melnikau[3], Alexander Urban[1,2], Jochen Feldmann[1,2], and Yury Rakovich[3] — [1]Chair for Photonics and Optoelectronics, Ludwig-Maximilians-Universität München, Amalienstr. 54, 80799 Munich, Germany — [2]Nanosystems Initiative Munich (NIM), Schellingstr. 4, 80799 Munich, Germany — [3]Centro de Física de Materiales (MPC, CSIC-UPV/EHU), Donostia International Physics Center (DIPC), Po Manuel de Lardizabal 5, Donostia-San Sebastian 20018, Spain

We have performed femtosecond transient absorption spectroscopy on cyanine based molecular J-aggregates covering the surface of gold nanorods. By changing the aspect ratio of the rods or choosing J-aggregates with different HOMO-LUMO transition energies, the coupling between excitonic and plasmonic resonances can be tuned and controlled. We have analyzed the nonlinear optical responses of purely excitonic, purely plasmonic and hybrid excitonic-plasmonic transitions. The transient behavior of the absorption changes at the hybrid transition frequencies gives further insight into coupling mechanisms between excitons and plasmons.

O 11.4 Mon 15:45 MA 004

**Short-range surface plasmonics on atomically flat thin single gold nanocrystals: Electron emission from a 60 nm spot at 800 nm wavelength** — •Bettina Frank[1], Philip Kahl[2], Thomas Weiss[1], Liwei Fu[3], Michael Horn von Hoegen[2], Frank Meyer zu Heringdorf[2], and Harald Giessen[1] — [1]4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany — [2]Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany — [3]Institute of Applied Optics, University of Stuttgart, Germany

We observe short-range surface plasmons in atomically flat single gold nanocrystals with a thickness in the 20-40 nm range. The crystals are grown electrochemically on atomically flat silicon wafers and structured with FIB-milled patterns on the surface. Sub-20 fs laser pulses at 800 nm in normal incidence geometry excite long-range as well as short-range surface plasmons. The latter ones possess plasmon wavelengths in the 140-180 nm range and exhibit considerably reduced propagation velocity. Using PEEM we can image these plasmons, statically as well as in a time-resolved fashion. Using circular grating patterns, nanofocusing down to 60 nm is experimentally observed.

This work was supported by DFG (SPP1391), BMBF, BW Stiftung, and ERC.

O 11.5 Mon 16:00 MA 004

**Nonlinear Plasmo-Emission of Electrons from Focused Surface Plasmon Polaritons** — •Philip Kahl, Daniel Podbiel, Andreas Makris, Simon Sindermann, Michael Horn-von Hoegen, and Frank-J. Meyer zu Heringdorf — Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany

In a photoemission electron microscope with normal incidence light geometry we recently observed high-order photoemission of electrons from focused surface plasmon polaritons (SPPs) on a silver film. The SPPs are excited at concentric circular gratings, have convex wave fronts and propagate from opposite directions into the center of the inlying disc. By combining sub 20 fs laser pulses and a home-built Mach-Zehnder interferometer to a pump-probe experiment we are able to temporarily resolve the propagation of these SPPs, the formation of a standing wave at the center and the reversal of the wave front curvature of the SPPs. The fact that the circles have diameters larger than 40 microns guarantees that the laser is not present anymore when the SPPs reach the center. Hence, the electrons are emitted from the plasmonic field alone, which is why we call this effect plasmo-emission. We also captured energy-filtered photoelectron images and analyzed the kinetic energy spectra of the electrons originating from the standing wave fringes at the focal spot. The spectra indicate photoemission orders of up to five.

O 11.6 Mon 16:15 MA 004

**Shaping and spatiotemporal characterization of sub-10-fs pulses focused by a high-NA objective** — •Sebastian Goetz[1], Monika Pawlowska[1], Christian Dreher[1], Matthias Wurdack[1], Enno Krauss[2], Peter Geisler[2], Gary Razinskas[2], Bert Hecht[2,3], and Tobias Brixner[1,3] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Nano-Optics and Biophotonics Group, Experimentelle Physik 5, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [3]Röntgen Center for Complex Material Systems (RCCM), Am Hubland, 97074 Würzburg, Germany

For the investigation of ultrafast processes on the nanoscale by far-field radiation, the temporal resolution of femtosecond laser pulses has to be combined with the spatial resolution of a high-NA microscope. We combine confocal microscopy with phase and amplitude pulse shaping of few-cycle NIR pulses using an LCD pulse shaper in $4f$ single-pass geometry. By utilizing the pulse compression algorithm PRISM, a pulse length of 10 fs could be achieved at the focus position. The capability of the setup is demonstrated by investigating the influence on the diffraction-limited focus of a high-NA objective, LCD imperfections and spatio-temporal coupling. By scanning of gold nanorods through the focal plane, position-dependent reflections within the focus reveal the spectrally resolved intensity profile and the spatial dependency of the pulse arrival time. The ability to shape the light fields and the availability of high peak powers open the path to all-optical control of near-field propagation in the linear and nonlinear regimes.

O 11.7 Mon 16:30 MA 004

**Local Nonlinear Spectroscopy of Single Gold Nanostructures** — •Daniela Wolf, Thorsten Schumacher, and Markus Lippitz — Experimental Physics III, University of Bayreuth

While higher harmonics generation is a commonly known effect and is used in many applications, the origin of the higher harmonics light generated in plasmonic nanostructures is still not fully understood. Contrary to the luminescence from gold structures, higher harmonics generation is a coherent process so that interference effects come into play when more complex structures are considered. In our experiments, we investigate the response of different gold nanostructures upon excitation with infrared light. The homogeneous luminescence background as well as the interference effects in the third harmonic signal can be observed in spectrally resolved backfocal plane images. In combination with calculated interference patterns from a dipole model, this method allows conclusions about the spatial origin of THG.

O 11.8 Mon 16:45 MA 004

**Second-harmonic generation with double resonant hybrid plasmonic/dielectric antennas** — •Heiko Linnenbank[1], Yevgen Grynko[2], Jens Förstner[2], and Stefan Linden[1] — [1]Physikalisches Institut, Universität Bonn, Germany — [2]Institut für Elektrotechnik und Informationstechnik, Universität Paderborn, Germany

In several studies it has been shown that the excitation of plasmonic resonances in gold nanostructures with ultrashort light pulses can give rise to large second and third harmonic signals. Here, we demonstrate that the second harmonic generation efficiency of metallic nanostructures can be increased by depositing a dielectric material with a large second order nonlinear coefficient in the hot spots of the structures. By varying the geometry of the nanostructures and by performing nonlinear spectroscopy we rule out that the enhancement of the second harmonic signal is due to a trivial shift of the plasmonic resonance frequency caused by the incorporation of the dielectric material. Furthermore, we have performed nonlinear experiments with double-resonant metallic nanostructures that exhibit plasmonic resonances at both the frequency of the pump light and the generated second harmonic light. Compared to metallic nanostructures which are only resonant to the pump light, the double-resonant structures give rise to larger second harmonic signals. Moreover, they also allow to control the polarisation properties of the generated light.

O 11.9 Mon 17:00 MA 004

**Frequency doubling with second harmonic resonant plasmonic nanostructures** — •Heiko Linnenbank and Stefan Linden — Physikalisches Institut, Universität Bonn, Germany

Second harmonic generation from lithographically defined metallic nanostructures has been a topic of large interest in recent years. In order to take advantage of local field enhancement effects, the samples are typically designed such that one of the plasmonic modes of the respective metallic nanostructure is resonant to the incident pump wave. In contrast, the second harmonic signal usually is not resonant to one of the higher order plasmonic modes. Here we show that also the opposite scheme can be employed for enhanced second harmonic generation. For this purpose, we have performed nonlinear spectroscopic experiments with different metallic nanostructures where rather the second harmonic light drives a plasmonic resonance than the pump field. Our findings can be explained in the framework of the anharmonic oscillator model where the characteristic parameters are extracted from linear extinction measurements.

O 11.10 Mon 17:15 MA 004

**Nonlinear plasmonics of aluminum nanoantennas resonant at the second harmonic frequency** — •Lili Gui, Jaco Fuchs, Bernd Metzger, Dominik Floess, Maxim Nesterov, and Harald Giessen — 4th Physics Institute and Research Center SCoPE, University of Stuttgart, 70569 Stuttgart, Germany

Localized surface plasmon resonances can boost significantly the optical nonlinearity of metallic nanoparticles due to the strongly confined and enhanced electromagnetic near-field. Although some double-resonant and multi-resonant configurations have been employed in order to achieve large nonlinear conversion efficiencies, there has been so far no quantitative investigation to illustrate the role of the plasmonic resonance of the nanoantenna at the harmonic frequency. It is still controversial whether the contribution of the harmonic resonance is adverse, as a loss mechanism due to more absorption, or beneficial, due to higher radiation efficiency.

Through comprehensive experimental studies of the second-harmonic spectroscopy of aluminum nanorods resonant at the second harmonic, we demonstrate that the contribution of the harmonic resonance is higher with regards to increased radiation efficiency than to increased absorption loss, with a clear evidence of larger overall second-harmonic-generation efficiency. The nonlinear response of the nanoantennas can be well explained by an analytic anharmonic oscillator model and nicely reproduced with finite-element simulations.

O 11.11 Mon 17:30 MA 004

**Applying the Otto geometry to observe second-harmonic generation from a surface plasmon resonance** — •Karsten Pufahl[1], Jan Heckmann[1], Nicolai B. Grosse[1], Liuyang Sun[2], John Sipe[3], Xiaoqin Li[2], and Ulrike Woggon[1] — [1]Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — [2]Department of Physics, University of Texas-Austin, USA — [3]Department of Physics, University of Toronoto, Canada

The Otto geometry enables the probing of material surfaces using evanescent fields having well-defined k-vectors. We have demonstrated this technique in the nonlinear optical regime to investigate how the excitation of a surface-plasmon (SP) resonance leads to enhanced second-harmonic generation (SHG) from a silver surface. The analysis of SHG in k-space allows one to infer SP propagation length and the enhancement of the near-field, while being free to vary the air gap which sets the SP-to-photon coupling strength. In contrast to the Kretschmann geometry where one is limited to investigating thin films at a fixed coupling strength, the Otto technique has the additional advantage that surface wave phenomena can also be explored in bulk and opaque samples.

O 11.12 Mon 17:45 MA 004

**Electron tunneling mediated amplification of radiative plasmon decay** — •xiao wang, kai braun, dai zhang, heiko peisert, hilamar adler, thomas chassé, and alfred meixner — Institute of physical and theoretical chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Here we demonstrate electron tunneling mediated amplification of photoluminescence (PL) from an Au-Au junction in a combined tip enhanced near-field optical and scanning tunneling microscope. Luminescence spectra were collected from the same Au-Au junction with different bias voltages with and without laser illumination. Without optical excitation the luminescence spectra show typical plasmon modes in the spectral range from 700-1050 nm excited by inelastic electron tunneling. Under laser illumination at 634 nm, at low bias voltages the PL is dominated by the radiative decay of the laser excited electron-hole pairs from the sp/d interband transition with a single band at 690 nm. At higher bias voltages, the luminescence increases dramatically, showing both the band from electron-hole recombination and the plasmon-modes from inelastic tunneling. The increase of the luminescence from inelastic tunneling is more than an order of magnitude and is attributed to the laser induced hot-electron population closely above the Fermi-level to inelastic tunneling having a higher radiative decay rate than the conducting electrons from the sp-band.

## O 12: Inorganic/Organic Interfaces: Growth II

Time: Monday 15:00–18:15 Location: MA 005

O 12.1 Mon 15:00 MA 005

**Many-Body Dispersion Effects in the Adsorption of Atoms and Molecules at Metal Surfaces** — •Victor Ruiz and Alexandre Tkatchenko — Fritz-Haber-Institut der MPG, Theory Department, Berlin, Germany

Van der Waals (vdW) interactions play an essential role in the structure and stability of atoms and molecules adsorbed at inorganic surfaces. Several promising methods have been developed in recent years for an efficient modeling of these ubiquitous interactions in molecules and solids. However, most of these methods are still based on an effective pairwise treatment of vdW interactions, ignoring the often important many-body contributions to the vdW energy. Here we show that the inclusion of many-body effects in vdW interactions enables us to achieve quantitative predictions in the adsorption energies of atoms and molecules on metal substrates. For this, we employ the recently developed many-body dispersion method coupled with density-functional theory (DFT+MBD) [1,2], which includes many-body effects in the long-range correlation energy to all orders in the dipole approximation. We study the influence of MBD effects on the adsorption structures, energies, and perpendicular vibrational frequencies of a Xe monolayer on transition metal surfaces. We futher study the adsoption of PTCDA ($C_{24}H_8O_6$) on Au(111), and compare to recent measurements of the adsorption energy and vertical adsorption height. [1] Phys. Rev. Lett. 108, 236402 (2012); [2] J. Chem. Phys. 140, 18A508 (2014).

O 12.2 Mon 15:15 MA 005

**LEEM investigation of the initial growth of heteromolecular layers** — •Caroline Henneke[1], Daniel Schwarz[1,2], and Christian Kumpf[1] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and Jülich Aachen Reseach Alliance (JARA)-Fundamentals of Future Information Technology — [2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA

One crucial issue for the performance of organic materials in electronic devices is the ability to specifically design the interfaces between different active layers according to their functional purpose. Heteromolecular films are of highest interest in this context, in particular their initial growth and the structure formation of the first molecular layer since this layer acts as a template for further growth.

The molecules Copper-II-phthalocyanine (CuPc) and 3,4,9,10-perylen-tetra-carboxylic-acid dianhydride (PTCDA) form well-ordered molecular monolayer structures when deposited on Cu(001). We present details of the growth kinetics of the molecular films and their dependence on the temperature and molecular concentrations on the surface during the deposition process. The growth was investigated in situ with LEEM and the geometric structure with LEED.

O 12.3 Mon 15:30 MA 005

**Structural and optical investigation of weakly interacting commensurate organic-organic interfaces in SnPc/PTCDA heterolayers on Ag(111)** — •Marco Gruenewald, Julia Peuker, Matthias Meissner, Falko Sojka, Roman Forker, and Torsten Fritz — Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, Jena 07743, Germany

We report on structural and electronic properties of highly-ordered ultrathin layers of the dye molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and tin(II)-phthalocyanine (SnPc) stacked on Ag(111). The thin films have been structurally characterized by low energy electron diffraction (LEED) and low temperature scanning tunneling microscopy (LT-STM) as well as optically by in situ differential reflectance spectroscopy (DRS) [Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 108, 34-68 (2012)]. Depending on the coverage and on the substrate temperature the SnPc adlayers on top of 1 ML PTCDA/Ag(111) form either three different commensurate registries (with each unit cell different in size and number of molecules) or show a 2D-gas-like behavior. By means of DRS we found that the molecules in all phases show monomer behavior pointing to a rather weak electronic interaction at the organic-organic interface in contrast to conclusions recently drawn for a similar commensurate heterointerface with CuPc instead of SnPc [PRL 108, 106103 (2012)]. Thus, commensurism at organic-organic interfaces cannot necessarily be linked to strong electronic interaction. Additionally, for SnPc films with thicknesses beyond 1 ML we found intermediate phases prior the formation of a SnPc bulk structure.

O 12.4 Mon 15:45 MA 005

**Vibrational properties of stacked and intermixed (CuPc + PTCDA) layers on Ag(111)** — •Sebastian Thussing and Peter Jakob — Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

The vibrational properties and thermal evolution of stacked and intermixed CuPc and PTCDA layers deposited on Ag(111) have been investigated using IR absorption spectroscopy, SPA-LEED, and TDS. For the mixed layers four different monolayer phases have been found depending on the CuPc:PTCDA ratio. Ordering of cold deposited layers sets in after annealing to 250 K and prevails up to 500 K. All mixed phases display characteristic spectroscopic signatures in vibrational spectra. The monolayer phases of CuPc and PTCDA show pronounced interfacial dynamical charge transfer (IDCT). Interestingly, IDCT is attenuated for mixed layers, especially for the respective minority species. This is attributed to energetic shifts of the partially filled 'former LUMO' as a result of intermolecular coupling (through metal charge transfer). For stacked (bi)layers thermal annealing leads to interlayer exchange for CuPc on PTCDA as well as for PTCDA on CuPc which we attribute to the extra energy gain provided by intermixing and charge transfer between the constituents within the monolayer. For PTCDA on CuPc intermixing is found already for T $>$ 200K, while the reverse stacking is stable up to 450K.

O 12.5 Mon 16:00 MA 005

**Heteroorganic layers of CuPc and PTCDA on the Ag(110) surface** — •Kathrin Schönauer[1,2], Serguei Soubatch[1,2], and Frank Stefan Tautz[1,2] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — [2]JARA - Fundamentals of Future Information Technology, Germany

The application potential of organic semiconductors for molecular electronics makes them interesting for fundamental research. Layers consisting only of one type of molecules have been investigated extensively over the last decades. Layers consisting of two different types of organic molecules, e.g. CuPc and PTCDA on the Ag(111) surface [1], are now subject of experiments. In this case, not only the interaction between the metal and the organic substance but also the molecule-molecule interaction is in the focus of research. We present investigations on mixed layers of CuPc and PTCDA on the Ag(110) surface, which is meant to be more reactive than the Ag(111) surface. The lateral arrangement is studied by low temperature scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The analysis of local electronic properties was done using scanning tunneling spectroscopy (STS).

[1] Stadtmüller et al., PRL 108, (106103) 2012

O 12.6 Mon 16:15 MA 005

**Single Iron-Phthalocyanine molecules on Fe/W(001): A non-contact atomic force microscopy study at low temperature in UHV** — •Josef Grenz, Alexander Schwarz, and Roland Wiesendanger — Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany

While magnetic exchange force microscopy (MExFM) has been achieved on various substrates [1,2], the detection of a magnetic signal stemming from a single molecule employing atomic force microscopy (AFM) has not been observed so far. Recent work on Cobalt-Phthalocyanine (CoPC) on Fe/W(110) utilizing spin-polarized scanning tunneling microscopy revealed a strong hybridization of the molecular orbitals and substrate 3d states depending on the molecular adsorption, which affects the magnetic properties of the molecule [3]. In this study we deposit single in the gas phase paramagnetic Iron-Phthalocyanine (FePC) molecules on Fe/W(001) and find 7 different adsorption geometries using non-contact atomic force microscopy (nc-AFM). Particularly, we were able to identify the adsorption sites of the central Fe ion for the different geometries on the antiferromagnetic Fe monolayer on W(001), which will influence the magnetic properties of the molecule in its adsorbed state.

[1] U. Kaiser *et al.*, Nature **446**, 522 (2008).

[2] R. Schmidt *et al.*, Nano Lett. **9**, 200 (2009).

[3] J. Brede *et al.*, Phys. Rev. Lett. **105**, 047204 (2010).

O 12.7 Mon 16:30 MA 005

**Quantitative test of the "surface trans-effect" in an adsorbed metal-organic complex** — •Peter S. Deimel[1], David A. Duncan[1], Tien-Lin Lee[2], Luke A. Rochford[3], Pardeep K. Thakur[2], D. Phil Woodruff[3], Francesco Allegretti[1], and Johannes V. Barth[1] — [1]Physics Department E20, TU München, Germany — [2]Diamond Light Source, Didcot, UK — [3]University of Warwick, Coventry, UK

On-surface coordination chemistry is an emerging field, which holds promise for nanotechnology, molecular spintronics and catalysis [1]. Previous work provided evidence for a "surface trans-effect" where the interaction [2] and even the magnetic coupling [3] between the metal ion of adsorbed metal-organic species and the underlying substrate can be affected by ligation in *trans* position. Corresponding marked changes in height of the metal center with respect to the substrate were theoretically predicted [2].

We present the first quantitative analysis of this effect using normal incidence X-ray standing waves. For iron phthalocyanine on Ag(111) we observe a distinct increase in height of the Fe ion upon $NH_3$ ligation, whereas the tetrapyrrole macrocycle is effectively unperturbed. Our results provide a test-bed for modeling schemes and structure-functionality correlations relevant for technological applications.

[1] J. V. Barth, Surface Science **603** (2009), 1533;

J. M. Gottfried and H. Marbach, Z. Phys. Chem. **223** (2009), 53.

[2] W. Hieringer et al., J. Am. Chem. Soc. **133** (2011), 6206.

[3] Ch. Wäckerlin et al., Nat. Commun. **1** (2010), 61.

O 12.8 Mon 16:45 MA 005

**Adsorption of MoMo-Methyl on Cu(111)** — •Jobynson Kollamana[1], Benjamin Stadtmüller[1], Johannes Stöckl[1], Anneken Grün[2], Manuel Zimmer[2], Markus Gerhards[2], Mirko Cinchetti[1], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center Optimas — [2]Department of Chemistry, University of Kaiserslautern

Metal-organic compounds are promising materials for new types of spintronic devices. While the magnetic and electronic properties of organic molecules in the gas phase are well understood, their behavior on metallic surfaces strongly depends on the interaction in these systems. Therefore, we studied the geometric and electronic properties of (sub)monolayer films of Molybdenum(II) acetate dimer (MoMo-Methyl) adsorbed on Cu(111) by scanning tunneling microscopy and complementary techniques.

For coverages below 1.0ML, the MoMo-Methyl molecules arrange in chains, oriented along high symmetry directions of the Cu(111) surface. Increasing the coverage to one monolayer results in the formation of long range ordered structures with domain sizes of several micrometers.

In addition, the electronic properties of these films were studied by scanning tunneling spectroscopy and photoelectron spectroscopy. Comparing these results to predictions for free MoMo-Methyl molecules allow to reveal the influence of the molecule-substrate interaction on the molecular properties.

O 12.9 Mon 17:00 MA 005

**Temperature-driven demixing of a two-dimensional metal-organic network** — •Rico Gutzler[1], Sören Krotzky[1], Claudius Morchutt[1,2], Vijay Vyas[1], Bettina V. Lotsch[1,3], and Klaus Kern[1,2] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Switzerland — [3]Ludwig Maximilians University and Center for Nanoscience, Munich, Germany

The great majority of reported surface-confined self-assembled molecular networks exhibit a crystalline structure. Under certain conditions, however, do non-crystalline networks form without long-range order, resembling two-dimensional glasses. Here we report a two-component metal-organic network that self-assembles at room temperature into such a glassy state on a crystalline surface. Scanning tunnelling microscopy reveals how an organic semiconducting molecule functionalized with two nitrile groups coordinates coadsorbed iron atoms to create a disordered porous layer. This binary mixture is then exposed to an annealing step, which upon cooling leads to the separation of the two components into spatially separate homogeneous and crystalline domains of either molecules or metal atoms. The first glassy state is thermondynamically not as stable as the second demixed state, although the demixing is accompanied by an entropy penalty equal to the entropy of mixing. The thermodynamic implications of this observation are discussed.

O 12.10 Mon 17:15 MA 005

**Spectroscopic investigation of free base and Manganese 5,10,15-tris(pentafluorophenyl)corrole on Ag(111)** — Mateusz Paszkiewicz[1], •Stefan Müllegger[2], Uwe Gerstmann[4], Hazem Aldahhak[4], Eva Rauls[4], Stefano Tebi[2], Wolfgang Schöfberger[3], Wolf Gero Schmidt[4], Reinhold Koch[2], Johannes Barth[1], and Florian Klappenberger[1] — [1]TUM, Physik department E20,Garching, Germany — [2]JKU, Solid state physics department, Linz, Austria — [3]JKU, Institute of organic chemistry, Linz, Austria — [4]University of Paderborn, Physik department, Paderborn, Germany

In our work we present the first X-ray spectroscopic investigation of free base 5,10,15-tris(pentafluorophenyl)corrole (TPFC) and manganese 5,10,15-tris(pentafluorophenyl)corrole (MnTPFC) on the Ag(111) surface. Our study is based on X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy measurements and combined with density functional theory (DFT) simulations. For both species we characterized all relevant regions and edges. Our analysis indicates a mixed 3+/4+ state of the Mn inside the MnTPFC. Furthermore, polarization-dependent NEXAFS measurements indicate for both molecules a low degree of order in the multilayer. In contrast, the first monolayers in contact with the silver substrate adsorb highly ordered, with the tetrapyrrolic macrocycle almost parallel to the surface, the residual tilt being ca. 20°. The three pentafluorophenyl groups are tilted by ~45° with respect to the surface.

O 12.11 Mon 17:30 MA 005

**Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin on Cu(111)** — Michael Stark, Stefanie Ditze, Michael Lepper, Liang Zhang, Hannah Schlott, Florian Buchner, Michael Röckert, Min Chen, Ole Lytken, Hans-Peter Steinrück, and •Hubertus Marbach — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

Based on a combined scanning tunneling microscopy and X-ray photoelectron spectroscopy study we present detailed insights into pronounced changes of long-range order and intramolecular conformation during the self-metalation of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) to CuTTBPP on Cu(111). 2HTTBPP adsorbed on Cu(111) at room temperature forms a peculiar entropically stabilized supramolecular ordered phase: the molecules arrange in alternating rows, with two distinct appearances in STM, which are assigned to concave and convex intramolecular conformations [1,2]. Upon metalation, the porphyrin literally "pops up" from the surface, due to a drastically reduced molecule-substrate interaction [3].

[1] S. Ditze et. al, JACS, 136 (2014) 1609
[2] H. Marbach, H.-P. Steinrück, Chem. Commun., 50 (2014) 9034
[3] M. Stark et al., Chem. Commun., 50 (2014) 10225

O 12.12 Mon 17:45 MA 005

**Engineering of large-pore metal coordination networks from de-novo synthesized porphyrins** — •Yuanqin He[1], Felix Bischoff[1], Knud Seufert[1], Willi Auwärter[1], Daphne Stassen[2], Davide Bonifazi[2], and Johannes Barth[1] — [1]Physik Department E20, Technische Universität München, James Frank Str. 1, D-85748 Garching, Germany — [2]Department of Chemistry and Namur Research College, University of Namur, Belgium

Molecular self-assembly using designed building blocks is a versatile method to fabricate nanostructures with tunable properties, wherein intermolecular interaction is a key factor that determines the structure. Here we present a low-temperature STM study on the self-assemblies of two differently substituted porphyrin species on Ag(111), namely (5,10,15,20)tetra-biphenylcyano porphyrin (2H-TPCN) and (5,10,15,20)tetra-pyridylphenylporphyrin (2H-TPyPP). Their distinct terminal substituents and the coordination to metal atoms, when adding Cu adatoms, induce different organic and metal-organic patterns. This allows us to explore the influence of the intermolecular interactions on the self-assembly and the formation of metal-organic coordination networks. Furthermore Monte-Carlo simulations are performed for these two systems, perfectly reproducing all the patterns observed in the experiment. The experimental results in combination with the phase transition diagram derived from the simulation can give us a hint on the ratio between the coordination bond and vdW force, which can be further used to design molecular building blocks and self-assembly protocols.

O 12.13 Mon 18:00 MA 005

**Impact of the bonding motif on the chirality transfer of DiOH[6]Helicene** — •Thomas Nijs[1], David Schweinfurth[2], Aneliia Wäckerlin[1], Aisha Ahsan[1], Sylwia Nowakowska[1], François Diederich[2], Carlo Thilgen[2], and Thomas A. Jung[1,3] — [1]University of Basel, Switzerland — [2]ETH Zurich, Switzerland — [3]Paul Scherrer Institute, Switzerland

Chirality plays an important role in biological processes as it generally affects molecular recognition by shape or geometry. Therefore, it needs to be crucially controlled, for example in pharmaceutical applications.

In order to address the impact of the intermolecular bonds and their strength on the chirality transfer [1], we employ an intrinsically chiral hexahelicene with two hydroxylic functional units [2]. We study the self-assembly at Ag(111) surface at sub-monolayer coverages under the regime of two different bonding motifs: H-bonding and metal-coordination. During deposition onto Ag(111) partial dehydrogenation occurs and H-bonded trimers are formed with a distinct chiral arrangement. By annealing in presence of Co adatoms added to the sample by sublimation, full dehydrogenation occurs and metal coordination bonds are established - while maintaining a trimeric motiv. Importantly however, the system emerges into a new self-assembly pattern of the opposite chirality. The morphology of the self-assembly is investigated by STM and the bonding motif is investigated by surface chemical analysis i.e. XPS.

[1] A. Shchyrba et al., JACS, 135, 15270-15273 (2013)
[2] T. Nijs et al., manuscript in preparation

# O 13: Electronic Structure of Surfaces II

Time: Monday 15:00–18:15 Location: MA 041

**Invited Talk** O 13.1 Mon 15:00 MA 041

**Advanced spin-resolved momentum microscopy** — •Christian Tusche — Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Angle resolved photoemission spectroscopy (ARPES) is an universal tool to probe the electronic structure of solids. Conventional electron spectrometers measure the distribution of photoelectrons in a limited angular interval, which makes complete mapping of band structures a time consuming task. Here, we discuss the recent approach to this issue by momentum microscopy. A momentum microscope captures the complete $2\pi$ solid angle of emission directions into a high resolution ($k_x$, $k_y$) image of the full surface Brillouin zone of a solid. This efficient measurement scheme intrinsically provides comprehensive quantitative information beyond high-symmetry directions.

Of particular importance is the spin of the electron, that gives rise to phenomena like ferromagnetism, spin-polarized surface states, and the discovery of new material classes like topological insulators. So far, however, the spin was only inefficiently probed in photoemission experiments, resulting in a rather low figure of merit ($10^{-4}$) for spin-resolved ARPES. This longstanding problem is defeated by introducing the novel concept of spin-resolved momentum microscopy: In combination with an imaging spin filter, we measure more than 5000 spin-resolved points in the full $k_{||}$-space, simultaneously. We will discuss examples ranging from the spin-resolved Fermi surface of ferromagnets to highly polarized states in topological insulators.

O 13.2 Mon 15:30 MA 041

**Strongly anisotropic spin-orbit splitting in a 2-dimensional electron gas** — •Matteo Michiardi[1], Marco Bianchi[1], Maciej Dendzik[1], Jill Miwa[1], Moritz Hoesch[2], Timur K. Kim[2], Peter Matzen[1], JianLi Mi[3], Martin Bremholm[3], Bo Brummerstedt Iversen[3], and Philip Hofmann[1] — [1]Department of Physics and Astronomy, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark — [2]Diamond Light Source, Harwell Campus, Didcot, OX11 0DE, United Kingdom — [3]Center for Materials Crystallography, Department of Chemistry, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark

Near-surface two-dimensional electron gases (2DEG) on the topological insulator $Bi_2Te_2Se$ are induced by electron doping and studied by angle-resolved photoemission spectroscopy. A pronounced spin-orbit splitting is observed for these states. The $k$-dependent splitting is strongly anisotropic to a degree where a large splitting can be found in the $\bar{\Gamma}\bar{M}$ direction while the states are hardly split along $\bar{\Gamma}\bar{K}$. We show that this strong anisotropy can be explained by expanding the $\mathbf{k}\cdot\mathbf{p}$ hamiltonian for 2DEGs to include the possibility of band structure anisotropy as well as both isotropic and anisotropic third order Rashba splitting. The interplay of band structure, higher order Rashba effect and tuneable doping offers the opportunity to engineer not only the size of the spin-orbit splitting but also its direction.

O 13.3 Mon 15:45 MA 041

**Epitaxial $Sb_2Te_3/Bi_2Te_3$ heterostructures: a new (route to) topological p-n junction** — •Markus Eschbach[1], Ewa Mlynczak[1], Jens Kellner[2], Jörn Kampmeier[1], Martin Lanius[1], Christian Weyrich[1], Gregor Mussler[1], Natalya Demarina[1], Thomas Schäpers[1], Lukasz Plucinski[1], Detlev Grützmacher[1], Markus Morgenstern[2], and Claus M. Schneider[1] — [1]Forschungszentrum Jülich GmbH, Peter Grünberg Institut, 52425 Jülich, Germany — [2]II. Physikalisches Institut B, RWTH Aachen University, 52074 Aachen, Germany

Recently, in the field of 3D Topological Insulators various attempts have been carried out to tune the chemical potential and, more specifically, the Dirac point to a desired energetic position i.e. to engineer the electronic bandstructure for the purpose of designing future spintronic devices. Here we show the first direct experimental proof, by angle-resolved photoemission, of the realization of a topological p-n junction made of a heterostructure of two different 3D TI materials $Bi_2Te_3$ and $Sb_2Te_3$ grown on Si(111). In the experiment we observe an energetic shift of the entire electronic structure of about 200 meV when decreasing the upper $Sb_2Te_3$ layer from a thickness of 25 QL to 6 QL. On one hand, we consider surface doping and the creation of a ternary alloy at the surface and on the other hand the creation of a depletion region and a built-in electric field at the interface of the two TI materials to be responsible for the shift. The latter contribution is supported by solving Schrödinger and Poisson equations self-consistently for a 1D model system.

O 13.4 Mon 16:00 MA 041

**Spin-resolved electronic structure of BiTeI** — •Henriette Maass[1], Christoph Seibel[1], Hendrik Bentmann[1], Christian Tusche[2], Taichi Okuda[3], Thiago Peixoto[1], Oleg Tereschchenko[4], Jürgen Kirschner[2], and Friedrich Reinert[1] — [1]Experimentelle Physik VII, Universität Würzburg, D-97074 Würzburg — [2]Max-Planck-Institut für Mikrostrukturphysik, Am Weinberg 2, D-06120 Halle — [3]Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, Japan — [4]Institute of Semiconductor Physics, 636090, Novosibirsk, Russia

The non-centrosymmetric lattice structure and large spin-orbit interaction in bismuth tellurohalides lead to large Rashba-type spin-splittings in the bulk and surface electronic structure of these materials. The resulting spin structure is predicted to be highly dependent on the orbital character of the electronic states [1]. Deploying a spin- and angle- resolving photoelectron spectrometer based on very-low-energy electron diffraction [2] and a momentum microscope with an imaging spin filter [3] we investigated the photoelectron spin polarization of the surface band structure of BiTeI for a subset of energies and momenta. Our experiments reveal a peculiar spin-structure yielding evidence for an orbital dependence of the Rashba-splitting. In particular we find evidence for a correlation between the photoelectron spin and the orbital character of the Rashba surface band.

[1] Z. Zhu *et al.*, New J. Phys. **15**, 023010, (2013)
[2] T. Okuda *et al.*, Rev. of Sci. Instr. **82**, 103302, (2011)
[3] C. Tusche *et al.*, Ultramicroscopy **130**, 70-76, (2013)

O 13.5 Mon 16:15 MA 041

**Electronic and spin structure of topological surface state in Sn-based ternary topological insulators** — •Maia G. Vergniory[1], Tatyana V. Menshchikova[2], Igor V. Silkin[3], Yuri M. Koroteev[3], Sergey V. Eremeev[3], and Evgueni V. Chulkov[4] — [1]Max-Planck-Institut für Mikrostrukturphysik, Halle, 06120 Germany — [2]Tomsk State Univeristy, Tomsk, 634050 Russia — [3]Institute of Strength and Materials Science, Siberian Branch, Tomsk, 634021 Russia — [4]Donostia International Physics Center, Donostia-San Sebastian, 20018 Spain

We report the bulk and surface electronic properties and spin polarization of a new rich family of Sn-based ternary complex topological insulators studied by means of first principles calculations. These compounds exist in different stoichiometries: SnxAyBz (A:Sb and Bi) (B: Te and Se). The crystal structure of these compounds is characterized by alternating along hexagonal axis quintuple, septuple and nonuple layer van der Waals bonded building blocks. We reveal that the bulk band gap in these systems is about 100 meV and the spin polarization near the Dirac point is up to 85%. Within the same family, for some of these compounds, which crystal structure has ionic-covalent bonded Bi2Te3 and crystalline topological insulator SnTe atomic layers within building block, the complex SOI-induced bulk band inversion caused by competition of band inversions in Bi2Te3 and in SnTe layers occurs and results in inherently nonlinear dispersion of the topological surface state.

O 13.6 Mon 16:30 MA 041

**Warping Effects on Spin and Electronic Structure of the Topological Surface State in $\alpha$-Sn** — •M. R. Scholz[1], A. Fleszar[2], G. Li[2], F. Adler[1], S. Glass[1], L. Dudy[1], J. Aulbach[1], S. Muff[3], J.-H. Dil[3], M. Bianchi[4], M. Michiardi[4], P. Hofmann[4], W. Hanke[2], R. Claessen[1], and J. Schäfer[1] — [1]Phys. Inst. and RCCM, Univ. Würzburg — [2]Inst. f. Theo. Physik u. Astronomie, Univ. Würzburg — [3]Swiss Light Source, Paul-Scherrer-Institut Villigen — [4]Aarhus University

The strain-induced insulating phase of $\alpha$-Sn was proposed to be of non-trivial topology in 2007 [1] and subsequently experimentally established by our group in 2013 [2]. Soon after the discovery of the topological insulators of the Bi$_2$X$_3$ family of materials the influence of the 3-fold symmetry of the crystal on spin texture and electronic structure of the topological surface state (TSS) has been dicussed, and is still a subject of current research. Here, we want to report on a detailed investigation of the influences of the diamond lattice symmetries on the TSS in $\alpha$-Sn. Our results from angle-resolved photoemission show that the TSS deviates from the ideal shape of a Dirac cone with circular constant energy contours. Moreover, spin-resolved photoemission reveals a lifting of the perpendicular locking of spin and momentum similar to the case of Bi$_2$X$_3$, while, in contrast, the spin remains fully within the surface plane. The experimental results are in nice agreement with our own DFT calculations. [1] Fu and Kane Phys. Rev. B **76**, 045302 (2007); [2] Barfuss et al., Phys. Rev. Letters **111**, 157205 (2013)

O 13.7 Mon 16:45 MA 041

**Probing the Surface Properties of the Topological Insulator TlBiSe$_2$ by Photoelectron Diffraction, Scanning Tunneling Spectroscopy and Ab-Initio Theory** — •Eike F Schwier[1], Clément Didiot[2], Kenta Kuroda[3], Roland Stania[4,5], Jun Zhang[5], Elia Razzoli[2], Mao Ye[1], Hideaki Iwasawa[1], Matthias Muntwiler[5], Philipp Aebi[2], Akio Kimura[6], Kenya Shimada[1,6], Hirofumi Namatame[6], and Masaki Taniguchi[1,6] — [1]Hiroshima Synchrotron Radiation Center, Japan — [2]U Fribourg, Switzerland — [3]U Marburg, Germany — [4]U Zürich, Switzerland — [5]PSI, Villigen, Switzerland — [6]U Hiroshima, Japan

It was recently found that the cleaved surface of the 3D topological insulator TlBiSe$_2$ is decorated with island-like structures[1]. In our study we deployed a combination of photoelectron diffraction (PED) as well as ab-initio theory and scanning tunneling spectroscopy to probe the properties of the surface. By comparing our PED measurements with multiple scattering calculations and taking into account different surface topographies we were able to unambiguously answer the question of the islands chemical composition and to estimate the island-substrate out-of-plane lattice constant. Using ab-initio calculations, we were further able to explain the emergence of the surface core-level shift in Tl 5d by comparing different surface terminations and Tl coverages. We will also present results from STS measurements on and between the islands in order to shine some light on the islands influence on the Dirac cone formation and its spin polarization.

[1] K. Kuroda et al., PRBB 88, 245308, 2013.

O 13.8 Mon 17:00 MA 041

**Spin-orbit interaction and Dirac cones in d orbital noble metal surface states** — •Ryan Requist[1], Polina M. Sheverdyaeva[2], Paolo Moras[2], Sanjoy K. Mahatha[3], Carlo Carbone[2], and Erio Tosatti[1,3,4] — [1]International School for Advanced Studies,Trieste, Italy — [2]Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Trieste, Italy — [3]International Centre for Theoretical Physics, Trieste, Italy — [4]IOM-CNR – Democritos, Trieste, Italy

We report a joint photoemission/ab initio study of spin-orbit effects in the deep d orbital surface states of a 24-layer Au film grown on Ag(111) and a 24-layer Ag film grown on Au(111), singling out a conical intersection (Dirac cone) in a large surface-projected gap at the time-reversal symmetric $\overline{M}$ points. Unlike the often isotropic dispersion at $\overline{\Gamma}$ point Dirac cones, the $\overline{M}$ point cones are strongly anisotropic. An effective $\mathbf{k} \cdot \mathbf{p}$ is derived to describe the anisotropic Rashba band splitting and spin polarization near the Dirac cone, and we discuss multiband tight binding models for surface states with spin-orbit interactions.

O 13.9 Mon 17:15 MA 041

**Rashba splitting of graphene-covered Au(111) revealed by quasiparticle interference mapping** — •Mikhail Fonin, Philipp Leicht, Julia Tesch, Felix Blumenschein, Philipp Erler, and Luca Gragnaniello — Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany

Although the Rashba-split bands are readily visible in angle-resolved photoemission, their observation at the local scale employing quasiparticle interference (QPI) mappings is challenging. Here, we report on low-temperature scanning tunneling microscopy/spectroscopy measurements on epitaxial graphene flakes on Au(111). Careful analysis of the QPI maps allows the discrimination between the electronic systems of graphene and Au(111). Beyond the scattering vectors, which can be ascribed to the elastic scattering within each of the systems, we clearly observe QPI features related to the scattering process between graphene states and the Au(111) surface state. This additional interband scattering process at the graphene/Au(111) interface allows the direct quntitative determination of the magnitude of the Rashba splitting of the Au(111) surface state, which cannot be evaluated from QPI measurements on pure Au(111). This experiment demonstrates a new local spectroscopic approach to investigate the band structure of surfaces with Rashba splitting.

O 13.10 Mon 17:30 MA 041

**Microscopic theory of the residual surface resistivity of Rashba electrons** — •Juba Bouaziz[1], Stefan Blügel[1], Hiroshi

Ishida[2], and Samir Lounis[1] — [1]Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany — [2]College of Humanities and Sciences, Nihon University, Sakura-josui, Tokyo 156, Japan

A microscopic expression of the residual electrical resistivity tensor is derived in linear response theory for Rashba electrons scattering at a magnetic impurity with cylindrical or non-cylindrical potential. We investigated the specific case of an Fe adatom deposited on Au(111) surface [1] and studied the evolution of the diagonal and off-diagonal elements of the resistivity tensor as function of the magnetization direction of the impurity and of the spin-orbit strength. We found that the longitudinal residual resistivity leads to an anomalous magnetoresistance while the transversal one to a planar Hall effect. In the limit of no spin-orbit interaction and a non-magnetic impurity of cylindrical symmetry the expression of the residual resistivity of a two-dimensional electron-gas has the same simplicity and form as for the three-dimensional electron gas [2] and can also be expressed in terms of scattering phase shifts.

[1] S. Lounis *et al.* Phys. Rev. Lett. **108**, 207202 (2012)
[2] J. Friedel, NuovoCimento Suppl. **7**, 287 (1958)

This work is supported by the HGF-YIG Programme VH-NG-717 (Functional Nanoscale Structure and Probe Simulation Laboratory).

O 13.11 Mon 17:45 MA 041

**Unconventional surface reconstruction of $Na_2IrO_3$ with persistent energy gap** — •Felix Lüpke[1,2], Soham Manni[3,4], Steven C. Erwin[5], Igor I. Mazin[5], Philipp Gegenwart[4], and Martin Wenderoth[1] — [1]IV. Physikalisches Institut, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany — [2]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and JARA-Fundamentals of Future Information Technology — [3]I. Physikalisches Institut, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany — [4]Experimental Physics VI, Center for Electronic Correlations and Magnetism, University of Augsburg, D-86159 Augsburg, Germany — [5]Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA

$Na_2IrO_3$ is an intriguing material for which theoretical predictions, so far unverified, have been made that the surface of $Na_2IrO_3$ should exhibit a clear signature of the quantum spin Hall effect. We studied the surface of $Na_2IrO_3$ using scanning tunneling microscopy, spectroscopy and density-functional theory calculations. We observed two types of surface terminations with different surface periodicity and Na content. By comparing bias-dependent experimental topographic images to simulated images, we determined the detailed atomistic structure of both observed surfaces. The found dramatic structural changes are highly unusual and cast doubt on any prediction of surface properties based on bulk electronic structure. Indeed, we found no indication of the predicted quantum spin Hall behavior.

O 13.12 Mon 18:00 MA 041

**Initial stages of the Fe2ZrSi Heusler alloy formation** — •Katerina Horakova[1], Jan Honolka[1], Jan Lancok[1], Vladimir Chab[1], and Petr Sajdl[2] — [1]Institute of Physics, Academy of Sciences of the Czech Republic, 182 21 Prague 8, Czech Republic — [2]Institute of Chemical Technology Prague, 166 28 Prague 6, Czech Republic

We measured the electronic structure of clean Zr (0001) surfaces before and after adsorption of submonolayer coverages of Si and Fe atoms. Measurements were done using k-space microscopy. Our aim is to study the initial stages of the formation of Fe2ZrSi Heusler alloys on this surface. Our work is motivated by a passivation process of zirconium, widely used in the nuclear power industry. Fe and Si are deposited sequentially on the clean Zr surface. The structure of the surface was analysed by LEED and XPS. Different chemical states of Zr were found as a function of temperature and the composition. On a clean surface we detected two different chemical states of the Zr, one corresponding to the metal Zr, and the second to the bond with hydrogen naturally trapped in the bulk. After Si deposition, a slight annealing at 400°C of the Si layer produces a new quasicrystalline structure connected with strong changes of the electronic structure at Ef. These changes are probably a result of Zr-Si-H bonding. The deposition of Fe and subsequent annealing produces a disordered layer only.

## O 14: Oxide Surfaces: Adsorption and Reactivity

Time: Monday 15:00–18:00 Location: MA 042

O 14.1 Mon 15:00 MA 042

**Adsorption energies of small molecules on metal oxide surfaces using the method of local increments** — •Wilke Dononelli and Thorsten Klüner — Carl von Ossietzky Universität Oldenburg,Ammerländer Heerstraße 114-118, 26129 Oldenburg

Obtaining highly accurate potential energy surfaces is still very demanding and one of the limiting factors in theoretical surface science. Nowadays density functional theory (DFT) with periodic boundary conditions is the most frequently used approach in theoretical surface science. However, the exact form of the exchange correlation functional is unknown and no systematic strategy of improving the results obtained in DFT calculations has been investigated. So far, only conventional quantum chemistry provides a well-defined hierarchy of methods for the systematic treatment of electron correlation effects.

The disadvantage of using high accurate post-Hartree-Fock methods like Moller-Plesset perturbation theory or the coupled-cluster method is the high computational cost of these methods. For example the CCSD method scales very bad with the size of the system. In order to decrease the size of the system, the method of increments was introduced by Stoll to calculate the correlation energy on an accurate level of theory.

In this study, the method of local increments is used in connection with an embedded cluster approach and wave function based quantum chemical ab initio methods [1] to describe the adsorption of small single molecules on the rutile(110) and MgO(001) surfaces.

[1] B. Paulus, Phys. Rep. 428, 1 (2006).

O 14.2 Mon 15:15 MA 042

**The role of defects in the adsorption of CO on $Co_3O_4$** — •M.Alexander Schneider[1], Pascal Ferstl[1], Lutz Hammer[1], M.Alif Arman[2], Edvin Lundgren[2], Jan Knudsen[3], Sascha Mehl[4], Arafat Toghan[4], Yaroslava Lykhach[4], and Jörg Libuda[4] — [1]Solid State Physics, FAU Erlangen-Nürnberg, Germany — [2]Division of Synchrotron Radiation Research, Lund University, Sweden — [3]The MAX IV Laboratory and Division of Synchrotron Radiation Research, Lund University, Sweden — [4]Physical Chemistry II, FAU Erlangen-Nürnberg, Germany

We studied the adsorption of CO on 3 nm thick $Co_3O_4(111)$ films grown on Ir(100) by means of XPS, IRAS and STM under ultrahigh vacuum conditions. At full saturation of the surface at 100 K both XPS and IRAS suggest that CO is bound in three different configurations. We find two distinctly different adsorption sites in which the molecule is weakly bound and desorbs from $Co_3O_4$ well below 300 K. A third stronger bound minority configuration resides at the surface even beyond room temperature. The latter might be related to surface defect sites which are investigated in detail by STM for the clean films. Possible configurations for the weakly bound CO molecules on the $Co_3O_4$ surface are also discussed.

O 14.3 Mon 15:30 MA 042

**Adsorption of carbon dioxide onto an iron oxide** — •Petr Dementyev, Casey O'Brien, Francisco Ivars, Swetlana Schauermann, and Hans-Joachim Freund — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Carbon dioxide is likely to play one of the key roles in clean energy technologies. Its conversion into methanol or other chemicals is a promising way for renewable energy storage. Since carbon dioxide molecules are inert, an important issue is to activate them. Herein we employ a combination of single-crystal adsorption calorimetry (SCAC) and infrared reflection-absorption spectroscopy (IRAS) to study carbon dioxide adsorption on iron oxide Fe3O4. SCAC is a method for probing energetics of adsorbate-surface interactions, while IRAS allows identifying chemical nature of surface species. Both instruments contain molecular beams what enables to conduct careful adsorption experiments under clean UHV conditions.

We probe two well-defined Fe3O4 (111) and (100) thin films. Both substrates as well as FeO film are grown epitaxially on Pt single crystal. Low-temperature SCAC measurements reveal that carbon dioxide transiently sticks to Fe3O4 whereas it does not interact with oxygen-terminated FeO and bare Pt. IRAS confirms that CO2 does react with the iron oxide. There are many features in the region of C-O stretching vibrations indicating coexistence of different species such as physisorbed CO2 and carbonates. Surface chemistry of CO2 seems to be strongly kinetically limited. Co-adsorption experiments show that water surface species block CO2 adsorption.

O 14.4 Mon 15:45 MA 042

**High chemical activity of a perovskite surface: adsorption of CO and H2O on Sr3Ru2O7** — •Florian Mittendorfer, Bernhard Stöger, Daniel Halwidl, Wernfried Mayr-Schmölzer, Josef Redinger, Michael Schmid, and Ulrike Diebold — Institut f. Angewandte Physik, TU Wien

In the recent years, complex transition metal oxide surfaces have received enormous attention, both due to the fundamental properties as well as their potential for applications in the field of energy storage and conversion. Yet only little is known about the chemistry of these materials. On the basis of density functional theory (DFT) calculations, I will present a theoretical study on the surface chemistry of Sr3Ru2O7, supported by experimental STM measurements. Surprisingly, the STM study shows a high chemical activity of the Sr3Ru2O7 surface [1]. We conclude that these observations are related to the facile adsorption of carbon monoxide (CO), which can easily be converted to a carboxylate-like COO species at the surface. With an adsorption energy of -2.2 eV, the latter structure shows a high chemical stability. We also find that H2O can be readily adsorbed at the surface, resulting in the dissociation of the water molecule. Yet the fragments display an attractive interaction, leading to complex adsorption patterns.

[1] B. Stoeger et al., Phys. Rev. Lett. 113 (2014) 116101

O 14.5 Mon 16:00 MA 042

**Surface chemistry of magnetite (001) surface: Adsorption of Formic Acid and Methanol.** — •Oscar Gamba[1], Heshmat Noei[2], Jiří Pavelec[1], Roland Bliem[1], Michael Schmi[1], Ulrike Diebold[1], Andreas Stierle[2], and Gareth Parkinson[1] — [1]Institute of Applied Physics, Vienna University of Technology, Wien, Austria — [2]DESY Nanolab & Physics Department, University of Hamburg, Hamburg, Germany

Understanding the surfaces of metal oxides and their interactions with organic molecules is a crucial aspect in research topics such as catalysis, and environmental science. Formic acid (HCOOH), and methanol (CH3OH), are often used as probe molecules to test the reactivity of metal oxide surfaces (1). Adsorption of both species can be molecular, as in the low temperature regime, but is frequently dissociative on surfaces that expose pairs of undercoordinated cations (2).

In this talk, the study of adsorption of formic acid and methanol on the Fe3O4(001) surface using XPS, LEED, IRRAS, and STM will be described. Both molecules adsorb molecularly at low temperature, and dissociatively at room temperature, yielding adsorbed formate and methoxy species respectively, together with surface hydroxyl groups. Formate adsorbs in a bidentate configuration at regular iron lattice sites producing a (1X1) overlayer. Methoxy adsorption is restricted to step edge and other defect sites where the coordinative undersaturation of the surface atoms is higher.

1.J. M. Vohs, Chemical Reviews 113 (6), 4136-4163 (2012). 2.J. M. Vohs and M. A. Barteau, Surface Science 176 (12), 91-114 (1986).

O 14.6 Mon 16:15 MA 042

**Carboxylic Acid Deprotonation on MgO(100)** — •Quratulain Tariq, Matthias Franke, Michael Röckert, Hans-Peter Steinrück, and Ole Lytken — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

Chemical functionalization of surfaces provides unique routes to obtain nanoscale supramolecular architectures, for novel technological applications. Only few attempts have been made to functionalize metal oxide surfaces by adsorption of organic molecules. A promising class of molecules to form supramolecular structures are aromatic carboxylic acids. Such species have been studied previously, on a variety of surfaces and both flat-lying and upright-standing adsorption configurations are possible. In the present work, we investigate the adsorption of phthalic acid (C6H4(COOH)2) on MgO(100) thin films on Ag(100), as a function of temperature and coverage, by X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), near-edge X-ray absorption fine structure (NEXAFS) and temperature programmed desorption (TPD). We find deprotonation of both carboxyl groups of the phthalic acid molecule upon heating and formation of a bidentate species with an upright standing orientation, stable between 350 and 500 K. The project is supported by the DFG through FOR 1878 (funCOS).

O 14.7 Mon 16:30 MA 042

**Density Functional Theory study of adatom and metal cluster adsorption on metal supported thin Zirconia films** — •Wernfried Mayr-Schmölzer, Florian Mittendorfer, and Josef Redinger — Center of Computational Materials Science, TU Vienna

Zirconium dioxide is a material with many interesting properties, which make it useful for various technological applications, for example as a solid electrolyte in solid-oxide fuel-cells or as an oxygen gas sensor. Therefore a detailed understanding of adsorption on zirconia films is crucial for these applications.

We present results of DFT calculations of adsorption of metal adatoms and clusters on a thin zirconium oxide film supported by a $Pt_3Zr$ substrate. This alloy is very stable and can be used to experimentally grow thin $ZrO_2$ films by oxidation. The calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) employing standard PBE and van-der-Waals density functionals.

The binding mechanism and interaction of adsorbed transition metal adatoms such as gold, silver, nickel and palladium was investigated. For gold we only find weak physisorption while the other metals show significantly higher adsorption energies. Additionally we present results of the adsorption of larger transition metal clusters on the oxide film and an analysis of their charged state.

This work has been supported by the Austrian Science Fund under the project number F4511-N16.

O 14.8 Mon 16:45 MA 042

**Surface etching of single crystalline ZnO by phosphonic acid based SAMs** — •Alexandra Ostapenko and Gregor Witte — Molekulare Festkörperphysik, Philipps-Universität Marburg, Renthof 7, 35032 Marburg, Germany

Self-assembled monolayers (SAMs) attachment have proven to be an effective way of tuning electronic interfacial properties or specifically link dye-molecules to transparent metal oxides. Organic-inorganic hybrid systems based on the latter approach have recently attracted significant research interest because of their promising use in photovoltaic application. The resulting device performance is expected to depend critically on the microstructure of the film. Widely used phosphonic acid based SAMs form surprisingly robust films on ZnO surfaces. However, it was found that during the film deposition phosphonic acid anchoring causes surface damaging resulting from dissolution-precipitation of ZnO. For the extended immersion times we observe the formation of star shaped surface defects of crystalline needles on single crystalline ZnO substrates. We show that the etching rate can be tuned directly by variations of pH-value during the immersion. Structure and composition of surface precipitations and their thermal stability were investigated combining atomic force spectroscopy, X-ray diffraction spectroscopy and thermal desorption spectroscopy. Preparative routes to optimize film formation avoiding surface etching were elucidated as well.

O 14.9 Mon 17:00 MA 042

**Formation of 1D adsorbed water structures on CaO(001)** — Xunhua Zhao, •Sergey V. Levchenko, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, DE

Understanding the interaction of water with oxide surfaces is of fundamental importance for basic and engineering sciences. Recently, a spontaneous formation of one-dimensional (1D) adsorbed water structures have been observed on CaO(001) [1]. Interestingly, at other alkaline earth metal oxides, in particular MgO(001) and SrO(001), such structures have not been found experimentally. We calculate relative stability of adsorbed water structures on the three oxides using density-functional theory with the hybrid functional HSE06 and *ab initio* many-body dispersion interaction correction [2], combined with the *ab initio* atomistic thermodynamics. Low-energy structures at coverages up to one monolayer are obtained with a first-principles genetic algorithm. Finite-temperature anharmonic vibrational spectra are calculated using *ab initio* molecular dynamics. We find a range of ($T$, *p*) conditions where 1D structures are thermodynamically stable on CaO(001). The orientation and vibrational spectra of the 1D structures are in agreement with the experiments [1]. The formation of the 1D structures is found to be actuated by a symmetry breaking in the adsorbed water tetramer, as well as by a balance between water-water and water-substrate interactions, determined by the lattice constant of the oxide.—[1] X. Shao, Y. Fujimori, M. Sterrer, H.-J. Freund, and N. Nilius, to be published; [2] A. Tkatchenko, R. A. DiStasio, Jr., R. Car and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (2012).

O 14.10 Mon 17:15 MA 042

**Formation of dendritic structures due to water ice on oxide surfaces under ambient conditions** — •Oğuzhan Gürlü[1], Kivanç Esat[1], and Özgür Birer[2] — [1]Istanbul Technical University, Istanbul, Turkey — [2]Koç University, Istanbul, Turkey

We have studied the chemical and morphological properties of nanoscale chromium oxide particles on glass and silicon oxide surfaces. Furthermore we investigated their interaction with water from the ambient atmosphere. We found out that dendritic structures due to water on these surfaces can from spontaneously. Our systematic studies of dosing such surfaces with humidified air revealed formation of further fractal structures due to water condensation and evaporation. The growth of these structures was observed under an ambient optical microscope in real time. When these samples were transferred to an atomic force microscope (AFM), dendrites due to water ice could still be observed, also under ambient conditions. AFM data showed that these structures could be as high as several hundredths of nanometers, proving them to be three-dimensional. Depending on the density of the oxide particles on glass or silicon oxide surfaces, shapes and sizes of the dendrites were observed to differ. Despite the counter intuitive nature of such formations, an explanation could be brought to their formation by use of Electrostatic Force Microscopy (EFM).

O 14.11 Mon 17:30 MA 042

**The interaction of water molecules with hematite(0001) surface** — •Roman Ovcharenko and Elena Voloshina — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2 12489 Berlin, Germany

The interaction of water with oxide surfaces is ubiquitous, as water is always present either as a reactant or just an "innocent spectator". The wetting process is predominantly govern by several factors, such as ambient conditions, surface termination and valence band structure. The precision *ab initio* calculation of the latter two properties of the $\alpha$-Fe$_2$O$_3$ surface is a serious challenge posed to theory due to Fe 3d electrons, unusual hybridisation, huge surface relaxations, big super cells and magnetism. The situation becomes even more complicated since taking into account on-site Coulomb interactions drastically changing the structure of the valence band top, that allows anyone to consider hematite as charge-transfer insulator in contrary to the prediction of pure GGA approach.

In this study we present the detailed *ab initio* theoretical investigation of the single water molecule behaviour on the hematite(0001) surface. The electronic structure has been treated within DFT approach with PBE-GGA exchange-correlation functional. To take into account Fe 3d strong electronic correlation we adopt DFT+U approach formalised by Dudarev and D2 theory proposed by Grimme has been applied to account for dispersion interaction between water molecule and the surface termination.

O 14.12 Mon 17:45 MA 042

**Water adsorption on non-polar ZnO surfaces: from single molecules to multilayers** — •stephane kenmoe and p. ulrich biedermann — Max-Planck-Institut für Eisenforschung GmbH Max-Planck-Straße 1 D-40237 Düsseldorf

The interface between water and ZnO plays an important role in many domains of technological relevance. Following the vital role of adsorbed water on substrate properties and the fascinating properties of interfacial water, there is a great interest in characterizing this interface. We use DFT to study the possible aggregation regimes that can form on the ZnO non-polar low-index (10-10) and (11-20) surfaces. We study the adsorption of water monomers, small water clusters like water dimers, water chains, ladder-like water structures, water thin films and water multilayers. Based on this, trends in binding energy as well as the binding mechanisms are analyzed to understand the driving forces and the nature of the fundamental interactions that stabilize the adsorbed layers.

## O 15: Scanning Probe Techniques: STM/AFM

Time: Monday 15:00–18:15 Location: MA 043

O 15.1 Mon 15:00 MA 043

**Switching a four-atom Si quantum dot with the tunneling current and atomic force by means of scanning probe microscopy** — Shiro Yamazaki[1], Keisuke Maeda[1], Yoshiaki Sugimoto[1], Masayuki Abe[1], Vladimir Zobac[2], Pablo Pou[3], Lucia Rodrigo[3], Pingo Mutombo[2], Ruben Perez[3], •Pavel Jelinek[1,2], and Seizo Morita[1] — [1]Osaka University, Japan — [2]Institute of Physics of the CAS, Prague, Czech Republic — [3]Universidad Autonoma de Madrid, Spain

Most of present switching mechanisms employ the electronic excitation using scanning tunneling microscopy (STM). But only few realizations of mechanical switches using non-contact atomic force microscopy (NC-AFM) have been reported so far. Here we show that simultaneous combination of the tunneling current (STM) and atomic force (AFM) provides new possibilities to control atomic configuration of nanostructures. First we use atomic manipulation to engineer bi-stable silicon quantum dot (QD) consisting of four buckled atoms on the Si(111)-7x7 surface. We show that application of the force and the current induces the opposite upward and downward switching of atoms in the Si4-QD. This allows us to perform controlled switching between different logical states of Si-QD by the tunneling current and/or the force. What more, simultaneous application of the current and force allows us controlling switching rates. We believe that selective application of two different mechanisms opens new horizons for nanoscale switching devices or atomic manipulation.

O 15.2 Mon 15:15 MA 043

**Quantifying the virtual ground of a STM pre-amplifier** — •Nirmalesh Kumar Sampath Kumar, Alferd J Weymouth, and Franz J Giessibl — Institute of Experimental and Applied Physics, University of Regensburg, Universitatstraße 31, 93053 Regensburg, Germany

In AFM, it is normal to apply a bias voltage between the tip and the sample, most often to compensate for the contact potential difference. In order to perform simultaneous STM, the tunneling current must be measured. This usually involves a preamplifier that holds its current input terminal at a virtual ground that is ideally equal to real ground. Limitations of amplifier bandwidth, gain and slew rate lead to time-dependent deviations of virtual ground from zero, causing a time-dependent variation of the electrostatic force between tip and sample. These time-dependent deviations can lead to artifacts in apparent dissipation and even to an apparent "self" excitation of the cantilever. Here, we monitor virtual ground and discuss the effect of virtual ground deviations to apparent dissipation.

O 15.3 Mon 15:30 MA 043

**Atomic-scale dissipation in atomic force microscopy imaging of TlBiSe$_2$** — •Florian Pielmeier, Julian Berwanger, and Franz J. Giessibl — Institut für Experimentelle und Angewandte Physik der Universität Regensburg, 93053 Regensburg, Deutschland

The surface termination of cleaved TlBiSe$_2$(111) was recently studied by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) [1,2]. Both methods revealed the unusual termination of the surface which is composed of hexagonally ordered Tl islands. Besides the atomic resolution in the frequency shift signal of our cantilever we also observe a distinct atomic-scale dissipation signal on the order of 10 meV/cycle. The dissipation is reduced at the atomic sites which are surrounded by a ring of increased dissipation. We attribute the ring-like structure of the dissipation pattern to lateral jumps of the weakly bonded Tl atoms of the surface. [1] K. Kuroda et al., Phys. Rev. B 88, 245308 (2013), [2] F. Pielmeier et al., submitted.

O 15.4 Mon 15:45 MA 043

**3D visual feedback during molecular manipulation** — •Philipp

Leinen[1,2], Matthew F. B. Green[1,2], Taner Esat[1,2], Christian Wagner[1,2], F. Stefan Tautz[1,2], and Ruslan Temirov[1,2] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — [2]JARA-Fundamentals of Future Information Technology

The scanning probe microscope is the tool of choice for the manipulation of single molecules on surfaces. With increased molecular complexity the number of degrees of freedom of such systems increases likewise. The respective high-dimensional potential energy surfaces call for the use of customized tip-trajectories for successful manipulation. Here, we present an intuitive approach to the task of SPM-based manipulation of large organic molecules. In brief, we connect a motion tracking and a 3D visualization device to a low-temperature non-contact atomic force microscope / scanning tunneling microscope (nc-AFM/STM). As a proof of principle application we demonstrate the controlled removal of single molecules from a monolayer of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA). The mutual hydrogen bonds in such a layer can only be broken if a specific tip-trajectory is used [1]. The motion tracker allows to find such a trajectory within minutes in a trial and error approach. Using immersive 3D glasses we provide the experimenter with a visualization of the current as well as previous tip trajectories and thus allow a systematic search by selective variation.

[1] M. F. B. Green, T. Esat, C. Wagner, P. Leinen, A. Grötsch, F. S. Tautz, and R. Temirov, *Beilstein J. Nanotechnol.* **5**, 1926 (2014).

O 15.5 Mon 16:00 MA 043

**3-D force and current mapping on PTCDA/Ag(111): the effect of inherent charge at the probe Xe atom** — •Oleksandr Stetsovych[1], Prokop Hapala[1], Ondřej Krejčí[1], Martin Ondráček[1], Martin Švec[1], and Pavel Jelínek[1,2] — [1]Institute of Physics, ASCR, Praha, Czech Republic — [2]Graduate School of Engineering, Osaka University, Japan

The combination of STM and dynamic AFM with functionalized tips allows the investigation of structural and electronic properties of organic molecules with high resolution. In this work, we employ Kolibri sensor with Xe-functionalized tip to acquire simultaneous 3D maps of the force, tunneling current and dissipation over the PTCDA deposited on Ag(111). The detailed contrast features of the force maps at various tip-sample separations are compared to a numerical model. The model describes relaxation of the Xe atom on the probe due to Pauli repulsion and electrostatic interaction with the surface.

Moreover, we observe a specific contrast difference between two independent measurements with Xe-functionalized tips. With a support of the model, it is possible to attribute the varying contrast to an inherent charge on the Xe-atom probe. By a careful comparison of the experimental and simulated data, we can analyze the electrostatic forces acting between the tip and molecule.

O 15.6 Mon 16:15 MA 043

**Chemical identification of atoms in an organic molecule using high-resolution atomic force microscopy** — •Nadine Jacoba van der Heijden[1], Prokop Hapala[2], Jeroen Rombouts[3], Joost van der Lit[1], Pingo Mutombo[2], Pavel Jelinek[2], and Ingmar Swart[1] — [1]Condensed Matter and Interfaces, Utrecht University, The Netherlands — [2]Institute of Physics of the Czech Academy of Science, Prague, Czech Republic — [3]VU University, Amsterdam, The Netherlands

Scanning probe techniques, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), can provide detailed information about the geometric and electronic structure of surfaces and molecules with atomic spatial resolution. However, current methods lack one important capability essential to realize the full potential of these techniques in molecular electronics and chemistry: sensitivity towards element, valence and functional group.

Here, we show that AFM combined with force-distance spectroscopy (FDS) and theoretical calculations can be used to achieve this goal. The central idea is that the force versus distance spectra dependend on the chemical nature of the atom atop of which the spectrum is acquired. By acquiring a 3D force grid over a model molecule, we demonstrate that chemical sensitivity can indeed be obtained.

O 15.7 Mon 16:30 MA 043

**Force Field Analysis of STM/AFM Tips for Atomic Manipulation** — Matthias Emmrich, Maximilian Schneiderbauer, •Ferdinand Huber, Alfred John Weymouth, and Franz Josef Giessibl — Institute for Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany

Atomic manipulation of single atoms and molecules by scanning tunneling microscopy (STM) relies on the force field the tip exerts on the adsorbate that is to be moved. We use combined STM and atomic force microscopy (AFM) operating at low temperature to analyze the force field between metallic tips and a CO molecule adsorbed on a Cu(111) surface [1]. We relate the force field of the tip to its suitability for reliable atomic manipulation and we find that the STM channel alone can lead to incorrect identifications of the pushing, pulling and sliding modes that have previously been identified. Circularly symmetric tips, obtained by poking, yield the most reliable manipulation. The symmetry of the force field can be assessed indirectly by evaluation of the manipulation pattern in the STM channel. In the first publication on manipulation forces [2], a lateral force of 160 ± 30 pN has been measured to move CO across Cu(111) at a temperature of 5 K. Here, we find that 96 pN suffices at a temperature of 7.5 K, suggesting that thermal excitation assists atomic manipulation.

[1] M. Emmrich, M. Schneiderbauer, F. Huber, A. J. Weymouth and F. J. Giessibl, *submitted* (2014)

[2] M. Ternes, C. P. Lutz, C. F. Hirjibehedin, F. J. Giessibl and A. J. Heinrich, Science **319**, 1066 (2008)

O 15.8 Mon 16:45 MA 043

**Mapping intra-molecular charge distribution by distortions in high-resolution AFM/STM microscopy** — •Prokop Hapala[1], Martin Ondracek[1], Stefan Tautz[2], Ruslan Temirov[2], and Pavel Jelinek[1] — [1]Institute of Physics , Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague, 16253, Czech Republic — [2]Institut fur Bio- und Nanosysteme 3, Forschungszentrum Julich, 52425 Julich

Distribution of electron charge in molecules is a central property for chemistry since it indicates nature of bonding. Ionic bonds, polar covalent and non-polar covalent bonds of different bond order distinguish from each other by different charge distribution. At the same time, the internal charge transfer in molecules caused by presence of atoms with different electronegativity can help with identification of these atoms. In this work, we extend our simple mechanical model [1] for simulation of high-resolution AFM and STM images by incorporation of electrostatic potential obtained from DFT calculation. We will demonstrate that distortions observed in high-resolution STM/AFM experiments, including STM images of PTCDA, IETS images of CoPc [2,3] and bond order discrimination in C60 [4], are considerably affected by electrostatic force between local charge density in sample and atomic probe-particle (CO or Xe) attached to tip. [1] Hapala, P. et al., Phys. Rev. B 90, 085421 (2014). [2] Chiang, C. et al., Science 344, 885-8 (2014). [3] Hapala, P. et al., Phys. Rev. Lett. 113, 226101 (2014). [4] Gross, L. et al., Science 337, 1326-9 (2012).

O 15.9 Mon 17:00 MA 043

**Probing the Polar Nature of Bonds by means of Atomic Force Microscopy** — •Florian Albrecht[1], Martin Fleischmann[2], Manfred Scheer[2], Martin Ondráček[3], Pavel Jelinek[3], and Jascha Repp[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany — [2]Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany — [3]Institute of Physics of Czech Academy of Science, 16253 Prague, Czech Republic

Recently, Kelvin probe force spectroscopy (KPFS) has been shown to be a powerful tool to detect charge distributions with sub molecular resolution [1, 2]. We performed KPFS measurements in a low temperature combined scanning tunneling and atomic force microscope with functionalized tips on different types of molecules - some of them exhibiting polar bonds. Whereas KPFS represents the charge distribution with moderate resolution for large tip-molecule separations, it fails for short distances. We therefore introduce a novel technique, in which the dependence of the electric field on tip-sample distance is exploited to map out charges. Thereby, we were able to resolve the intramolecular charge distribution with unprecedented lateral resolution.

[1] F. Mohn, et al., Nature Nano. 7, 227 (2012)

[2] B. Schuler, et al., Nano Letters 14, 3342 (2014)

O 15.10 Mon 17:15 MA 043

**Response of a Kelvin probe force microscope to charge switching dynamics** — •Martin Ondracek, Prokop Hapala, and Pavel Jelinek — Institute of Physics , Academy of Sciences of the Czech Republic, Prague, Czech Republic

Atomic or molecular structures which are capable of switching between two or more different charge states are of much interest as prospective building blocks for nanoelectronic devices. Kelvin probe force microscopy (KPFM), as a local and charge-sensitive probe, is a well-suited tool for studying such structures. Indeed, charge switching has been already observed for Au atoms on NaCl using an atomic force microscope [L. Gross et al., Science 324, 1428; J. Repp et al., Science 305, 493]. However, the time scale of charging and discharging can vary over several orders of magnitude, depending on the particular structure, tip distance, voltage bias, substrate conductivity etc. When the charge dynamics is too fast to be probed in real time, it can still manifest itself as a deviation of the measured curves from perfect Kelvin parabolas and as a contribution to the the dissipation signal. We have developed a simple numerical simulator that models the charge dynamics and interaction of KPFM with the chargeable structure. This enables us to predict the dependence of the characteristic features showing up in KPFM measurements on the time scales of charging and discharging as well as on the instrumental time scales of KPFM: the oscillation period of the cantilever, response time of the feedback loop, and the acquisition time of one data point in the KPFM measurement.

O 15.11 Mon 17:30 MA 043

**Intermolecular Contrast in Atomic Force Microscopy Images without Intermolecular Bonds** — Sampsa K. Hämäläinen[1], Nadine van der Heijden[2], Joost van der Lit[2], Stephan Hartog[2], Peter Liljeroth[2], and •Ingmar Swart[1] — [1]Department of Applied Physics, Aalto University School of Science, Finland — [2]Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

Atomic force microscopy (AFM) finds increasing use in the study of molecules on surfaces. This development started with the demonstration of imaging the chemical structure of organic molecules with atomic resolution.[1] Recently, features described to hydrogen bonds have also been reported. [2] These *inter*molecular bonds primarily have an electrostatic origin and may include some covalent character and other attractive interactions. However, it is not clear why these should yield significant repulsive contrast in AFM.

A recent theoretical study showed that the intermolecular features can be explained by the flexibility of molecule-terminated tips.[3] We probed this effect by carrying out atomic force microscopy experiments on a model system that contains regions where intermolecular bonds should and should not exist between close-by molecules. Intermolecular features are observed in both regions, demonstrating that intermolecular contrast cannot be directly interpreted as intermolecular bonds.[4]

[1] L. Gross et al. Science, 325, 1110 (2009). [2] J. Zhang et al. Science 342, 611 (2013). [3] P. Hapala et al., Phys. Rev. B 90, 085421 (2014). [4] S.K. Hämäläinen et al., Phys. Rev. Lett. 113, 186102 (2014).

O 15.12 Mon 17:45 MA 043

**Image Distortions of Molecules in Atomic Force Microscopy with Carbon Monoxide Terminated Tips** — •Nikolaj Moll, Leo Gross, Bruno Schuler, Alessandro Curioni, and Gerhard Meyer — IBM Research – Zurich, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland

Using functionalized tips, the atomic resolution of a single organic molecule can be achieved by atomic force microscopy (AFM) operating in the regime of short-ranged repulsive Pauli forces while the van-der-Waals and electrostatic interactions only add a diffuse attractive background [1]. The underlying mechanisms of image distortions in AFM with CO-terminated tips are identified and studied in detail [2]. Parts of a molecule appear different in size, which primarily originates from the charge density. Further, tilting of the CO at the tip, induced by van der Waals forces, enlarges the apparent size of parts of the molecule by up to 50 %. Moreover, the CO tilting in response to local Pauli repulsion causes a significant sharpening of the molecule bonds in AFM imaging. With these image distortions it is possible to distinguish different bond orders of individual carbon-carbon bonds in organic molecules by AFM.

[1] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, Science 325, 1110 (2009).

[2] N. Moll, B. Schuler, S. Kawai, F. Xu, L. Peng, A. Orita, J. Otera, A. Curioni, M. Neu, J. Repp, G. Meyer, and L. Gross, Nano Lett. (2014).

O 15.13 Mon 18:00 MA 043

**Development of cryogen-free low temperature scanning probe microscope by using a closed cycle cryostat** — •Byoung Choi, Stefan Ulrich, and Ryan Murdick — RHK Technology Inc. Troy, MI 48083, USA

Low temperature scanning tunneling microscope and atomic force microscope (LT-STM/AFM) based on a closed cycle cryostat (CCC) has been recently developed. We could realize to have the microscope thermally linked but mechanically decoupled to the cryostat by using a rubber bellows filled with Helium heat exchange gas. It enables atomically resolved topographic and spectroscopic measurements on various surfaces. At the temperature as low as 14K, the tip-sample distance fluctuation has been detected as low as 2 picometer after 8 hours of cooling. With stable conditions of both microscope and controller, we could record more than 64 by 64 scanning tunneling spectra grid for over 10 hours. The lateral drift during the measurement was as low as 1 nanometer without a counter heater or a temperature controller. We will also present the high stability and reproducibility of the CCC-LT-STM/AFM with the atom resolved imaging of Si, Pt, Au and KBr surfaces with an STM and AFM combined imaging and spectroscopic technique. These results demonstrate that the CCC-LT-STM/AFM is an instrument enabling experiments on a variety of surfaces and materials at sub-angstrom resolution without using any liquid cryogen.

## O 16: Graphene: Theory (HL with O/TT)

Time: Monday 15:00–17:15 Location: ER 164

O 16.1 Mon 15:00 ER 164

**The decoupling of epitaxial graphene on SiC by hydrogen intercalation: an *ab initio* study** — •Lydia Nemec[1], Patrick Rinke[1,2], Volker Blum[3], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Aalto University, Helsinki, Fi — [3]Duke University, Durham, NC, USA

Large-scale ordered epitaxial graphene can be grown on various substrates, out of which silicon carbide (SiC) is one of the most promising. The exact material properties of graphene depend on the growth conditions and its interaction with the substrate. By hydrogen intercalation of epitaxial graphene on the Si-face of SiC the graphene layer decouples from the substrate forming quasi-free-standing monolayer graphene (QFMLG) [1].

We performed an density functional theory study of QFMLG on the polar 6H-SiC(0001) surface based on a van der Waals corrected semilocal exchange-correlation functional using the all-electron numeric atom-centered basis function code FHI-aims. We find an adsorption height in excellent agreement with X-ray standing wave experiments, a very low buckling of the graphene layer, and a very homogeneous electron density at the interface. All these features improve the electronic properties of QFMLG compared to epitaxial graphene.

Using the insight gleaned on the Si-face, we present the structure of a hypothetical QFMLG phase on the C-face of SiC. We find that hydrogen intercalation is a promising option to control the SiC-graphene interface.

[1] C. Riedl, *et. al*, PRL 103, 246804 (2009).

O 16.2 Mon 15:15 ER 164

**Two-dimensional analysis of the double-resonant 2D Raman mode in bilayer graphene** — •Felix Herziger[1], Matteo Calandra[2], Paola Gava[2], Patrick May[1], Michele Lazzeri[2], Francesco Mauri[2], and Janina Maultzsch[1] — [1]Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany — [2]IMPMC, Université Pierre et Marie Curie, CNRS, 75252 Paris, France

The double-resonant 2D-mode Raman process in bilayer graphene has been discussed controversially in recent years. In this context, different models were proposed to explain the complex lineshape observed in experiments.

Using a two-dimensional first-principles calculation, we investigate the dominant contributions to the double-resonant Raman scattering cross-section of the 2D mode in bilayer graphene [1]. In contrast to previous works, we demonstrate that so-called 'inner' processes are, by far, the most dominant processes, as in single-layer graphene. Moreover, we show that the splitting between the two TO-derived phonon branches in bilayer graphene cannot be neglected for a consistent understanding of the 2D-mode lineshape. Additionally, we investigate the contributions from both TO branches to the symmetric and anti-symmetric scattering processes. Our results answer the long-standing question regarding the different contributions to the 2D-mode lineshape in bilayer graphene.

[1] F. Herziger, M. Calandra, P. Gava, P. May, M. Lazzeri, F. Mauri, and J. Maultzsch, Phys. Rev. Lett. 113, 187401 (2014)

O 16.3 Mon 15:30 ER 164

**Edge effects in the Raman spectra of atomically precise graphene nanoribbons: an ab-initio study** — Marzio De Corato$^{1,2}$, •Deborah Prezzi$^{2}$, Alice Ruini$^{1,2}$, and Elisa Molinari$^{1,2}$ — $^{1}$Department of Physics, Mathematics, and Informatics, University of Modena and Reggio Emilia, 41125 Modena, Italy — $^{2}$CNR-Nanoscience Institute, S3 Center, 41125 Modena, Italy

Bottom-up techniques have proven successful to achieve ultra-narrow and structurally well-defined graphene nanoribbons (GNRs) [1-2], where different edge shapes and terminations can be obtained by varying the molecular precursors. In this work we perform density-functional perturbation theory calculations to investigate the vibrational properties of GNRs with cove-type edge structure and variable width, similar to those produced in Ref. 2. By comparison with other prototype systems, we show that the phonon modes and the Raman spectra of these systems strongly depend on the specific edge morphology. This is particularly evident in the acoustic region, where the Radial-Like Breathing Mode (RLBM) shows sensible changes when the edge termination is modified. This makes the Raman spectrum of these GNRs very different from the case of both carbon nanotubes and ribbons with ideal armchair or zigzag edges, where the breathing mode depends on the lateral size only. Our results are in very good agreement with recent experimental data [2].

[1] J. Cai et al., Nature (London) 466, 470 (2010). [2] A. Narita et al., Nature Chem. 6, 126 (2014).

O 16.4 Mon 15:45 ER 164

**Controlling the localization of electrons in bilayer graphene** — •Maximilian Fleischmann, Sam Shallcross, and Oleg Pankratov — Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7B2, 91058 Erlangen

Two mutually rotated layers of graphene exhibit an electronic structure that depends profoundly on the rotation angle. The small angle regime in particular is associated with significant changes of the electronic properties of the bilayer: one finds localization on the moiré lattice and a significant reduction in the Fermi velocity near the Dirac point [1]. We investigate how the electronic properties in the small angle limit may be controlled by an external electric field directed perpendicular to the bilayer. We consider a uniform field as well as modulated fields with a period chosen to "connect" the Dirac cones of the two layers in momentum space. The latter electrostatic potentials may be realized by a proper choice of substrate. We find that electric fields can be used to control the degree of localization of the quasiparticles in the bilayer. A uniform field tends to delocalize the electron states; this effect is generally less pronounced for energies close to the Dirac point. In contrast, a modulated field favours electron localization throughout the low-energy spectrum.

[1] S. Shallcross et al., Phys. Rev. B 87, 245403, 2013.

O 16.5 Mon 16:00 ER 164

**Magnetic interactions in bilayer graphene** — •Nicolas Klier, Sam Shallcross, and Oleg Pankratov — Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7B2, 91058 Erlangen

The indirect exchange interaction between magnetic impurities, known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, is governed by the static spin susceptibility of the host system and therefore depends sensitively on the host electronic structure. For this reason, this interaction is particularly interesting for materials in which the underlying electronic spectrum is novel, such as single layer and bilayer graphene. We investigate the RKKY interaction for bilayer graphene at zero and at finite temperature, as well as for the case in which the bilayer is biased by a perpendicular electric field. At the edge of the energy gap between the two conduction (or valence) bands at the Dirac point we find a remarkable transition in the form of the RKKY interaction. For Fermi energies on either side of the gap the interaction takes asymptotically two different forms: the oscillatory or the anti-ferromagnetic. We show that at the Dirac point the sign of the RKKY interaction (ferromagnetic vs anti-ferromagnetic) can be controlled by an external electric field.

O 16.6 Mon 16:15 ER 164

**Is deformed graphene described by the Dirac-Weyl equation on a curved space-time?** — •Fabian Rost, Sam Shallcross, and Oleg Pankratov — Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7B2, 91058 Erlangen

It is well known that, at low energies, the quasiparticles of graphene are described by the wave equation of massless neutrinos: the Dirac-Weyl equation. Less well understood is whether the elastically deformed graphene can be described as the DW equation on a curved space-time as suggested in [1]. To answer this question we consider both a space-time description, and a low energy treatment derived from the tight-binding model, and compare them term by term in an expansion in the deformation tensor. We find that the low energy theory contains an infinite class of deformation-dependent terms that are absent in the space-time approach. Yet all terms present in the curved-space approach can be found in the low energy theory which follows from the tight-binding model.

[1] F. de Juan, A. Cortijo, and M.A.H. Vozmediano, *P*hys. Rev. B **76**, 165409, 2007.

O 16.7 Mon 16:30 ER 164

**Phase diagram of honeycomb lattice in Iionic-Hubbard model** — •Sahar Nabavi and Morad Ebrahimkhas — Department of Science, Mahabad Branch, Islamic Azad University, Mahabad 59135, Iran

Tight binding electrons on a honeycomb lattice are described by an effective Dirac theory at low energies. An alternate ionic potential ($\Delta$) generates a single-particle gap in the spectrum. We employ the dynamical mean field theory- iterative perturbation theory (DMFT-IPT) technique, to study the effect of on-site electron correlation ($U$) on energy gap of a honeycomb system. For a fixed ionic potential $\Delta$, we find that beyond a critical value $U_{c1}(\Delta)$ massive Dirac fermions become massed and we have gapped energy bands. Further increasing $U$ beyond $U_{c2}(\Delta)$, there will be another phase transition to the Mott insulating state. Therefore the competition between the single-particle gap parameter, $\Delta$, and the Hubbard $U$ between $U_{c1}(\Delta) < U < U_{c2}(\Delta)$ restores the semi-metallic nature. The width of the intermediate semi-metallic regime shrinks by increasing the ionic potential. However, at small values of $\Delta$, there is a wide interval of $U$ values for which the system remains semi-metal. The phase diagram and energy gap of the system are identified

O 16.8 Mon 16:45 ER 164

**Antiferromagnetic coupling of vacancies in graphene on SiO$_2$** — •Stephan Zimmermann$^{1}$, Sven Just$^{2}$, Marco Pratzer$^{2}$, Markus Morgenstern$^{2}$, Vladislav Kataev$^{1}$, and Bernd Büchner$^{1}$ — $^{1}$IFW Dresden, Institute of Solid State and Materials Research, 01069 Dresden, Germany — $^{2}$II. Institute of Physics B and JARA-FIT, RWTH Aachen, 52074 Aachen, Germany

Monolayer graphene grown by chemical vapor deposition and transferred to SiO$_2$ is used to introduce vacancies by Ar$^{+}$ ion bombardment at a kinetic energy of 50 eV. The density of defects visible in scanning tunneling microscopy is considerably lower than the ion fluence, implying that most of the defects are single vacancies as expected from the low ion energy. The vacancies are characterized by scanning tunneling spectroscopy on graphene and highly oriented pyrolytic graphite (HOPG). A peak close to the Dirac point is found within the local density of states of the vacancies similar to the peak found previously for vacancies on HOPG. The peak persists after air exposure up to 180 min, such that electron spin resonance (ESR) at 9.6 GHz can probe the vacancies exhibiting such a peak. After an ion flux of 10/nm$^{2}$, we find an ESR signal corresponding to a g factor of 2.001-2.003 and a spin density of 1-2 spins/nm$^{2}$. The peak width is as small as 0.17 mT indicating exchange narrowing. Consistently, the temperature-dependent measurements reveal antiferromagnetic correlations with a Curie-Weiss temperature of -10 K. Thus, the vacancies preferentially couple antiferromagnetically, ruling out a ferromagnetic graphene monolayer at ion induced spin densities of 1-2 nm$^{2}$.

O 16.9 Mon 17:00 ER 164

**Behaviour of the edge states of the $\nu = 0$ lowest Landau level in graphene beyond SU(4)-symmetry** — •Angelika Knothe[1,2] and Thierry Jolicoeur[2] — [1]Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — [2]Université Paris Sud, CNRS, LPTMS, UMR 8626, Orsay 91405 France

The $\nu = 0$ quantum Hall state of an infinite sheet of graphene is known to exhibit various different phases when the SU(4)-symmetry of spin and valley/sublattice isospin is broken by interactions and the Zeeman-effect [1]. The situation becomes even richer when considering the edge states close to the sharp boundaries of a finite piece of graphene: Recent theoretical [2] and experimental [3] works suggest that in finite samples the properties of the spin and isospin-texture and its excitations depend on the position within the lattice with respect to its edge. With the help of numerical Hartree-Fock calculations we theoretically investigate the behaviour of the edge modes of a $\nu = 0$ quantum Hall state of graphene. In our model-Hamiltonian we account for both, the influence of SU(4)-symmetric terms and such that break the symmetry, as well as for the presence of the boundary of the lattice. In doing so, we are able to understand the behaviour of different spin and isospin configurations as compared to the phases in the bulk or the predictions of a non-interacting single-electron theory [4].

[1] M. Kharitonov, Phys. Rev. B **85**, 155439 (2012) [2] G. Murthy *et al.*, Phys. Rev. B **90**, 241410(R) (2014) [3] G. Li *et al.*, Nature Commun. **4**, 1744 (2013) [4] D. A. Abanin *et al.*, Phys. Rev. Lett. **96**, 176803 (2006)

## O 17: Overview Talk (Eli Rotenberg)

Time: Tuesday 9:30–10:15 Location: HE 101

**Invited Talk** O 17.1 Tue 9:30 HE 101

**Angle-Resolved Photoemission Spectroscopy (ARPES) and its applications to novel 2D materials** — •Eli Rotenberg — The Advanced Light Source, E. O. Lawrence Berkeley National Lab, Berkeley CA 94720 USA

Angle resolved photoemission spectroscopy (ARPES) is a well-known and ideal technique for elucidating the basic electronic structure of materials, both simple and complex. Beyond this, it is able to illuminate more subtle aspects of the properties of conduction electrons, such as ground-state symmetry breaking and many-body interactions. The tuning, or control, of these properties in engineered materials is of tremendous relevance for the search for new materials with potentially useful properties, such as higher temperature superconductors or long-lived, topologically non-trivial states.

Because ARPES is a critical tool in the development cycle of such new materials, there is a wide interest in establishing tighter integration between ARPES and both ever more discerning light sources as well as complex in-situ sample preparation capabilities. I will provide a review of the ARPES technique and its application to new materials in this context, emphasizing the development of new instrumentation for small-spot ARPES (potentially down to 50 nm or so) and crystal growth of 2D materials using conventional and pulsed laser deposition techniques. Examples will be drawn from epitaxially-grown multilayer graphenes and oxides such as tetragonal CuO.

## O 18: Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces I

Time: Tuesday 10:30–12:30 Location: HE 101

**Topical Talk** O 18.1 Tue 10:30 HE 101

**Water adsorption on Ru(0001): A molecular perspective** — •Sabine Maier — Department of Physics, FAU Erlangen-Nürnberg, Germany

Water and its dissociation products play an important role in many areas of fundamental science and technological applications. The water molecules at the interface with metal surfaces are arranged differently than those in the bulk liquid or ice due to their strong bonding to the surface. Here, molecular level studies are presented using low temperature scanning tunneling microscopy, that offer new insights into the formation of a wetting layer and the water dissociation process on Ru(0001). We found a bonding motif of the first water layer consisting of rotated hexagonal molecular domains connected by pentagons and heptagons, which deviates significantly from the conventional ice-like water model.[1] Above 150K, we observed the formation of mixed water-hydroxyl structures following partial dissociation. The reaction path for the dissociation process and its energetics will be discussed.[2]

[1] S. Maier et al. Phys. Rev. B 85, 155434 (2012)

[2] S. Maier et al. Phys. Rev. Lett. 112, 126101 (2014)

O 18.2 Tue 11:00 HE 101

**Probing Water Structure at the $\alpha$-$Al_2O_3$(0001) Surface Using Interface Specific Vibrational Dynamics** — Yujin Tong, Harald Kirsch, Martin Wolf, and •R. Kramer Campen — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

$\alpha$-$Al_2O_3$(0001) surfaces exposed to water are ubiquitous in engineered applications and a useful model for more complicated alumino-silicate surface/water interaction omnipresent in the environment. Despite this ubiquity, gaining a molecular level understanding of water $\alpha$-$Al_2O_3$(0001) interaction has proven challenging. It has recently been proposed, based partly on simulation, that the first layer of water on this surface is essentially hydrophobic: while hydrogen bonding occurs within this first layer, neither surface aluminols nor the first layer of molecular water donate a hydrogen bond to overlying bulk liquid. Direct experimental evidence for such a non-wetted water layer has thus far proven elusive. Here we probe the existence of this layer using interface specific vibrational relaxation as a probe of surface water structure. We find, using an ultrafast time resolved infrared pump - vibrational sum frequency probe scheme, that the $T_1$ of OH groups at the $\alpha$-$Al_2O_3$(0001) surface is $\approx 8$ ps: intermediate between that of surface aluminols in contact with excess water ($< 1$ ps) and that of isolated surface OH groups on oxide surfaces ($> 100$ ps). This intermediate $T_1$ is the first direct experimental insight consistent with a non-wetted interfacial water layer on the $\alpha$-$Al_2O_3$(0001) surface.

O 18.3 Tue 11:15 HE 101

**A joint *first principles* and ATR-FTIR study of the vibrational properties of interfacial water at Si(100):H-$H_2O$ solid-liquid interfaces** — •lei yang[1], stefanie tecklenburg[1], andreas erbe[1], stefan wippermann[1], francois gygi[2], and giulia galli[3] — [1]Max-Planck-Institute for Iron Research, Duesseldorf, Germany — [2]University of California, Davis, Davis, United States — [3]University of Chicago, Chicago, United States

Understanding the structural and bonding properties of solid-liquid interfaces is crucial for a wide range of (photo-)electrochemical applications, such as e. g. solar water splitting and electrolysis. However, there are no experimental techniques presently available allowing one to directly probe the microscopic structure of solid-liquid interfaces. We present a joint investigation of the vibrational properties of interfaces between liquid water and prototypical semiconductor substrates, i.e. hydrogenated silicon surfaces. We carried out (ATR-FTIR) spectroscopy measurements and *ab initio* molecular dynamics simulations. The latter allowed us to interpret the experiments and to unravel specific bonding configurations and interactions of water molecules with the solid surfaces. Our study highlights the key role of coupled theory-experimental investigations on well controlled and characterized interfaces, in order to develop robust strategies to interpret experiments and validate theory. This work provides a solid basis for investigating ion solvation and chemical processes at the interface. G. G. and F. G. acknowledge DOE-BES Grant No. DE-SS0008939.

**Topical Talk** O 18.4 Tue 11:30 HE 101

**Using resonant inelastic soft x-ray scattering maps to study liquids, gases, and their interfaces** — •Lothar Wein-

hardt — IPS, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany — ANKA Synchr. Radiation Facility, KIT, Eggenstein-Leopoldshafen, Germany — Dep. of Chem., University of Nevada, Las Vegas, U.S.A. — ITCP, KIT, Karlsruhe, Germany

X-ray emission spectroscopy (XES) and Resonant Inelastic X-ray Scattering (RIXS) have recently been applied to study liquid and gaseous systems. Such experiments became possible with new specialized experimental setups and given a unique insight into the electronic and vibrational structure of these systems. In this way, information on solvent/solute interactions, hydrogen bonding, molecular symmetries, excited-state dynamics, and many other aspects could be gathered. Finally, interfaces between solids and a gas/liquid can be studied in an in-situ fashion, which is of particular relevance for a wide range of applied systems including catalysis, electrochemistry, or the influence of environmental conditions on surfaces. In this presentation, we will report on our recent progress on studying such systems using XES and RIXS. By the development of a high-transmission soft x-ray spectroscopy setup we are able to measure complete Resonant Inelastic soft X-ray Scattering (RIXS) maps. These maps give a comprehensive picture of the electronic structure of occupied as well as unoccupied electronic states of the studied system. We will demonstrate the power of this approach by discussing the results obtained on selected liquids, gases, solutions, as well as gas/solid- and liquid/solid interfaces.

**Topical Talk** O 18.5 Tue 12:00 HE 101

**Effect of flow on water organization at solid interfaces** — •Mischa Bonn — Max Planck Institute for polymer research, Mainz, Germany

At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water. Owing to its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has received much attention.

We elucidate the structure and structural dynamics of interfacial water using ultrafast surface-specific sum-frequency generation (SFG) vibrational spectroscopy. We make use of the fact that the SFG signal depends critically on the interfacial organization of water molecules. We attempt to bridge continuum models of laminar flow along interfaces, with molecular-level descriptions of the Stern and diffuse layer, which describe the near-surface distribution of ions.

For water at two different mineral interfaces, we report a dramatic effect of water flow water along the mineral surface on the organization of water at the interface. Our observations can be explained by considering the coupling between the flow and the dissolution chemistry at the interface. Even for low-soluble quartz at neutral pH, dissolution plays a key role in determining the interfacial water organization.

## O 19: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale I

Time: Tuesday 10:30–13:30 Location: MA 004

**Invited Talk** O 19.1 Tue 10:30 MA 004

**Electronic structure in the vicinity of strong non-adiabatic couplings** — •Eberhard K.U. Gross — Max Planck Institute of Microstructure Physics, Halle (Saale), Germany

The Born-Oppenheimer (BO) approximation is among the most fundamental ingredients of modern Condensed-Matter Theroy. Yet, some of the most fascinating phenomena such as the process of vision or phonon-driven superconductivity occur in the regime where the BO approximation breaks down. To tackle such situations one has to face the Hamiltonian of the complete system of interacting electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration. The resulting equations of motion for the nuclear and electronic wavefunctions lead to a unique definition of exact potential energy surfaces as well as exact geometric phases. We show an example [2] where the geometric phase associated with the conical intersection of BO surfaces has no counterpart in the true electron-nuclear wavefunction. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3], reminiscent of Tully surface hopping algorithms. Based on this observation we propose novel mixed-quantum-classical algorithms.

[1] Abedi, Maitra, Gross, PRL 105, 123002 (2010).

[2] Min, Abedi, Kim, Gross, PRL 113, 263004 (2014).

[3] Abedi, Agostini,Suzuki, Gross, PRL 110, 263001 (2013).

O 19.2 Tue 11:00 MA 004

**Towards First-Principles Modeling of Electrolytic Solvent Effects in Photo-Catalytic Water Splitting** — •Stefan Ringe[1], Sebastian Matera[2], Harald Oberhofer[1], and Karsten Reuter[1] — [1]Technische Universität München — [2]Freie Universität Berlin

Due to the complexity of the physical processes underlying photocatalytic surface reactions, ab-initio computational approaches have to overcome major challenges concerning accuracy and computational costs. In particular, an efficient description of electrolytic solvent effects—which are crucial for charge driven reactions—is highly necessary.

We present an implementation of the modified Poisson-Boltzmann (MPB) model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. In contrast to most implicit solvent models, this technique combines nonlinear dielectric solvent response with a statistical description of solvated finite-sized ions. This has been shown to capture a majority of electrochemical solvent effects appearing in heterogeneous photo-catalysis.[1]

We developed a self-consistent function-space oriented solution scheme for Poisson-Boltzmann-like equations which in contrast to common multi-grid solvers is able to exploit the specialized grids and optimized integration schemes of FHI-aims. We demonstrate the approach and its efficiency for the linearized Poisson-Boltzmann equation and a range of molecular systems. Finally, we discuss how the methodology can be employed for the solution of non-linear problems. [1] Kilic,M.S., Bazant, M.Z., *Phys. Rev. E*, *75*, **2007**, 021502.

O 19.3 Tue 11:15 MA 004

**Phonons in Molecular Crystals: The Role of Collective van der Waals Interactions** — •Johannes Hoja and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

By now, it is well established that dispersive van der Waals (vdW) interactions are crucial for the structure and stability of molecular crystals [1]. However, complete understanding of functionality of molecular crystals also requires a predictive description of response to external perturbations. Here we study the role of vdW interactions on phonons in molecular crystals. This subject is important since such low-frequency vibrations can be used to identify for instance drugs, explosives, and different polymorphic forms of molecular crystals. We studied the vibrational spectra of several molecular crystals with density-functional theory, including many-body dispersion interactions (DFT+MBD method). We find that long-range MBD effects can give rise to novel peaks in the phonon density of states [2], which can not be observed with a simple pairwise treatment of vdW interactions. We further discuss the nature of these vibrations and demonstrate a non-trivial connection between collective vdW interactions and entropy of molecular crystals.

[1] L. Kronik, A. Tkatchenko, Acc. Chem. Res. 47, 3208 (2014).

[2] A. M. Reilly, A. Tkatchenko, Phys. Rev. Lett. 113, 055701 (2014).

O 19.4 Tue 11:30 MA 004

**Converged Nuclear Quantum Statistics from Semi-Classical Path Integrals** — •Igor Poltavskyi and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The quantum nature of nuclear motions plays a vital role in the structure, stability, and thermodynamics of molecular systems. The standard approach to take nuclear quantum effects (NQE) into account is the Feynman-Kac imaginary-time path-integral molecular dynamics (PIMD). Conventional PIMD simulations require exceedingly large number of classical subsystems (beads) to accurately capture NQE, resulting in considerable computational cost even at room temperature due to the rather high internal vibrational frequencies of many molecules of interest.

We propose a novel parameter-free form for the PI partition function and estimators to calculate converged thermodynamic averages. Our approach requires the same ingredients as the conventional PIMD simulations, but decreases the number of required beads by roughly an order of magnitude. This greatly extends the applicability of *ab initio* PIMD for realistic molecular systems. The developed method has been applied to study the thermodynamics of $N_2$, $H_2O$, $CO_2$, and $C_6H_6$ molecules. For all of the considered systems at room temperature, 4 to 8 beads are enough to recover the NQE contribution to the total energy within 2% of the fully converged quantum result.

O 19.5 Tue 11:45 MA 004

**Can we get reliable quantum dynamics simulations for vibrational spectra in the condensed phase?** — •Mariana Rossi[1], David Manolopoulos[1], and Michele Ceriotti[2] — [1]University of Oxford, Oxford, UK — [2]EPFL, Lausanne, Switzerland

At the level of accuracy we can now achieve in first-principles calculations, the inclusion of more subtle nuclear quantum effects (NQE) in simulations become more relevant. However, their inclusion is challenging for anharmonic and dynamical processes, in particular in the condensed phase. We show a new method to approximate quantum corrections in time-dependent properties based on a path integral framework, called thermostatted ring polymer molecular dynamics (TRPMD) [1], which is immune to pathological problems of previously proposed methods. We perform a systematic comparison of TRPMD with other approaches that rely on different approximations to quantum dynamics, to assess their performance for the IR spectrum of HOD in $D_2O$ and water at different phases/temperatures [2]. Using an empirical potential energy surface (q-TIP4P/f), we find that the different techniques are largely consistent with one another, within a few tens of $cm^{-1}$. Comparison with classical molecular dynamics demonstrates the importance of NQE even up to 600K. The cross validation between these different approaches provides clues to limitations of their underlying approximations and paves the way for more reliable approaches to nuclear quantum dynamics that are feasible together with electronic structure methods. [1] M. Rossi, M. Ceriotti, D. Manolopoulos, JCP 140, 234116 (2014); [2] M. Rossi, et al., JCP 141, 181101 (2014)

O 19.6 Tue 12:00 MA 004

**Ultra-high temperature properties of ZrC: a fully-anharmonic ab-initio approach** — •Andrew Duff[1], Dominique Korbmacher[2], Albert Glensk[2], Blazej Grabowski[2], Joerg Neugebauer[2], and Mike Finnis[1] — [1]Department of Physics and Department of Materials, Thomas Young Centre, Imperial College London, Exhibition Road, London SW7 2AZ, UK — [2]Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, Düsseldorf 40237, Germany

As a binary end-member of many of the technologically highly interesting MAX phases, as well a useful refractory material in its own right, there is much to be gained from achieving a more accurate first-principles assessment of the behaviour of ZrC at ultra-high temperatures. Exploiting recent developments in finite-temperature density functional theory (DFT) calculations, we provide valuable data at temperatures where the available experimental data is of low accuracy. Within the framework of the UP-TILD approach [Grabowski 2007], the thermal expansion and heat-capacity of ZrC are calculated up to the melting-point. These fully anharmonic results are compared to calculations performed within the widely used quasi-harmonic approximation (QHA), which treats anharmonic effects in only an approximate manner. Sizeable deviations are found close to the melting point, consistent with the strongly anharmonic lattice vibrations present at such temperatures.

O 19.7 Tue 12:15 MA 004

**Quo vadis electronic friction? Assessing vibrational lifetimes beyond the independent atom approximation** — •Simon P. Rittmeyer[1], J. Iñaki Juaristi[2], Jörg Meyer[3], and Karsten Reuter[1] — [1]Technische Universität München, Germany — [2]Depto. & Centro de Física de Materiales (CSIC-UPV/EHU), San Sebastián, Spain — [3]Leiden University, Leiden, The Netherlands

The quest for a both accurate and numerically efficient first-principles-based treatment of electronically non-adiabatic adsorbate dynamics on metal surfaces is still ongoing. A promising candidate in this regard is the concept of electronic friction within the local density friction approximation (LDFA). The numerical efficiency of this approach stems from an intrinsic decomposition and mapping of the interacting system to independent atoms individually embedded in a free electron gas. This inherent simplicity has raised serious conceptual concerns about the accuracy of this theory. On the other hand, it is not clear how much these approximations actually affect the description of "real" observables. In this regard, vibrational lifetimes of high-frequency adsorbate modes on metal surfaces provide a sensitive measure to gauge a non-adiabatic theory. We thus target this observable applying the LDFA for several well-studied systems and discuss it by comparing the results to other theoretical approaches as well as experimental data. Moreover, we present a simple and computationally efficient strategy to extend the LDFA beyond the yet indispensable frozen-surface and independent-atom approximation.

O 19.8 Tue 12:30 MA 004

**Polynomial-oriented linear least squares fits of potential energy surfaces for quantum dynamics** — •Florian Habecker and Thorsten Klüner — Universität Oldenburg, Germany

The field TD-QM Molecular Dynamics is facing two major problems within the BO-approximation: I. Solution of the TISE for the electrons and II. Solution of the TDSE for the nuclei. Electronic structure calculations result in a K-dimensional PES (K: number of d.f. for the nuclei) on which the motion of the nuclei is simulated, subsequently.

For economical reasons, the number of sampling points calculated by QC methods is generally smaller than those needed in the QD calculation. Hence, an interface is required to link the two major tasks. Taking the scalar energies E with the corresponding geometry parameters as input, the output of such an interface is a function to calculate any points of the PES, i.e. interpolated and extrapolated values.

Following classical papers on $H_3^+$ [1 and refs. therein], the linear model function was chosen as a K-dimensional polynomial in this study. The lack of flexibility in this uniform ansatz was restored using appropriate non-linear variable transformations. Applying the method of LLS, precise fits can be calculated in a single non-iterative step. The capability of this approach was validated with a set of 7942 ab initio data points from a 3-D PES of a $CO/Ti_9O_{18}Mg_7^{14+}$-system [2]. Precise fits with chemical accuracy and better have been obtained for moderate expansions of the model function.

[1] W. Meyer, P. Botschwina, P. Burton, *J. Chem. Phys.* **84**, 891 (1986).
[2] H. Spieker, T. Klüner, *Phys. Chem. Chem. Phys.* **16**, 18743 (2014).

O 19.9 Tue 12:45 MA 004

**Representing Complex Potential Energy Surfaces by Artificial Neural Networks** — •Christopher Handley and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universit*at Bochum, D-44780 Bochum, Germany

Computer simulations of large systems are computationally costly, and in many cases intractable, when using ab initio methods. More efficient potentials are typically based on approximations specific for particular atomic interactions, and the fitting of these potentials is not straightforward. Neural Networks (NNs) can provide interatomic potentials that are comparable to the accuracy of quantum mechanical calculations [1,2]. They are flexible enough to fit complex functions to quantum mechanical training data and yield accurate energies and forces. Here, we present our recent work towards more transferable NN potentials. [1] C. M. Handley and P. L. A. Poplier, J. Phys. Chem. A, 114, 3371- 3383, (2010). [2] J. Behler, PCCP, 13, 17901-18232 (2011).

O 19.10 Tue 13:00 MA 004

**Kinetic Monte Carlo simulations of thin film growth with anisotropic particles** — •Miriam Klopotek, Martin Oettel, and Frank Schreiber — Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Thin film growth is a topic of fundamental experimental research, in particular for organic molecules with semiconducting properties. Thin films of organic molecules are composed of multiple 'imperfect' layers of the molecules, and the structures formed are of fundamental interest for various applications. Organic molecules are mostly highly anisotropic, rendering complex ordering at various length- and time-scales within the growing film that is not seen in the case of isotropic molecular/atomistic films [1]. We explore how this particle anisotropy affects the growth dynamics by means of computer simulations. We have developed a novel algorithm to simulate large-scale thin film growth with rod-like particles using an accelerated Monte Carlo technique called *kinetic Monte Carlo* [2]. We disuss the simulations and the most relevant findings arising from statistical observables related to the orientational order of the rods. To relate the non-equilibrium growth structures to equilibrium we performed equilibrium calculations of a single layer of rods, as well. [1] S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti, and O. Konovalov. Real-time observation of structural and orientational transitions during growth of organic thin films. *Phys. Rev. Lett.*, 96:125504, March 2006. [2] Andrea C. Levi and Miroslav Kotrla. Theory and simulation of crystal growth. *Journal of Physics: Condensed Matter*, 9(2):299, 1997.

O 19.11 Tue 13:15 MA 004

**Ti and N adatom diffusion on, and $N_2$ desorption from TiN(001) surfaces via *ab initio* and classical molecular dynamics** — •Davide G. Sangiovanni[1], Daniel Edström[1], Lars Hultman[1], Ivan Petrov[1,2], Valeriu Chirita[1], and Joe E. Greene[1,2] — [1]Thin Film Physics, IFM, Linköping University, Sweden — [2]University of Illinois, Urbana-Champaign, Illinois, USA

We use classical and *ab initio* molecular dynamics to investigate fundamental atomistic processes and surface properties responsible for TiN surface evolution during thin film growth. The rate of adatom migration and $N_2$ desorption events are determined as a function of temperature to extract activation energies, attempt frequencies, and diffusion coefficients. Ti adatoms ($Ti_{ad}$), highly mobile on TiN(001) terraces, diffuse among fourfold hollow sites, primarily along <100> channels via single and long jumps. $Ti_{ad}$ jumps on TiN(001) are highly correlated; an effect which leads to smaller diffusion coefficients than those determined via adatom random walks. Due to strong bonds formed with underlying N surface ($N_{surf}$) atoms, N adatoms ($N_{ad}$) are considerably less mobile on TiN(001) than Ti adatoms. After several $N_{ad}/N_{surf}$-pair exchange reactions, with very few $N_{ad}$ jumps among neighboring stable surface sites, the $N_{ad}/N_{surf}$ pair desorbs, leaving an anion surface vacancy which acts, in turn, as a catalyst for $N_2$ dissociative chemisorption. This pathway for $N_2$ desorption from TiN(001) is considerably more probable than N adatom recombination, which is kinetically hindered due to short-range $N_{ad}/N_{ad}$ repulsive interactions.

## O 20: Inorganic/Organic Interfaces: Growth III

Time: Tuesday 10:30–13:15 Location: MA 005

O 20.1 Tue 10:30 MA 005

**Tetrahydrofuran adsorption mechanism on Si(001)-c(4x2): A systematic density functional study.** — •slimane laref ralf tonner — Fachbereich Chemie, Hans Meerwein Straße, 35032 Marburg, Germany

The silicon surface plays a decisive role for semiconductor devices. Thereby, the adsorption of organic molecules on silicon can play a major role in increasing functionalizing these semiconductors and even improve device properties in the long term [1]. Small organic molecules preferably react with one dimer on the clean surface which is related to the unique reconstruction of the clean silicon (001) surface [2-5]. Recently, experimental results [6] showed that tetrahydrofuran (THF) molecules exhibited a two-step reactivity on the silicon surface. Starting from these findings, we carried out a systematic density functional theory study to elucidate the main chemical processes of THF on Si(001)-c(4x2). All computational investigations were carried out within Vienna ab initio simulation package [7]. However, for treating electron interactions all calculations were established by mean of Perdew, Burke and Ernzehof (PBE) for the exchange-correlation function [8]. In addition, for weak interaction we used semi-empirical dispersion correction terms (DFT-D3) with an advanced damping function [9]. We calculate the adsorption energies and the kinetic barriers as well as the key structures that characterize the chemical reactions on the surface. A notable conclusion of this study is that the dissociation of THF molecules is dominated by kinetic effects in terms of a barrierless dissociation across the dimer trough.

O 20.2 Tue 10:45 MA 005

**In-situ reflection anisotropy spectroscopy study of the MOCVD prepared Si(111) surface** — •Agnieszka Paszuk, Weihong Zhao, Matthias Steidl, Sebastian Brückner, Oliver Supplie, Anja Dobrich, Peter Kleinschmidt, and Thomas Hannappel — Technische Universität Ilmenau, FG Photovoltaik, Gustav-Kirchhoff-Str. 5, 98693 Ilmenau

Integrating III-V materials with Si substrates could combine the superior optoelectronic properties of the III-V compounds with the low-cost silicon technology. Further benefits may arise from applying nanowires which require less material than planar devices and might achieve efficiencies similar to today's best solar cells. By forming a p-n junction within Si substrates we could create a tandem solar cell exceeding the Shockley-Queisser limit associated with a single junction. Our approach is to grow a thin GaP buffer layer as a transition between silicon and the active III-V material. In dependence on the pre-growth Si(111) surfaces preparation, we are able to control the polarity of the GaP buffer. GaP films grown on the H-terminated Si(111) have A-type polarity, while GaP grown on Si(111) surface terminated with arsenic have B-type polarity. Here, we studied the preparation of the clean Si(111) or arsenic terminated surfaces in hydrogen ambient. By XPS we confirm complete oxide removal after high temperature annealing. Moreover, we can observe a change in the reflectance anisotropy (RA) spectrum after the deoxidation process, which depends on the Si surface termination and Si offcut direction. FTIR confirms Si surface termination by monohydride or arsenic.

O 20.3 Tue 11:00 MA 005

**Growth of $\alpha$-sexithiophene ($\alpha$-6T) on a textured rutile $TiO_2$(110) surface** — •Thorsten Wagner, Michael Mühlegger, Ebrahim Ghanbari, and Peter Zeppenfeld — Johannes Kepler University Linz, Austria

Titanium dioxide ($TiO_2$) is a wide band gap semiconductor with applications as photocatalyst, in solar energy converters, and in electronic devices based on organic thin films. In this work, we studied the growth of the prototype organic semiconductor $\alpha$-sexithiophene ($\alpha$-6T, $C_{24}H_{14}S_6$) on the (110) surface of rutile $TiO_2$ single crystals. In particular, we used the real-time imaging capabilities of Photoelectron Emission Microscopy (PEEM) to study side-by-side the growth of $\alpha$-6T on a well prepared part of the surface and on a part of the surface with was modified by ion bombardment. To texture the surface, first several cycles of oxygen exposure, annealing, and sputtering were carried out. Finally, one part of the sample was sputtered with $Ar^+$-ions for 5 min while the other part was protected by an aperture.

The ion bombardment of the $TiO_2$ surface introduces oxygen vacancies. Morphological changes of the surface and these oxygen vacancies can modify the growth of the organic dye molecules $\alpha$-6T as demonstrated by Ivanco *et al.* By imaging spectroscopy we can confirm the local modification of the $TiO_2$ surface upon sputtering. Local transients of the PEEM intensity were obtained during deposition of the organic material. Finally, the individual crystallites were probed by imaging spectroscopy to study their electronic properties.

O 20.4 Tue 11:15 MA 005

**Tuning the self-assembly of triarylamine derivatives on KBr(001)** — •Christian Steiner[1], Tim Sander[1], Maximilian Ammon[1], Natalie Hammer[2], Bettina Gliemann[2], Ute Meinhardt[2], Milan Kivala[2], and Sabine Maier[1] — [1]Department of Physics, FAU Erlangen-Nürnberg, Germany — [2]Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany

Electrically insulating surfaces generally have a lower surface energy than their metallic counterparts. As a consequence organic molecules without a specific bonding motif often lack sufficient interactions with the insulating surface, and tend to dewet or form unordered clusters along step edges.

Here, we present a low temperature non-contact AFM study on the adsorption geometry of hydrogen-bonding and halogen functionalized triarylamines on KBr(001). Dimethyl bridged triarylamines adopt a flat-lying adsorption geometry. The structure of the hydrogen-bonding networks is influenced by the underlying lattice geometry. In contrast, the more compact carbonyl bridged triarylamines favour an intermolecular $\pi$-$\pi$ interaction, which leads to a nearly upright adsorption geometry. The nearly upright molecules form linear aggregates along the [110]-direction. These results show that the adsorption geometry of triarylamines can be tuned by a suitable choice of functional groups, and that the molecule-surface interaction is not neglectable on KBr(001).

O 20.5 Tue 11:30 MA 005

**Self assembly of amino substituted carbonyl bridged triarylamines** — •Maximilian Ammon[1], Tim Sander[1], Patrick

Seitz[1], Christian Steiner[1], Milan Kivala[2], and Sabine Maier[1] — [1]Department of Physics, FAU Erlangen-Nürnberg, Germany — [2]Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany

Triarylamine derivatives are versatile building blocks for a variety of application-oriented molecular structures including organic field effect transistors [1] and optolelectronic devices [2]. Here we present a scanning tunneling and non-contact atomic force microscopy study at low temperatures on the self-assembly of triarylamines with amino and carbonyl functional groups. Self-assembled porous networks are expected to form due to the hydrogen-bonding motif, which we observe on Au(111). Its structure will be discussed based on scanning tunneling hydrogen microscopy [3] measurements. The self-assembly strongly depends on the surface reactivity and the molecule-surface interaction. Scanning tunneling microscopy measurements on Cu(111) also show a porous network, but indicate a binding motif based on metal ligand interaction. In contrast, the molecules adopt a nearly upright adsorption geometry, stabilized by intermolecular $\pi$-$\pi$-interactions, on KBr(001).

[1] K. Schmoltner et al., Polym. Chem. 4, 5337-5344 (2013).
[2] C. Liu et al., Chem. Eur. J. 18, 6928-6934 (2012).
[3] Weiss, C. et al., PRL 105, 086103 (2010).

O 20.6 Tue 11:45 MA 005

**Steering molecular self-assembly of biphenyl-dicarboxylic acid on Cu(111) by tuning the carboxylic hydrogen content** — •Tobias Schmitt, Lutz Hammer, and M.Alexander Schneider — Solid State Physics, Univ. Erlangen-Nürnberg, 91058 Erlangen, Germany

Molecular self-assembly is mainly controlled by a complex interplay between molecule-substrate interaction and intermolecular interactions such as hydrogen bonding. We report on the ordered phases of 4,4'-biphenyl-dicarboxylic acid (BDA) on Cu(111) using low temperature scanning tunneling microscopy in ultra-high vacuum. We deposit the molecules at various temperatures to introduce different degrees of thermally activated deprotonation. This leads to different (locally) ordered supramolecular structures. In the case of non-deprotonated BDA head-to-tail coupling between carboxylic groups dominates due to H-bond formation. This mechanism is observed also in semi-deprotonated structures. Fully deprotonated carboxylic groups, in contrast, form chevron-like structures by the interplay of intermolecular carboxylate-aromatic ring hydrogen bonds and carboxylate-copper interaction.

O 20.7 Tue 12:00 MA 005

**Adsorption Phenomena of Thioether-functionalized $\{Ni^{II}_4\}$ Coordination Complexes on Au(111)** — •Volkmar Hess[1], Frank Matthes[1], Daniel E. Bürgler[1], Claus M. Schneider[1], Kirill Yu. Monakhov[2], Claire Besson[2], Paul Kögerler[2], Alessio Ghisolfi[3], and Pierre Braunstein[3] — [1]Peter Grünberg Institute, Electronic Properties (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Institut für Anorganische Chemie, RWTH Aachen University, 52074 Aachen, Germany — [3]Laboratoire de Chimie de Coordination, Université de Strasbourg, 67081 Strasbourg, France

The anchoring and organization of sulfur-containing heterocyclic groups on metallic substrates is still barely explored. The chemical deposition of a cubane-type $\{Ni^{II}_4\}$ $(=[Ni_4(\mu_3\text{-}Cl)_4Cl_4(HL\cdot S)_4])$ coordination complex terminated by cyclic thioether functional groups from a dichloromethane solution on the Au(111) surface is investigated by STM imaging and surface chemical characterization via XPS, AES, and LEED, both immediately after deposition and after subsequent post-annealing steps. The results provide strong evidence for a partial decomposition of the complex upon deposition on the Au(111) surface that however leaves the magnetic cubane-like $\{Ni^{II}_4Cl_{4n}\}$ (n = 1 or 2) core of the complex intact. Only post-annealing above 500 K induces further decomposition and fragmentation of the $\{Ni^{II}_4Cl_{4n}\}$ core. The detailed insight into the chemisorption-induced decomposition pathway provides guidelines for realizing the deposition of thioether-functionalized molecules on metal surfaces.

O 20.8 Tue 12:15 MA 005

**Peptides as bio-organic building blocks for self-assembly on surfaces** — •Sabine Abb[1], Ludger Harnau[2,3], Stephan Rauschenbach[1], and Klaus Kern[1,4] — [1]Max-Planck-Institute for Solid State Reserach, Heisenbergstr. 1, Stuttgart — [2]Max-Planck-Institute for Intelligent Systems, Heisenbergstr. 3, Stuttgart — [3]IV. Institute for Theoretical Physics, University Stuttgart, Pfaffenwaldring 57, Stuttgart — [4]Ecole Polytechnique Fédérale de Lausanne, Switzerland

In the past decade, the self-assembly of molecules on surfaces via hydrogen bonding and metal coordination has been studied extensively with small, specifically designed organic molecules, yielding a huge variety self-assembled structures. Peptides and proteins are the building blocks of biological self-assembly employing the same bonding motifs. Electrospray ion beam deposition (ES-IBD) enables us to deposit these non-volatile molecules intact in ultra-high vacuum (UHV) where they can be investigated with high precision by STM.

Here, we report the self-assembly of angiotensin II, an 8 amino acid peptide, on metal surfaces. We deposited submonolayer coverage in vacuum by ES-IBD and subsequently investigated the assemblies by STM. While the peptide forms regular yet isolated trimer assemblies on Cu(111) surfaces, long range ordering into a chiral honeycomb network can be observed on Au(111). By a combination of high resolution STM and atomistic MD simulation, we are able to provide an atomistic model and highlight important aspects of peptides as bio-organic building blocks.

O 20.9 Tue 12:30 MA 005

**Racemate versus conglomerate: Chiral pentahelicene on Cu(111)** — •Anaïs Mairena[1], Johannes Seibel[1], Liying Ma[1], Alix F. Tröster[2], Konstantin Grenader[2], Andreas Terfort[2], and Karl-Heinz Ernst[1,3] — [1]Empa, Swiss Federal Laboratories for Materials Science and Technology, Dubendörf, Switzerland — [2]Goethe Universität Frankfurt am Main, Germany — [3]University of Zurich, Switzerland

We studied the 2D self-assembly of racemic pentahelicene ([5]H, C22H14) on Cu(111) with STM. Adsorption of [5]H leads to formation of homochiral pairs already at very low coverages, as observed with STM at 7 K. After deposition at room temperature and cooling to 50 K, two distinct long-range ordered structures have been observed at higher coverages (0,97% of ML). Both structures still have the homochiral pairs as building blocks. While one structure is racemic, i.e., it is composed of homochiral pairs with opposite handedness, the second structure consists of homochiral domains. At monolayer saturation coverage, only a conglomerate of homochiral domains prevails. The two types of homochiral domains are respectively tilted by + 15° and -15° compared to the Cu substrate. A surface-mediated selection mechanism is presented and discussed.

O 20.10 Tue 12:45 MA 005

**Pyrene derivatives on Au(111): the role of halogen substituents in self-assembled network formation** — •Van Bay Tran[1], Tuan Anh Pham[1], Fei Song[1], Manh Thuong Nguyen[2], and Meike Stöhr[1] — [1]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands — [2]The Abdus Salam International Center for Theoretical Physics, Strada Costiera 11, I-34151 Trieste, Italy

Halogen bonding is nowadays considered as an important tool for steering intermolecular interactions in supramolecular chemistry as well as crystal engineering. The formation of two dimensional (2D) molecular networks based on halogen bonding interactions has recently been reported at the solid-vacuum interface as well as at the solid-liquid interface. This is expected to open up new opportunities for the construction of organic thin film-based devices for future applications. However, the exact role of the halogen substituents in the structural formation of such networks attracts less attention and therefore, asks for more studies. In this work, we present the self-assembly of two bromine-functionalized pyrene derivatives on a Au(111) substrate by using scanning tunneling microscopy and low energy electron diffraction under ultrahigh vacuum conditions combined with density functional theory calculations. The study focuses on the influence of the halogen substituents on the resulting 2D molecular networks. Based on the theoretical calculations, the obtained self-assembled patterns are explained via optimizing the intermolecular interactions.

O 20.11 Tue 13:00 MA 005

**Covalently bonded networks by surface-confined coupling of copper-octabromotetraphenylporphyrin** — •Lars Smykalla[1], Pavel Shukrynau[1], Marcus Korb[2], Rasha K. Al-Shewiki[2], Heinrich Lang[2], and Michael Hietschold[1] — [1]Technische Universität Chemnitz, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany — [2]Technische Universität Chemnitz, Inorganic Chemistry, D-09107 Chemnitz, Germany

We demonstrate the on-surface synthesis of a two-dimensional covalent organic network starting from copper-2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin molecules. Results of this molecule on Au(111) [1] are compared to its adsorption on the more reactive and anisotropic Ag(110) surface. Splitting-off of bromine atoms bonded at the macrocyclic core of the porphyrin is monitored by X-ray photoelectron spectroscopy for different annealing steps. Upon annealing to high temperatures depending on the substrate, direct coupling between the reactive carbon sites of the molecules occurs which links the molecular macrocycles with phenyl groups of adjacent molecules. Thus, the initial, ordered, non-covalently interconnected supramolecular structure is completely transformed into a close-packed covalently bonded network of overall good quality. The structures are characterized using scanning tunneling microscopy. Lattice defects and the change of the electronic structure are discussed.

[1] L. Smykalla, P. Shukrynau, M. Korb, H. Lang, M. Hietschold: "Surface-confined 2D polymerization of a brominated copper-tetraphenylporphyrin on Au(111)", under review

## O 21: Graphene: Growth & Intercalation

Time: Tuesday 10:30–13:00 Location: MA 041

O 21.1 Tue 10:30 MA 041

**First-principles Study of the Origin of a Rippled Graphene Phase on Ir(001)** — •Mighfar Imam[1], Natasa Stojic[1,2], and Nadia Binggeli[1,2] — [1]The Abdus Salam International Centre for Theoretical Physics Strada Costiera 11, 34151 Trieste, Italy — [2]IOM-CNR Democritos, Trieste, I-34151, Italy

An interesting graphene phase on Ir(001) comprising ordered one-dimensional ripples of nanometer periodicity with exceptionally large buckling has recently been observed experimentally [1]. In this phase, chemisorbed lines of graphene, only a few nanometers wide, strongly bind to the substrate along Ir[010], while the whole graphene film markedly buckles between these periodic lines, resulting in graphene ripples along Ir[100]. We have performed a density functional theory study including the long range van der Waals interactions to investigate the microscopic mechanisms responsible for the formation of this new graphene phase on Ir(001). With our calculated trends of the chemisorption and rippling energies, we explain the appearance of a buckled chemisorbed phase with a specific nanometer periodicity. We have also analyzed the effect of changing graphene curvature on its electronic structure and chemisorption energy, finding a new feature in the conduction band close to the Fermi energy. This new feature in the conduction states is identified as the one largely responsible for the strong local chemisorption of graphene.

[1] A. Locatelli et al., ACS Nano, 7, 6955 (2013)

O 21.2 Tue 10:45 MA 041

**Graphene induced faceting of Ir(557)** — Christian Witt, Michael Horn-von Hoegen, and •Frank-J. Meyer zu Heringdorf — University Duisburg-Essen, Faculty for Physics and CENIDE, Lotharstrasse 1, 47057 Duisburg

With its great application potential due to the unique electronic structure and the mechanical properties, graphene holds promise for future carbon-based device architectures. Lately, a lot of effort has been invested into the growth of graphene on metal surfaces, due to the possibility to separate the graphene from the surface after growth. In some cases, however the interaction between graphene and the substrate, in conjunction with the elevated sample temperatures, results in a modification of the substrate surface morphology during growth. Here we investigate the modification of a regularily stepped Ir(557) surface during catalytic growth of graphene at various ethylene pressures and temperatures with low energy electron microscopy. Ir(557) is a vicinal (111) surface with a miscut of 9.45° in [001] direction. We find simultaneous growth of graphene flakes and nano-ribbons, depending on ethylene pressure and sample temperature. The nano-ribbons grow exclusively along the steps. Both, flakes and nano-ribbons, induce a faceting of the surface during growth. An intercalation of oxygen between the graphene and the faceted surface does not affect the already present facets. The orientation of the facets were determined by reciprocal space mapping and (ex-situ) AFM measurements.

O 21.3 Tue 11:00 MA 041

**Comparing graphene growth on Cu(111) vs. oxidized Cu(111)** — Stefano Gottardi[1], Kathrin Müller[1], Luca Bignardi[1], Juan Carlos Moreno Lopez[1], Tuan Anh Pham[1], Alexei Barinov[2], Jonas Björk[3], Petra Rudolf[1], and •Meike Stöhr[1] — [1]University of Groningen — [2]Sincrotrone Trieste — [3]Linköping University

The epitaxial growth of graphene on catalytically active metallic surfaces via chemical vapor deposition (CVD) is known to be one of the most reliable routes towards high quality large-area graphene. This CVD-grown graphene is generally coupled to its metallic support resulting in a modification of its intrinsic properties. Growth on oxides is a promising alternative that might lead to a decoupled graphene layer. Here, we compare graphene on a pure metallic to graphene on an oxidized copper surface, in both cases grown by a single step CVD process under similar conditions. Remarkably, the growth on copper oxide - a high-k dielectric material - preserves the intrinsic properties of graphene; it is not doped and a linear dispersion is observed close to the Fermi energy. Density functional theory calculations give additional insight into the reaction processes and help explaining the catalytic activity of the copper oxide surface.

O 21.4 Tue 11:15 MA 041

**Ir(111) surface state stability against Li adsorption: role of graphene** — •Petar Pervan[1], Ivo Pletikosić[2], Marin Petrović[1], Iva Šrut Rakić[1], Marko Kralj[1], Milorad Milun[1], Tonica Valla[2], and Predrag Lazić[3] — [1]Institut za fiziku, Bijenička 46, 10000 Zagreb, Croatia — [2]Department of Condensed Matter Physics & Materials Science, Brookhaven National Lab, Upton — [3]Institut Rudjer Bošković, Bijenička 54, 10000 Zagreb, Croatia

Surface states (SS) are known to be extremely sensitive to the presence of defects or adsorbates with the effect that any surface state would disappear in response to submonolayer coverage of adsorbates. Moreover, adsorbates can induce a change of the surface potential which in turn may strongly affect its binding energy. In this work we report on the Li intercalation of graphene on Ir(111) and its influence on the Ir surface state at the K point studied by means of the Low Energy Electron Diffraction (LEED), the Angle Resolved Photoemission Spectroscopy (ARPES) and the Density Functional Theory (DFT). We have found that at all stages of the Li intercalation the integrity of the surface state at the K point has been preserved. Despite the increase of the SS binding energy its spectral intensity and the width were constant at all Li concentrations. This finding suggests an unperturbed surface state coherence at the K point. Away from the K point the surface state exhibits strong hybridization with graphene pi bands which is accompanied by the opening of the band gap at higher binding energy with respect to the hybridisation point.

O 21.5 Tue 11:30 MA 041

**Chemical Functionalization of Graphene via Hyperthermal Molecular Reaction** — Girjesh Dubey[1], Roberto Urcuyo[1], Sabine Abb[1], Gordon Rinke[1], Marko Burghard[1], •Stephan Rauschenbach[1], and Klaus Kern[1,2] — [1]Max-Planck-Institute for Solid State Research, Stuttgart, Germany — [2]Institut de Physique de la Matière Condensée, EPFL, Lausanne, Switzerland

Covalent functionalization represents a viable pathway for tailoring graphene's electronic properties, for instance to open a band-gap. It furthermore enables subsequent chemical coupling for applications in molecular diagnostics and molecular electronics. In this study, chemical vapor deposited (CVD) graphene is covalently functionalized though electrospray ion beam deposition (ES-IBD) of hyperthermal molecular cation beams of 4,4-azobis(pyridine). The one-step, room temperature ion-surface reaction process takes place in high vacuum ($10^{-7}$ mbar), and requires a threshold kinetic energy of 165 eV of the molecular ions. The covalent attachment of the molecules is proven by the effect of thermal annealing, which removes the intense D peak in the Raman spectrum of the functionalized graphene. Based up X-ray photoelectron spectroscopy data, we conclude that the attached species are azopyridinium groups. A high functionalization degree of 3% of the carbon atoms of graphene is attained after 3-5 hours of ion exposure of $2 \times 10^{14}$ azopyridinium/cm$^2$ of which 50% bind covalently.

G. Dubey et al.: *J. Am. Chem. Soc.* **136**, 13482-13485 (2014)

O 21.6 Tue 11:45 MA 041

**Quantum interference on the doped graphene/SiC systems** — •Mykola Telychko[1], Pablo Merino[2], Pingo Mutombo[1], Martin Ondraček[1], Prokop Hapala[1], Oleksandr Stetsovych[1], Martin Švec[1], and Pavel Jelínek[1] — [1]Institute of Physics ASCR, Cukrovarnicka 10, Praha, Czech Republic — [2]Max Planck Institute for Solid State Research, Heisenberg Strasse 1, 705669 Stuttgart

We report methodology for co-doping of epitaxial graphene grown on the SiC(0001) substrate by boron and nitrogen atoms. Nitrogen doping was achieved using direct nitrogen ion implantation into the graphene lattice and subsequent thermal stabilization. Boron doping was achieved by introducing the additional source of boron atoms during growth process of the graphene/SiC(0001).

Atomically-resolved low-temperature STM/AFM measurements of well-defined single substitutional nitrogen and boron dopants reveal that nitrogen dopants in graphene lattice feature a strong destructive quantum interference effect, tunable by changing the tip-sample separation. The current dependence on the tip position is successfully modelled by DFT and STM simulations for the both types of dopants. Absence of the destructive interference over the boron dopants allows clear chemical discrimination between the N and B atoms.

O 21.7 Tue 12:00 MA 041

**Scanning Tunneling Microscopy of epitaxial Graphene with single ion-implanted Boron, Nitrogen and Carbon atoms** — •Philip Willke[1], Anna Sinterhauf[1], Julian Amani[2], Sangeeta Thakur[3], Thomas Kotzott[1], Steffen Weikert[2], Kalobaran Maiti[3], Hans Hofsäss[2], and Martin Wenderoth[1] — [1]IV. Physikalisches Institut, Universität Göttingen, Germany — [2]II. Physikalisches Institut, Universität Göttingen, Germany — [3]Department of Condensed Matter Physics and Materials' Science, TIFR, Mumbai, India

Using scanning tunneling microscopy and spectroscopy we investigate the structural and electronic properties of single substitutional atoms in SiC-graphene. These are prepared by low-energy ion implantation, which we use as a suitable method for boron and nitrogen incorporation in graphene [1,2]. We find, that boron and nitrogen atoms lead to an effective doping of the graphene sheet and allow to reduce or raise the position of the Fermi level, respectively. The electronic properties of the doping atoms are additionally addressed. To reveal the defect creation in the doping process $^{12}C^{+}$ carbon ions, that only introduce defects and no impurity atoms, are studied as a reference. Moreover, we perform magnetotransport measurements to investigate the influence of the microscopic structure on the graphene transport properties. This work was supported by DFG priority program 1459 "Graphene".

[1] P. Willke et al., Appl. Phys. Lett. 105, 111605 (2014)

[2] U. Bangert et al., Nano Lett. 13(10) (2013)

O 21.8 Tue 12:15 MA 041

**Reversible Hydrogenation of Graphene on Ni(111) - Synthesis of 'Graphone'** — •Julian Gebhardt[1], Wei Zhao[2], Florian Späth[2], Karin Gotterbarm[2], Christoph Gleichweit[2], Hans-Peter Steinrück[2], and Andreas Görling[1] — [1]Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — [2]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Understanding the adsorption and reaction between hydrogen and graphene is of fundamental importance for developing graphene-based concepts for hydrogen storage and for the chemical functionalization of graphene by hydrogenation. Recently, theoretical studies of single-sided hydrogenated graphene, so called graphone, predicted it to be a promising semiconductor for applications in graphene-based electronics. Here, we report on the synthesis of graphone bound to a Ni(111) surface. We investigate the formation process by X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and density-functional theory calculations, showing that the hydrogenation of graphene with atomic hydrogen indeed leads to graphone, i.e., a hydrogen coverage of 1 ML (4.2 wt%). In addition, the dehydrogenation of graphone was shown to be possible by XPS and TPD measurements. The complex desorption process was attributed to coverage-dependent changes in the activation energies for the associative desorption of hydrogen as molecular $H_2$.

O 21.9 Tue 12:30 MA 041

**Towards Understanding the Wetting of Nanostructured Surfaces** — •Mausumi Chattopadhyaya and Alexandre Tkatchenko — Fritz Haber Institut der MPG, Berlin, Germany

Water is arguably the most important liquid. Understanding how water interacts with nanostructures leads to many fundamental questions both in theory and experiment. On the experimental side, it has been widely quoted that the contact angle of water on graphite is in the range of 90°-95°. However, careful measurements using ultra high vacuum techniques lead to drastically different values of 35±4°. From theory point of view, a precise description of water interacting with nanostructured surfaces seems to require the highest levels of correlated quantum-chemical methods. Here, we study the interaction of water with layered materials with the aim to determine the contact angle of water on different nanostructured surfaces. This demands a precise calculation of the surface energy of the nanostructure and the interaction energy between water and the surface. We have carried out systematic calculations of water interacting with few-layer graphene and h-BN surfaces. These calculations have been done using pairwise Tkatchenko-Scheffler(TS) scheme and many-body dispersion (MBD) method within density functional theory (DFT). Remarkably, our results suggest that the binding energy of a water molecule does not depend on the number of graphene or h-BN layers. We finally discuss the current work aiming to understand the contact angle of water on a range of nanostructured surfaces.

O 21.10 Tue 12:45 MA 041

**Fingerprinting graphene: self-assembly by breaking the rules of surface science** — •Samuel Grandthyll[1], Stefan Gsell[2], Michael Weinl[2], Matthias Schreck[2], Karin Jacobs[1], and Frank Müller[1] — [1]Saarland University, Experimental Physics, 66041 Saarbruecken, Germany — [2]University of Augsburg, Experimental Physics 4, 86135 Augsburg, Germany

Epitaxial graphene is expected to be the only synthesis route to obtain large-area sheets of this silicon substitute for the engineering of future nano electronic devices on an industrial scale. So far, there are different recipes to obtain epitaxial graphene, using either intrinsic carbon, as released by the selective desorption of silicon from a SiC surface, or using extrinsic carbon, as via the chemical vapor deposition (CVD) of simple hydrocarbons on transition metal surfaces. In addition, even ex-situ deposition of liquid precursors (LPD) provides well-ordered graphene monolayers. In order to explore the limits of self-assembly in LPD synthesis, we show that graphene formation on transition metal surfaces is an extraordinarily robust mechanism that also works when carbon is provided in the maximal undefined way, namely by using a human fingerprint as a precursor. Our results show that "fingerprinting" graphene provides well-ordered monolayers of the same quality as in case of using ultrapure synthetic single precursors. The unique directedness of the self-assembly process of graphene on transition metals by liquid precursor deposition therefore offers a simple synthesis route for epitaxial graphene [1].

[1] F. Müller et al., Langmuir 30 (2014), 6114-6119

# O 22: Ultrafast Surface Dynamics

Time: Tuesday 10:30–13:00 Location: MA 042

**Invited Talk** O 22.1 Tue 10:30 MA 042

**Electron dynamics at molecule-semiconductor interfaces** — •Katrin R. Siefermann — Leibniz-Institute of Surface Modification (IOM), Leipzig, Germany

Charge transfer processes across hybrid interfaces, such as formed by the connection of molecules to semiconductors, play an increasingly important role in a variety of emerging technologies. Detailed understanding of interfacial charge transfer in these systems, however, remains a major challenge for experiments and theory.

In my talk I will present a new approach to monitor photo-induced electron transfer from a molecule to a semiconductor material with sub-picosecond temporal resolution and from the perspective of well-defined atomic sites [1]. Combining femtosecond time-resolved X-ray photoelectron spectroscopy with constrained density functional theory, we are able to identify the nature of an intermediate electronic state that precedes free charge carrier generation in a film of dye-sensitized ZnO nanocrystals after photoexcitation of the dye with visible light. The findings demonstrate a new capability to monitor charge transfer in complex hybrid materials. This presentation will further include our latest results of electron dynamics at interfaces.

[1] K. R. Siefermann, C. D. Pemmaraju, S. Neppl, A. Shavorskiy, et al., J. Phys. Chem. Lett. 5, 2753-2759 (2014).

O 22.2 Tue 11:00 MA 042

**Time-resolved hard-x-ray photoelectron spectroscopy at the x-ray free-electron laser SACLA** — •Lars-Philip Oloff[1,2], Masaki Oura[2], Ashish Chainani[2], and Kai Rossnagel[1,2] — [1]Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24118 Kiel, Germany — [2]RIKEN, SPring-8 Center, Sayo-cho, Hyogo, 679-5148, Japan

Time-resolved hard x-ray photoelectron spectroscopy (trHAXPES) is established as a novel ultrafast spectroscopy technique using the x-ray free-electron laser SACLA (Japan) [1,2]. The technique extends time-resolved photoemission into the hard x-ray regime and, as a core-level spectroscopy, combines atomic-site and chemical-state specificity with femtosecond time-resolution and bulk sensitivity. It can thus open novel opportunities for probing ultrafast electron dynamics in strongly excited materials, at buried interfaces, and in electronic devices under *in operando* conditions.

The viability of trHAXPES using 8 keV x-ray free-electron laser radiation is demonstrated by a systematic investigation of probe and pump pulse-induced vacuum space-charge effects. The measured time and excitation energy dependencies of spectral shifts and broadenings are compared to the results of $N$-body numerical simulations and simple analytic (mean-field) models.

[1] M. Oura *et al.*, J. Synchrotron Rad. **21**, 183 (2014)

[2] L.-P. Oloff *et al.*, New J. Phys., in press (2014)

O 22.3 Tue 11:15 MA 042

**Narrowband high harmonic pulses for trARPES using frequency-upconverted Ti:Sapphire lasers** — •S. Emmerich[1], S. Eich[1], A. Stange[3], A.V. Carr[2], J. Urbancic[1], T. Popmintchev[2], M. Wiesenmayer[1], K. Jansen[3], A. Ruffing[1], S. Jakobs[1], T. Rohwer[3], S. Hellmann[3], C. Chen[2], P. Matyba[2], L. Kipp[3], K. Rossnagel[3], M. Bauer[3], M.M. Murnane[2], H.C. Kapteyn[2], S. Mathias[1], and M. Aeschlimann[1] — [1]University of Kaiserslautern and Research Center OPTIMAS, 67663 Kaiserslautern, Germany — [2]JILA, University of Colorado and NIST, Boulder, CO 80309-0440, USA — [3]Institute of Experimental and Applied Physics, University of Kiel, D-24098 Kiel, Germany

trARPES using femtosecond XUV high harmonics has recently emerged as a powerful tool for investigating ultrafast quasiparticle dynamics in correlated-electron materials. However, the full potential of this approach has not yet been achieved because, to date, high harmonics generated by 800 nm wavelength Ti:Sapphire lasers required a trade-off between photon flux, energy and time resolution. Photoemission spectroscopy requires a quasi-monochromatic output, but dispersive optical elements that select a single harmonic can significantly reduce the photon flux and time resolution. Here we show that shorter wavelength driven high harmonic extreme-ultraviolet trARPES is superior to using 800 nm laser drivers since it eliminates the need for any spectral selection, thereby increasing photon flux and energy resolution while preserving excellent time resolution [Eich et al., J. Electron Spectrosc. 195 (2014) 231-236].

O 22.4 Tue 11:30 MA 042

**Thermalization dynamics in graphite - Phonon-phonon interaction vs. supercollision** — •Ankatrin Stange, Christian Sohrt, Lexian Yang, Gerald Rohde, Petra Hein, Lars Oloff, Kerstin Hanff, Kai Rossnagel, and Michael Bauer — Institute of Experimental and Applied Physics, University of Kiel, Germany

Recent studies reported on a defect-assisted (supercollision) process yielding an enhanced coupling between optically excited electrons and acoustic phonons in graphene [1,2] and accelerating electron-lattice thermalization down to timescales in the few picosecond regime. In this work we address the question to what extent also the relaxation dynamics in the parent compound graphite is governed by supercollision. Time- and angleresolved photoelectron spectroscopy is used to monitor the transient carrier population in the $\pi$-bands at the $H$ point at absorption of intense near-infrared laser pulses. In correspondence to other works the relaxation due to interaction with the lattice proceeds on two characteristic timescales: A fast (≈250 fs) cool down of the electron gas arising from the interaction of the electronic system with strongly coupled optical phonons (SCOPs) [3] is followed by a picosecond dynamics that can consistently be reproduced within a three-temperature model only if the coupling between SCOPs and acoustic phonons is taken into account [3]. In contrast, the supercollision model clearly fails in describing the recorded electron temperature transients.

[1] J. C. W. Song *et al.*, Phys. Rev. Lett. **109**, 106602 (2012)

[2] J. C. Johannsen *et al.*, Phys. Rev. Lett. **111**, 027403 (2013)

[3] T. Kampfrath *et al.*, Phys. Rev. Lett. **95**, 187403 (2005)

O 22.5 Tue 11:45 MA 042

**Second Harmonic Spectroscopy in the Reststrahlen Band of SiC Using an Infrared Free Electron Laser** — •Alexander Paarmann, Alexey Melnikov, Sandy Gewinner, Wieland Schoellkopf, and Martin Wolf — Fritz Haber Institute of the Max Planck Society, Berlin

We experimentally study the efficiency of optical second harmonic generation in the highly reflective Reststrahlen spectral region of the wide-band gap semiconductor 6H-SiC, employing tunable picosecond mid-infrared laser pulses generated from the FHI free electron laser. The Reststrahlen region, located between longitudinal and transversal optical phonon resonances, provides a unique window to study nonlinear effects in the phononic response of a crystal. We observe sharp resonances of the second harmonic signal at both transverse and longitudinal optical phonon fundamental frequencies, the latter being unexpected since no resonance in the optical nonlinearity is predicted for longitudinal modes. We discuss the underlying mechanism of local field enhancement, which is tightly linked to the largely dispersing linear optical properties in the Reststrahlen band. The negative real part of the dielectric function results in rapidly attenuated evanescent waves in this region, making these experiments sensitive to a thin near-surface layer. The resulting large amplitude atomic motions induced by intense mid-infrared laser excitation opens the door to future studies of nonlinear phononic response at semiconductor surfaces and interfaces.

O 22.6 Tue 12:00 MA 042

**Experimental determination of the potential energy curve of diethyl ether on Si(001)** — Marcel Reutzel[1], Marcus Lipponer[1], •Michael Dürr[1,2], and Ulrich Höfer[1] — [1]Philipps University, 35037 Marburg — [2]Justus Liebig University, 34392 Giessen

The adsorption dynamics of organic molecules on semiconductor surfaces is in most cases controlled by a precursor or intermediate state. For molecules containing a heteroatom such as nitrogen or oxygen, this intermediate state involves lone pair electrons of the heteroatom and, in the case of Si(001), the empty dangling bond of the lower silicon atom. Most recently, we have shown that in the case of ether molecules one can isolate this datively bonded intermediate at low temperatures; at elevated temperatures cleavage of the O-C bond of the otherwise inert ether group was observed [1].

Here we show that, using optical second harmonic generation, we

can follow in situ the conversion of diethyl ether from the intermediate to the final adsorption configuration. Measuring the kinetics as a function of surface temperature allows us to determine the associated energy barrier. Complementary information is obtained from sticking probabilities measured by means of molecular beam experiments. The dependence of the initial sticking probability on surface temperature reveals the energy difference between the conversion and desorption barrier out of the datively bonded intermediate state. Combination of the two results give full information on the potential energy curve for the adsorpton of diethyl ether on Si(001).
[1] G. Mette, *et al.*, ChemPhysChem **15**, 3725 (2014).

O 22.7 Tue 12:15 MA 042

**Polarization dependent photoinduced voltage in $\mathbf{Sb_2Te_3}$** — •Thomas Schumann[1], Maria Mansurova[2], Fabio Boschini[3], Cinja Seick[2], Gregor Mussler[4], Tobias Kampfrath[5], and Markus Münzenberg[1] — [1]Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald,Germany — [2]I.Physikalisches Institut,Georg-August Universität Göttingen,Germany — [3]Dipartimento di Fisica,Politecnico di Milano, Italia — [4]Peter-Grünberg Instiut,Forschungszentrum Jülich,Germany — [5]Abteilung für Physikalische Chemie,Fritz-Haber-Institut Berlin(MPG),Germany

Topological insulators potentially open up a novel route in spin based electronics. The energy momentum landscape of the Dirac cone provides, via spin-momentum locking, a control of the directionality of spin currents [1]. Its femtosecond control with light pulses has been demonstrated. The used excitations are realized with femtosecond laser pulses (at 1.55 eV) with different pump-pulse polarization. We demonstrate coherent femtosecond control of the dynamics in presence of the pump-pulse and the DC detection of helicity dependent photo currents. Both are compared to possible optical transitions in ab-initio calculations.

Furthermore we thank the DFG-SPP1666.

[1] J. W. McIver et al., Nat. Nanotech. 7, 96(2012)

O 22.8 Tue 12:30 MA 042

**Development of Ultrafast Low-Energy Electron Diffraction** — •Max Gulde[1], Simon Schweda[1], Gero Storeck[1], Anastassia Rissanou[2], Sebastian Schramm[1], Manisankar Maiti[1], Hak Ki Yu[3,4], Alec Wodtke[3], Vagelis Harmandaris[2], Sascha Schäfer[1], and Claus Ropers[1] — [1]4th Physical Institute, University of Göttingen, Göttingen, Germany — [2]Department of Applied Mathematics, University of Crete, 71409 Heraklion, Greece — [3]Max Planck Institute for Biophysical Chemistry, 37077 Göttingen, Germany — [4]Institute for Physical Chemistry, University of Göttingen, 37077 Göttingen, Germany

Ultrafast electron diffraction experiments have offered intriguing insights into atomic-scale structural dynamics in bulk media on their fundamental time scales [1]. In contrast, comparable time-resolved studies in quasi two-dimensional systems such as surfaces and interfaces remain challenging, despite recent accomplishments [2, 3]. Here, we introduce ultrafast low-energy electron diffraction (ULEED) in transmission as a powerful new tool for ultrafast surface science [4]. In particular, we present a detailed experimental and theoretical account of the relaxation of a polymer superstructure on free-standing graphene from a highly out-of-equilibrium state. Finally, first data from a ULEED experimental setup operated in back-reflection is presented.

[1] B. J. Siwick et al., Science 302, 1382-1385 (2003).
[2] S. Schäfer et al., J. Chem. Phys. 135, 214201 (2011).
[3] A. Hanisch-Blicharski et al., Ultramicroscopy 127, 2-8 (2013).
[4] M. Gulde et al., Science 345, 200 (2014).

O 22.9 Tue 12:45 MA 042

**Velocity map imaging of ultrafast electron emission from fs-laser illuminated nanoscale metal tips** — Alexander Bainbridge and •William Bryan — Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP, UK

We have recently demonstrated velocity map imaging (VMI) of photoelectron emission from a metal nanotip illuminated with a strong field laser pulse [1]. We will present theoretical and experimental results demonstrating the simultaneous momentum resolution of electrons emitted from gas and solid targets. Above threshold ionization from krypton gas facilitates momentum calibration, and tunnelling from a metal nanotip exhibits a hemispherical momentum distribution defined by discrete photon absorption. Numerical simulations show VMI condition are maintained over a wide range of instrument configurations such that momentum focusing is independent of the emission location.

Forthcoming experiments will involve cryogenic sharpening of nanotips to a single atom, traditionally observed with field ion microscopy. As the nanotip approaches a single atom, the observed velocity map image will tend towards that of a gas phase atom, showing recollisional interference. This hybrid of real-space and momentum-space imaging will be decisive in the design of next-generation femtosecond electron diffraction and microscopy instruments.

[1] A R Bainbridge and W A Bryan, New J. Phys. 16 (2014) 103031

## O 23: Plasmonics and Nanooptics: Structure, Fabrication and Characterization

Time: Tuesday 10:30–13:15 Location: MA 043

O 23.1 Tue 10:30 MA 043

**Large-area spectrally selective plasmonic perfect absorber sensor fabricated by laser interference lithography** — •Shahin Bagheri, Nikolai Strohfeldt, Andreas Tittl, and Harald Giessen — 4th Physics Institute and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

We employ laser interference lithography to create homogeneous wire and rectangle arrays and utilize them for manufacturing of large-area plasmonic perfect absorbers [1]. Geometry and periodicity of such tailored nanostructures can be precisely controlled by adjusting the interference conditions in single- and double-exposure processes, resulting in spectrally selective perfect absorption of light from the visible to the mid-infrared wavelength range. We also demonstrate the applicability of our fabrication method for detection schemes by measuring the hydrogen sensing performance of a palladium-based perfect absorber operating in the visible wavelength range. Due to the large-area and fast fabrication process, our method offers a great potential for low-cost commercial nanophotonic and plasmonic devices in industrial applications.

[1] S. Bagheri et al., Adv. Opt. Mater. **2**, 1050-1056 (2014)

O 23.2 Tue 10:45 MA 043

**Light trapping and enhanced absorption in femtosecond-laser materials processed amorphous thin-film silicon** — Dominik Differt[1], •Walter Pfeiffer[1], Babak Soleymanzadeh[1], and Helmut Stiebig[1,2] — [1]Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany — [2]Institut für Innovationstransfer an der Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany

Efficient thin-film solar cells balance the reduced absorption in thin absorber layers by means of various photon management strategies that often involve nanotextured interfaces. We report broadband absorption enhancement in femtosecond (fs) laser materials processed thin amorphous silicon. The absorption of a single amplified fs laser pulse (30 fs, 795 nm, 75 mJ $\mathrm{cm}^{-2}$) creates a thin nanotextured microcrystalline surface layer. Coherent scattered light micro-spectroscopy in combination with spectral interferometry reveals that incident radiation is trapped for about 100 fs in localized photonic modes in the laser processed area. This trapping explains the enhanced absorption and the observed local Raman yield enhancement. The lateral correlation length of the light trapping modes indicates very efficient light scattering in the processed layer that leads to strong localization of light in the absorber layer. Consequently, fs materials processing offers an interesting pathway towards advanced photon management in amorphous silicon based thin-film solar cells.

O 23.3 Tue 11:00 MA 043

**Extreme Ultraviolet Proximity Lithography for fast, flexible and large-scale fabrication of infrared antennas** — •Georg Kunkemöller[1,3], Tobias W.W. Mass[2], Ann-Katrin U. Michel[2], Hyun-Su Kim[3], Sascha Brose[1], Serhiy Danylyuk[1], Thomas Taubner[2], and Larissa Juschkin[3] — [1]TOS, RWTH Aachen University — [2]I. Institute of Physics (IA), RWTH Aachen University — [3]Chair for Experimental Physics of Extreme-Ultraviolet EUV, RWTH Aachen University

Recently, several lithographic approaches to improve throughput and costs for the fabrication of infrared antennas by using parallel processes were presented [1-4]. In this contribution, we present Extreme ultraviolet (EUV) proximity lithography as a comparable advantageous technique for the fabrication of large arrays of infrared antennas. Using Fresnel-diffraction, this method offers the potential of a great variety of structures [5]. Depending on deposure time and gap between mask and resist, different dumbbell-shaped structures can be fabricated using only a single mask-geometry. Characterization via SEM imaging and FTIR spectroscopy show a good agreement to lithograpy- and FDTD simulations and turns this fabrication method to a promising tool for a large-area fabrication of infrared nanostructures.

[1] Hoffmann et al. *J. Phys. Chem. C* **2013** 117, 11311-11316
[2] Cataldo et al. *ACS Nano* **2012** 6, 979-985
[3] Aksu et al. *Nano Lett.* **2010** 10, 2511-2518
[4] Bagheri et al. *Adv. Opt. Mat.* **2014** 2, 1050-1056
[5] Danylyuk et al. *J. Vac. Sci. Technol. B* **2013** 31, 021602

O 23.4 Tue 11:15 MA 043

**Fabrication and Characterization of Plasmonic Nanocone Antennas for Strong Spontaneous Emission Enhancement** — •Björn Hoffmann[1], Simon Vassant[1], Xue-Wen Chen[1], Stephan Götzinger[1,2], Vahid Sandoghdar[1,2], and Silke Christiansen[1,3] — [1]Max Planck Institute for the Science of Light, Erlangen, Germany — [2]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [3]Helmholtz Centre Berlin for Materials and Energy, Berlin, Germany

Plasmonic nano-antennas have attracted remarkable attention due to their ability to strongly modify the excitation and emission channels of quantum emitters. Metallic nanocones are a promising candidate for a strong enhancement of spontaneous emission while keeping high quantum efficiencies. Here, we report on the precise fabrication of gold nanocones with tunable dimensions to tailor their plasmon resonance to specific applications. Therefore, we developed a focused ion beam (FIB) etching procedure that offers precise control over the height, diameter and tip radius of the cones. We measured the plasmon resonance spectra of gradually etched cones and were able to reproduce the spectra by BOR-FDTD simulations. The cones show reproducible plasmon resonances between 580 - 700 nm and exhibit theoretical radiative Purcell factors above 500, which renders them promising structures for spontaneous emission enhancement.

O 23.5 Tue 11:30 MA 043

**Creating metallic nanostructures by electron beam induced deposition (EBID) for plasmonic applications** — •Caspar Haverkamp[1], Katja Höflich[1], and Silke Christiansen[1,2] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — [2]Max Planck Institute for the Science of Light, Erlangen, Germany

During EBID a gas-injection system (GIS) inserts a precursor Gas into the vacuum chamber of an scanning electron microscope (SEM). The molecules which adsorb, desorb and diffuse at the substrate surfaces and are locally decomposed by the electron beam. While the volatile part is pumped out the non-volatile part forms the deposit onto the substrate. By controlling the electron beam movement via a patterning engine various shapes can be realized. As precursor gas the metal-organic compound dimethyl-(acetylacetonate) Gold(III), short Me2Au(acac) is used, resulting in nanometer-sized gold particles embedded in a carbonaceous matrix. Since the metal content of this material is very low, two approaches are discussed how to overcome this drawback. The first one is to decrease the carbon content of the structure by an in-situ post-treatment with water vapor irradiated by the electron beam. The splitting of the water molecules by the electron beam results in reactive oxygen species which react with the carbon of the EBID structure creating volatile carbon oxides. The second approach is to use the EBID structure as template and achieving the plasmonic response by a metallic coverage .

O 23.6 Tue 11:45 MA 043

**Cathodoluminescence of sharp Au- and Ag-tips in the vicinity of a Au-film** — •Martin Grüsser, Xinzhou Ma, and Rolf Schuster — Institute of Physical Chemistry, Condensed Matter Division, Karlsruhe Institute of Technology (KIT), Germany

Sharp metal tips acting as optical antennas play an important role in many experimental applications. The locally enhanced electromagnetic field allows, e.g., for tip-enhanced raman spectroscopy [1, 2] on the single molecule level. In addition to the lightning-rod effect, also surface plasmons localized at the tip apex and gap plasmons between a tip and a sample surface [3] contribute to the field enhancement.

To investigate the local excitation of surface plasmons and gap plasmons in the tip-surface system we employ, cathodoluminescence upon electron irradiation in a scanning electron microscope (SEM), which accesses the radiative modes of the electron excited plasmons. The distance between tip and surface is controlled by a scanning tunneling microscope, mounted inside the vacuum chamber of the SEM. We observed enhanced photon emission upon electron irradiation near the tip-surface gap, on both the tip as well as on the sample side. Spectra upon irradiation of tip or sample show strong differences in intensity and peak position, e.g. a redshift for smaller tip-surface distances and evolution of additional peaks, which may depend on the formation of gap plasmons.

[1] R. M. Stöckle et al., Chem. Phys. Lett. 2000, 318, 131. [2] B. Pettinger et al., Annu. Rev. Phys. Chem. 2012, 63, 379. [3] Z. Yang, J. Aizpurua, H. Xu, J. Raman Spectrosc. 2009, 40, 1343.

O 23.7 Tue 12:00 MA 043

**Nanowire-film gap plasmon waveguides for spaser resonators** — •Friedemann Gädeke, Günter Kewes, and Oliver Benson — AG Nano Optik, Institut für Physik, Humboldt-Universität zu Berlin

Surface plasmon amplification by stimulated emission of radiation (spaser) might be an essential part of future nano-photonic devices. Spasers are subwavelength sized light sources and could be used in quantum information technology or nano-lithography [1].

We report on numerical and experimental investigations on an ultracompact resonator design for spasers. We use organic gain media in a waveguide which is formed by a gap between a gold film and a gold nanowire. The design follows Ref. [2] and [3] and includes emitter-free spacing layers between active medium and metal [4] which will be benefitial to achieve lower spasing thresholds. We optimize our design towards a well defined energy distribution in the gap and low propagation losses. We present a feasible fabrication technique based on relatively simple and quick methods like spin-coating, ellipsometry and stamping as well as first fluorescence studies.

[1] Stockman, M. I., Journal of Optics 12, 024004 (2010) [2] Oulton, R. F. et al., Nature 461, 629-632 (2009) [3] Russell, K. J. et al., Nature Photonics 6, 459-462 (2012) [4] Kewes, G. et al., Arxiv 1408.7054 (2014)

O 23.8 Tue 12:15 MA 043

**Material contrasts of layered Phase Change Materials in s-SNOM** — •Martin Lewin, Benedikt Hauer, Ann-Katrin U. Michel, and Thomas Taubner — Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany

Phase Change Materials (PCM) show at least two stable states in the solid phase with significantly different physical properties. They can be switched reversibly by optical or electronical means, which enables their use for storage and logical applications [1].

Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is based on an illuminated metal coated tip being scanned over a sample. Due to the local detecting approach, the optical properties of the sample can be analysed wavelength-independently on a nm-scale [2].

Hence, s-SNOM can be used to investigate the switching in nanometre sized phase change devices: We could show that it is possible to distinguish amorphous and crystalline regions of AgInSbTe even below 100 nm of capping layer. Firstly, the material contrasts of a bare 30 nm thick layer of AgInSbTe with and without capping layer are analysed. Secondly, correlative TEM and s-SNOM analyses are performed of a sandwiched amorphous layer with crystalline spots. The found complex material contrasts are explained by theoretical calculations taking into account the layered structure of the sample.

[1] M. Wuttig and N. Yamada, Nature Mater. 6, pp. 824-832 (2007) [2] F. Keilmann and R. Hillenbrand, Phil. Trans. R. Soc. Lond. A 362, pp. 787-805 (2004)

O 23.9 Tue 12:30 MA 043

**Surfactant-Controlled Kinetic Overgrowth of Gold Rods into Gold-Core Silver-Shell Rodboids to Induce Controlled Internal Mirror Charges** — •Tobias König, Moritz Tebbe, Martin Mayer, Christian Kuttner, and Andreas Fery — Physical Chemistry II, University of Bayreuth, 95447 Bayreuth, Germany

We present the surfactant-controlled overgrowth of gold nanorods into gold-core silver-shell nanoparticles (rodboids) to gain low growth rates for full control of the kinetic process. In gold-core silver-shell rodboids not much attentions has been paid to the overlap region of the intraband gaps of gold and silver (326 to 515 nm). In this optical region, the gold core acts as a retarding element because of the much higher damping in the core compared to the silver shell. Electromagnetic simulations show that the silver shell induces mirror charges at the core/shell interface which results in a similar signature as an antibonding mode. An excitation outside the overlap region yields in-phase oscillations of the surface charges (signature of a bonding mode). In contrast to plasmonic hybridization, the energetic splitting of the two modes is weaker so that both modes are present in the optical spectrum. Consequently, full control over the kinetic process allows for precise tailoring of the resonance wavelengths of both modes. Tailored rodboids represent ideal candidates as a building block for metamaterials and are suitable for application as optical sensor, light harvesting, and information technology.

O 23.10 Tue 12:45 MA 043

**Strongly Coupled Plasmonic Modes of Self-Assembled Particles Lines in the Context of Ensemble-Averaging and Disorder** — •Christian Kuttner, Christoph Hanske, Moritz Tebbe, Tobias König, and Andreas Fery — Physical Chemistry II, University of Bayreuth, 95447 Bayreuth, Germany

We present ensembles of gold nanoparticle arranged in single and double lines on solid substrates.[1] These linear assemblies were formed by template-assisted self-assembly[2,3] of monodisperse protein-coated gold nanoparticles in wrinkle templates. The substrates exhibit high structural regularity on centimeter-squared areas which allow for characterization of their extinction cross-sections by conventional UV/vis/NIR spectroscopy.

Modeling based on electrodynamic simulations shows a clear signature of strong plasmonic coupling with an interparticle spacing of 1-2 nm. We find evidence for well-defined plasmonic modes of quasi-infinite chains.[1] Beyond elementary simulations on the individual chain level, we introduce an advanced model taking parameters like the chain length distribution, ensemble-averaging, as well as interchain disorder into account.[1]

[1] C. Hanske et al. Nano Lett. 2014, in press.

[2] C. Lu et al. Soft Matter, 2007, 3, 1530-1536.

[3] N. Pazos-Perez et al. Chem. Sci., 2010, 1, 174-178.

O 23.11 Tue 13:00 MA 043

**New details about monocrystalline goldflakes for plasmonic applications** — •Thorsten Feichtner[1], Muhammad Bashouti[1], Björn Hoffmann[1], Achmed Salaheldin[2], Mirza Mačković[3], Christel Dieker[3], Peter Richter[4], Ovidiu Gordan[4], Dietrich Zahn[4], Erdmann Spieker[3], and Silke Christiansen[1,5] — [1]Max Planck Institute for the Science of Light (MPL), 91058 Erlangen, Germany — [2]Universität Erlangen-Nürnberg, Institute of Particle Technology, 91058 Erlangen, Germany — [3]Universität Erlangen-Nürnberg, Center for Nanoanalysis and Electron Microscopy (CENEM), 91058 Erlangen, Germany — [4]Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany — [5]Helmholtz Centre Berlin for Materials and Energy (HZB), 14109 Berlin, Germany

Wet-chemical synthesis of nm-thin, large area gold flakes is a viable method to realize a flat, monocrystalline raw material for fabricating high quality plasmonic devices. Transmission electron microscopy (TEM) proved the gold flakes being single crystalline except for twin boundary formation parallel to the flake surface. Micro-ellipsometry allowed to determine their complex dielectric constant for the first time. The flakes were polished by focused ion beam (FIB) milling and analyzed with electron backscatter diffraction (EBSD). The gold flakes remain monocrystalline down to a thickness of ≈10 nm allowing state-of-the-art nanofabrication processing to obtain nano-antennas or other desired plasmonic structures at sizes and structure perfections impossible with evaporated, poly-crystalline gold thin films.

## O 24: Catalysis: Structural Effects

Time: Tuesday 10:30–13:15 Location: MA 144

O 24.1 Tue 10:30 MA 144

**Theoretical and in-situ studies for the dissociation of water on an active Ni/CeO$_2$ catalyst: Importance of strong metal-support interactions for the cleavage of O−H bonds** — •M. V. Ganduglia-Pirovano[1], D. López-Durán[1,2], J. Carrasco[1,2], Z. Liu[3], S. D. Senanayake[3], T. Duchoň[4], V. Matolín[4], and J. A. Rodriguez[3] — [1]Inst. de Catálisis y Petroleoquímica, CSIC, Spain — [2]CIC Energigune, Álava, Spain — [3]Brookhaven Natl. Lab., N.Y., U.S. — [4]Faculty of Math. and Phys., Charles Univ., Praha, Czech Rep.

Water dissociation is crucial in numerous heterogeneous catalytic reactions on oxide-supported transition-metal catalysts. Here, supported by a combination of density-functional theory and experimental results, we elucidate the effect of the support on O−H bond cleavage activity for nickel/ceria systems. Ambient-pressure O1s photoemission spectra at low Ni loadings on CeO$_2$(111) reveal a substantially larger amount of OH groups as compared to the bare oxide support. Our computed activation energy barriers for water dissociation show an enhanced reactivity of Ni adatoms on CeO$_2$(111) compared with larger Ni particles and extended Ni(111) surfaces. At the origin of this support effect is the ability of ceria to stabilize oxidized Ni$^{2+}$ reactive species by accommodating electrons in localized $f$-states. The fast dissociation of water on Ni/CeO$_2$ has a dramatic effect on the activity and stability of this system as a catalyst for the water-gas shift reaction [1,2].

[1] J. Carrasco et al., J. Phys. Chem. C, 117, 8241 (2013).

[2] J. Carrasco et al., Angew. Chem. (2015), DOI: 10.1002/anie.201410697R2.

O 24.2 Tue 10:45 MA 144

**Alumina model supports on NiAl(110) studied by High-Pressure STM** — •Rik Mom[1], Joost Frenken[2], and Irene Groot[1] — [1]Huygens-Kamerlingh Onnes Laboratory, Leiden, The Netherlands — [2]ARCNL, Amsterdam, The Netherlands

Modern research on the atomic- and molecular-scale working mechanisms of industrial catalysis increasingly involves efforts to extend the use of traditional surface science characterization tools to high pressures and to increase the complexity of the investigated model catalysts.

In order to mimic the alumina that is often used to support catalytic nanoparticles, ultrathin alumina films have been developed on single crystal metal surfaces. Because of its high degree of crystallinity and good conductivity, the Al2O3/NiAl(110) system has received particular interest[1].

Here, we investigate the stability of this thin-film support under high pressures, e.g. 1 bar, of various gasses. We used high-pressure STM[2] to follow the structural evolution of the film and post-mortem XPS to inspect the end result. Our observations show that alumina films on NiAl(110) are stable under 1 bar of H2, O2 and H2S. Under millibar levels of H2O, film growth occurs in defective areas, gradually expanding these over the surface. Experiments using thicker alumina films with the same level of crystallinity show that film thickness has little effect on the reactivity towards water. [1] G.H. Simon et al., J. Phys.: Condens. Matter 24, 084007 (2012) [2] C.T. Herbschleb et al., Rev. Sci.Instr. 85, 083703 (2014)

O 24.3 Tue 11:00 MA 144

**Tuning Excitability by Alloying: The System Rh(111)/Ni/O$_2$+H$_2$** — •Tim Smolinsky, Mathias Homann, Florian Lovis, and Ronald Imbihl — Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Germany

Catalytic oxidation of hydrogen on Rh(111) is a bistable system but through alloying with nickel the system becomes excitable [1]. Varying the nickel coverage from zero up to several monolayers we studied chemical wave patterns and adsorbate-induced Ni segregation in the $10^{-6}$ and $10^{-5}$ mbar range at temperatures between 323 K and 773 K with photo electron emission microscopy (PEEM). The surface was characterized with Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). Already small Ni coverages lead to excitable behavior and at high Ni coverages 3D-NiO particles start to nucleate on the surface. Nickel is apparently highly mobile in the top layers of the crystal. Shape, velocity and wavelength of the pulses depend on the nickel coverage. A bifurcation diagram showing the dependence of the system behavior on the nickel coverage was constructed.

[1] F. Lovis, T. Smolinsky, A. Locatelli, M. Á. Niño and R. Imbihl, J. Phys. Chem. C 116 (2012) 4083-4090.

O 24.4 Tue 11:15 MA 144

**Near-ambient pressure XPS investigation of the oxidation of liquid Gallium and Platinum-Gallium alloys** — •Mathias Grabau[1], Sandra Krick-Calderón[1], Florian Rietzler[1], Florian Maier[1], Nicola Taccardi[2], Hans-Peter Steinrück[1], and Christian Papp[1] — [1]Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — [2]Lehrstuhl für Chemische Reaktionstechnik, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

The oxidation of the liquid samples of gallium and gallium based platinum alloys (2 and 5 wt% Pt) by molecular oxygen at temperatures between 300 and 550 K was examined using near ambient pressure XPS. Gallium oxide films of different thickness were prepared on the surface of the liquid samples under isothermal and isobaric conditions; the growth was monitored in situ. The thickness of the prepared oxide films increased to up to 30 Å with rising temperature and O2 pressure. The gallium oxide films were found to be stable in UHV up to temperatures just below 740 K. Enrichment of metallic platinum in the grown gallium oxide films was found for the examined alloys. The enrichment of platinum in the oxide films was found to be independent of the composition of the alloy, the film thickness, and the temperature and pressure during growth of the oxide films.

We acknowledge the financial support of the Cluster of Excellence 'Engineering of Advanced Materials'.

O 24.5 Tue 11:30 MA 144

**$H_2$ activation on Pt-$CeO_2$ mixed oxides for fuel cell applications** — •Armin Neitzel[1], Yaroslava Lykhach[1], Tomas Skála[2], Nataliya Tsud[2], Mykhailo Vorokhta[2], Kevin Charles Prince[3], Vladimir Matolín[2], and Jörg Libuda[1] — [1]FAU Erlangen-Nürnberg, Germany — [2]Charles University in Prague, Czech Republic — [3]Elettra-Sincrotrone Trieste, Italy

We investigated $H_2$ activation on Pt-$CeO_2$ mixed oxides as a function of Pt content by means of synchrotron radiation photoelectron spectroscopy and resonant photoemission spectroscopy. Pt-$CeO_2$ mixed oxides were prepared by co-deposition of metallic Pt and Ce in oxygen atmosphere on well-ordered $CeO_2$(111) buffer layers on Cu(111) at 110 K. Mixed oxides contain $Pt^{2+}$, $Pt^{4+}$, $Ce^{4+}$ and fractions of $Ce^{3+}$ ions. $Pt^{2+}$ ions are stabilized at (100) nanofacets at the surface of nanostructured $CeO_2$ films. Thermal stability of nanostructured Pt-$CeO_2$ mixed oxides depends strongly on the Pt concentration. Annealing to 700 K in UHV leads to partial reduction of $Pt^{2+}$ ions to metallic Pt particles once their number exceeds that of the (100) sites. $H_2$ dissociation occurs only in presence of metallic $Pt^0$ on the Pt-$CeO_2$ substrates. Below 300 K, $H_2$ activation yields hydroxyl groups which prevent hydrogen spillover from Pt to the substrate. Above 350 K, reduction of $Pt^{2+}$ is accompanied by formation of oxygen vacancies due to the reaction of hydrogen with oxygen provided by the reverse oxygen spillover from the substrate to the Pt particles.

O 24.6 Tue 11:45 MA 144

**Microkinetics of the Deacon process over $RuO_2$(110): Rate-determining steps and diffusion limitations** — •Zhen Yao, Farnaz Sotoodeh, and Karsten Reuter — Technische Universität München

$Cl_2$ is widely used in many chemical industries which produce HCl as byproduct. For a sustainable operation recycling HCl back to high purity $Cl_2$ is therefore mandatory. In the corresponding oxidative Deacon process ($4HCl + O_2 \rightarrow 2\ Cl_2 + 2H_2O$) $RuO_2$ shows unique activities. Ultimately aiming for cheaper substitutes comprising earth-abundant metals, an atomic-scale understanding of what makes up for the special performance of $RuO_2$ represents a first step.

We contribute to this endeavor by analyzing the Deacon reaction network on a $RuO_2$(110) model catalyst with microkinetic simulations. Specific targets are the role of the trench-like surface geometry of $RuO_2$(110), as well as the identification of the rate-limiting steps under varying operation conditions. For this we compare different mean-field and kinetic Monte Carlo models, and employ both first-principles and empirically determined rate constants.

O 24.7 Tue 12:00 MA 144

**Comparison of mean-field and kinetic Monte Carlo microkinetic models of CO methanation on Rh(211): Influence of lateral interactions between adsorbates** — •Mie Andersen[1], Andrew J. Medford[2,3], Thomas Bligaard[2,3], Jens K. Nørskov[2,3], and Karsten Reuter[1,2,3] — [1]Theoretical Chemistry, Technische Universität München, Germany — [2]SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, CA, USA — [3]Department of Chemical Engineering, Stanford University, CA, USA

In heterogeneous catalysis microkinetic modeling is often carried out in the mean-field approximation (MFA), which assumes a rapid mixing of the adsorbates and leads to a uniform distribution of all atomic and molecular species on the surface. Here, we loosen some of the underlying assumptions inherent in the MFA by moving to a full kinetic Monte Carlo (KMC) description of relevant surface processes such as adsorption, diffusion, reaction, and desorption. Using CO methanation on Rh(211) as a test case and energetic input from density functional theory calculations, we compare the predicted coverages and turnover-frequencies between mean-field and KMC microkinetic models. Further, we discuss simple first-order models for lateral interactions between adsorbates [1], where the statistically correct description of fluctuations and correlations in the coverage and binding sites of adsorbates in KMC is expected to outperform the MFA.

[1] Journal of Catalysis 307, 275-282 (2013)

O 24.8 Tue 12:15 MA 144

**Stabilization of $CH_2$ on Ru(0001) by hydrogen co-adsorption** — •Xunhua Zhao[1], Harald Kirsch[1], Zefeng Ren[1,2], R. Kramer Campen[1], Sergey V. Levchenko[1], Martin Wolf[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]Present address: Peking University, Beijing, CN

Based on indirect experimental evidence, $CH_2$ was proposed as a buidling block for hydrocarbon chain growth on the Ru(0001) surface during the Fischer-Tropsch process. However, previous calculations agreed that $CH_2$ is not stable on Ru(0001) at the reaction conditions, and should quickly convert into CH. Employing density-functional theory, we show that this disagreement can be reconciled if coadsorbed hydrogen is present on the surface. All possible $CH_x$+$H_y$ configurations with adsorbates at hollow sites are calculated. $CH_x$ dissociation barriers are obtained using the string method. We further demonstrate, by calculating the surface phase diagram for one-carbon species on Ru(0001) as a function of $H_2$ chemical potential, that the stablization of $CH_2$ by co-adsorbed hydrogen requires non-equilibrium conditions. The calculated barrier for the $CH_2$ dissociation in the presence of hydrogen is significantly increased, and is close to the one recently measured by vibrational sum-frequency generation spectroscopy [1]. Our results also explain why $CH_2$ was not observed when C or CH are hydrogenated on Ru(0001) [2], although it is observed after methane decomposition.—[1] H. Kirsch, X. Zhao, Z. Ren, S. V. Levchenko, M. Wolf, and R. K. Campen, J. Catal. **320**, 89 (2014); [2] T. K. Shimizu *et al.*, J. Chem. Phys. **129**, 244103 (2008).

O 24.9 Tue 12:30 MA 144

**Controlling $CH_2$ dissociation on Ru(0001) through surface site blocking by adsorbed hydrogen** — •Harald Kirsch[1], Xunhua Zhao[1], Sergey V. Levchenko[1], Martin Wolf[1], Zefeng Ren[2], and R. Kramer Campen[1] — [1]Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin, Germany — [2]International Center for Quantum Materials and School of Physics, 100871 Beijing, China

Understanding the relative stability of $CH_x$ species on surfaces is necessary for mechanistic description of such important catalytic chemistry as the Fischer-Tropsch synthesis or the steam reforming process of methane. Here we investigate the thermal stability of surface bound $CH_2$ radical on Ru(0001). We produce a $CH_2$ covered surface in UHV at low temperatures ($< 250$ K) by employing a supersonic molecular beam source for $CH_4$ dissociation and characterize $CH_2$ population using vibrational sum frequency spectroscopy ($> 5$ cm$^{-1}$ resolution). By this approach we experimentally quantify the barrier of the reaction $CH_2 \rightarrow CH + H$ via an Arrhenius analysis and find an activation energy of 65 ± 6 kJ/mol, which is $> 4\times$ higher than previous computational results [1]. Our density functional theory calculations show, that this disagreement can be reconciled if 3 coadsorbed H atoms per $CH_2$ are present in our experiment [2] and that such hydrogen coverages require non-equilibrium with respect to the overlying gas phase.

[1] I.M. Ciobica et al, J. Phys. Chem. B **104**, 3364 (2000); [2] H.

Kirsch, X. Zhao, Z. Ren, S. V. Levchenko, M. Wolf, and R. K. Campen, J. Catal. **320**, 89 (2014)

O 24.10 Tue 12:45 MA 144

**Dissociation of carbon monoxide on Co(0001) - an in situ scanning tunneling microscopy study at high pressures and high temperatures** — •Bernhard Böller, Martin Ehrensperger, and Joost Wintterlin — Ludwig-Maximilians-Universität, Munich, Germany

The dissociation of carbon monoxide on Co surfaces is a key element in the discussion of the mechanism of the cobalt-catalyzed Fischer-Tropsch synthesis. We have investigated a Co(0001) single crystal at 493 K in CO pressures up to 0.85 mbar using high pressure scanning tunneling microscopy (STM). Ex situ photoelectron spectroscopy (XPS) was used to detect the resulting surface carbon. At CO pressures higher than 0.05 mbar XPS showed significant amounts of surface carbon, indicating dissociation of CO. Because of the high activity of the cobalt surface and the unavoidable presence of traces of contaminants at elevated pressures, extensive experiments were preformed to exclude other sources than CO dissociation for the surface carbon. As the coverage of carbon increased, the in situ STM data showed the evolution of new surface features. Starting from local changes they finally covered most of the surface, forming a (5x5) superstructure. Most likely a carbon-induced surface reconstruction is involved in these processes. Additionally, after exceeding a certain coverage, surface carbide started to form. Simultaneous structure changes near the steps indicate transport processes of cobalt atoms.

O 24.11 Tue 13:00 MA 144

**In Situ Scanning Tunneling Microscopy of a Co(0001) Fischer-Tropsch model catalyst** — •Martin Ehrensperger, Bernhard Böller, and Joost Wintterlin — Ludwig-Maximilians-Universität, Munich, Germany

The low temperature Fischer-Tropsch process produces long chain hydrocarbons over cobalt catalysts, starting from syngas, a mixture of hydrogen and carbon monoxide. Whereas the reaction mechanism has been intensively discussed, key questions about molecular processes and the structure of the catalyst surface remain unanswered. We have investigated a Co(0001) single crystal in 10 mbar of syngas at 493 K with in situ high temperature and high pressure scanning tunneling microscopy (STM). Methane was catalytically produced on the cobalt surface, as proven by quadrupole mass spectrometry. The STM data show a metallic surface. The surface was neither transformed into a surface oxide or carbide nor was it reconstructed. A reorganization of the surface morphology during reaction, as has often been postulated, was not observed under the applied experimental conditions. The STM images are in agreement with reversibly bound molecules that form a mobile mixed adsorbate layer on a flat metallic surface. Using ex situ x-ray photoelectron spectroscopy only low amounts of carbon and oxygen were detected.

## O 25: Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces II

Time: Tuesday 14:00–16:00 Location: HE 101

**Topical Talk** O 25.1 Tue 14:00 HE 101

**First-Principles Microkinetic Modeling at Solid-Liquid Interfaces: First Steps** — •Karsten Reuter — Technische Universität München, Germany

Over the last decade first-principles based microkinetic models have become a common tool to describe solid-gas processes like heterogeneous catalysis or crystal growth. For processes at solid-liquid interfaces such modeling is in its infancy. Challenges arise already in the efficient treatment of solvation effects or in the determination of individual rate constants, where extended time-scale simulations are required to capture the often complex and rough free energy barriers.

In this talk I will review our first steps to address corresponding challenges, focusing on water/aspirin as a showcase application. For corresponding active pharmaceutical ingredients knowledge of their intrinsic dissolution rates is a cornerstone to optimize the pharmacokinetics. We achieve this goal within a spiral-growth microkinetic model that draws on dissolution rate constants obtained within a novel hyperdynamics-metadynamics molecular simulation approach.

**Topical Talk** O 25.2 Tue 14:30 HE 101

**Structure of metal electrode-electrolyte interfaces determined from first principles** — •Axel Gross — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany — Helmholtz Institut Ulm - Elektrochemische Energiespeicherung, 89069 Ulm, Germany

The theoretical description of electrode-electrolyte interfaces from first principles is hampered by the complexity of the interface structures and the liquid nature of the electrolyte requiring computationally expensive statistical averaging. Despite these obstacles, significant progress has been made in the modeling in recent years. In this contribution, I will present our attempts to contribute to this progress by systematically increasing the complexity of the considered systems [1, 2]. The electrolyte can be described either as a thermodynamic reservoir or using implicit of explicit solvent models. Using these approaches, the equilibrium coverage of specifically adsorbed anions such as halides as a function of the electrode potential will be addressed. This represents an integral part of the realistic modeling of electrochemical double layers. Additionally, on metal electrodes such as platinum the adsorption of H or OH - depending on the electrode potential - has to be considered in the presence of an aqueous electrolyte. Finally, the structure of organic electrolytes on metal electrodes that is governed by weak dispersion forces will be discussed [2, 3].

[1] Axel Groß *et al.*, J. Electrochem. Soc. **161**, E3015 (2014).
[2] Nicolas Hörmann *et al.*, J. Power Sources **275**, 531 (2015).
[3] F. Buchner *et al.*, ACS Nano **7**, 7773 (2013).

**Topical Talk** O 25.3 Tue 15:00 HE 101

**Synchrotron x-ray determination of ion distributions at liquid interfaces** — •Jean Daillant — Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, F-91192 Gif sur Yvette Cedex, France

The interfacial behavior of ions is of key importance in a number of phenomena ranging from microfluidics to chemistry in the atmosphere and from protein stability to the transport of pollutants in water.

Beyond Coulombic interaction, the polarisability and hydration of the ions as well as water interfacial structure are important, leading to ion specificity, i.e. possibly dramatically different behavior for ions like $Cl^-$ and $I^-$. Understanding these effects requires measurements to access the surface composition at the relevant nanometric length-scale.

Investigating the surface composition of alkali-halide aqueous solutions using grazing incidence x-ray fluorescence, differences in concentration over a few angstrom could be resolved, with, for example $I^-$ or $Br^- > Cl^-$. These results could be explained by including a short-range potential accounting for short-range solvent mediated couplings.

Polarization of the liquid-Hg aqueous electrolyte induces extremely large decrease in surface energy with strong ion specificity. Using x-ray reflectivity, we could determine the interfacial structure, demonstrating an accumulation of ions at the Hg surface. Our results challenge the long-standing approximation that assimilates the Hg surface to a smooth, chemically inert surface with a uniform surface charge density.

Finally, using the standing wave technique which allows both high spatial and element sensitivity, we have investigated ion distributions in nano-channels, and I will discuss the first results we have obtained.

**Topical Talk** O 25.4 Tue 15:30 HE 101

**Modelling of electrical double layers at metal oxide electrodes** — •Michiel Sprik[1] and Jun Cheng[2] — [1]Department of Chemistry, University of Cambridge, Cambridge UK — [2]Department of Chemistry, University of Aberdeen, Aberdeen, UK

Oxide surfaces exchange protons with an aqueous electrolyte and can therefore carry a net proton charge. The adsorbed protons at low pH can be partially or fully discharged by conduction electrons or the deprotonated anionic groups at high pH by holes. The "intrinsic" equilibrium constants for this process (acidities, ionization and dehydrogenation free energies) can be computed for charge neutral surfaces. We have developed such a method using Density Functional Theory based Molecular Dynamics (DFTMD, for an application to rutile titania see Angew Chem Int Ed Engl (2014) 53, 12046). An electrode with net excess or deficit proton charge can be described in first approximation by a triple layer model consisting of the charged electrode surface, ionic counter charge on the electrolyte side (a Helmholtz layer at high ionic strength) and a space charge layer on the electrode side. After a summary of our DFTMD method, we will outline in this talk how the equilibrium constants computed by the DFTMD simulation can be used in an analytic model for an "electron coupled proton adsorption isotherm". The additional parameter in this model is the capacitance of the Helmholtz layer. Such a parametrized isotherm should enable us to analyse the effect of double layers on the (photo) electrocatalytic properties of metal oxides as will be shown for the example of the oxidation of adsorbed water molecules.

## O 26: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale II

Time: Tuesday 14:00–15:45 Location: MA 004

**Invited Talk** O 26.1 Tue 14:00 MA 004

**First-principles theories of electron-plasmon and electron-spin fluctuation interactions in nanomaterials** — •Johannes Lischner — Imperial College, London, United Kingdom

The GW method includes an accurate treatment of many-electron interaction effects beyond density-functional theory and is the state-of-the-art approach for computing spectral functions and quasiparticle energies in nanomaterials. These quantities are measured in photoemission and tunneling experiments. Despite its great success, the GW approach has certain shortcomings and I will discuss two topics that require going beyond GW: i) plasmon satellites in spectral functions and ii) the coupling of quasiparticles to spin fluctuations.

Plasmon satellites in recent photoemission experiments on doped graphene have been interpreted in terms of novel plasmaron excitations, strongly coupled plasmon-hole states, predicted by GW theory. Using a cumulant expansion of the Green's function to include higher-order electron-electron interaction effects and an accurate description of the substrate, I will demonstrate that no plasmaron states need to be invoked to explain the experiments. Similar conclusions are drawn for tunneling spectra of semiconductor quantum-well two-dimensional electron gases. I will also discuss the interaction of quasiparticles with spin fluctuations in iron selenide and demonstrate that significant coupling constants can give rise to superconducting transition temperatures consistent with experimental findings.

O 26.2 Tue 14:30 MA 004

**Charge separation dynamics and opto-electronic properties of a diaminoterephthalate-C60 dyad** — •Stefano Pittalis[1], Alain Delgado[1], Jörg Robin[2], Lena Freimuth[3], Jens Christoffers[3], Christoph Lienaua[2], and Carlo Andrea Rozzi[1] — [1]Istituto Nanoscienze - CNR, Modena, Italy — [2]Institut fuer Physik and Center of Interface Science, Carl von Ossietzky Universität, Oldenburg, Germany — [3]Institut fuer Chemie and Center of Interface Science, Carl von Ossietzky Universität, Oldenburg, Germany

A novel dyad composed of a diaminoterephthalate scaffold, covalently linked to a Fullerene derivative, is explored as a nanosized charge separation unit powered by solar energy. Its opto-electronic properties are studied and the charge separation rate is determined. Simulations of the coupled electronic and nuclear dynamics in the Ehrenfest approximation are carried out on a sub 100 fs time scale after photoexcitation in order to gain insights about the mechanisms driving the the charge separation. In particular, the role of vibronic coupling and of the detailed morphology are highlighted.

O 26.3 Tue 14:45 MA 004

**Transfering spin into an extended $\pi$-orbital of a large molecule – ab-initio study of Au-PTCDA:Au(111)** — •T. Deilmann[1], T. Esat[2], B. Lechtenberg[3], P. Krüger[1], C. Wagner[2], R. Temirov[2], F.B. Anders[3], F.S. Tautz[2], and M. Rohlfing[1] — [1]Institut für Festkörpertheorie, Universität Münster, Germany — [2]Peter Grünberg Institute (PGI-3), FZ Jülich, Germany — [3]Lehrstuhl für Theoretische Physik II, TU Dortmund, Germany

The combination of an organic molecule with an unpaired spin offers a large variety of interplay between spins and orbitals, with high sensitivity to structural and environmental details. Recently, a single Au atom on a PTCDA monolayer physisorbed on Au(111) has been investigated experimentally; it exhibits a Kondo peak in the STS spectrum.

In this talk we discuss ab-initio mean-field electronic spectra (which will then serve as input data for a subsequent NRG calculation to describe the Kondo effect). Based on ab-initio structural data (in agreement with observed STM images) we evaluate the electronic spectra by many-body perturbation theory within the *GW* approximation, as well as, a simplified LDA+*GdW* approach [1]. For gas-phase PTCDA and Au-PTCDA, both methods agree well with one another and with available measurements. For Au-PTCDA on Au(111), a full *GW* calculation is too expensive due to the substrate. LDA+*GdW*, on the other hand, fully allows to incorporate the substrate polarizability in the self energy inside the molecule and leads to good agreement with the experimental data.

[1] M. Rohlfing, *Phys. Rev. B* **82**, 205127 (2010).

O 26.4 Tue 15:00 MA 004

**Quasi-particle band structure of the transition-metal-based zero-gap semiconductors** — •Murat Tas[1], Ersoy Sasioglu[2], Iosif Galanakis[3], Christoph Friedrich[2], and Stefan Blügel[2] — [1]Department of Basic Sciences, İstanbul Kemerburgaz University, 34217 İstanbul, Turkey — [2]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — [3]Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece

Zero-gap semiconductors (SCs) are promising materials for a variety of applications ranging from spintronics to thermoelectricity. Using the *GW* approximation within the framework of the FLAPW method, we study the quasi-particle band structure of a number of transition-metal-based zero-gap SCs XX′YZ, where X, X′ and Y are the transition metal elements, and Z is an *sp* element. We find that, in contrast to *sp*-electron based SCs such as Si and GaAs, the many-body renormalization has a minimal effect on the electronic band structure of these systems. It turns out that for many compounds the change of the band gap is less than 0.2 eV, which makes the starting point PBE a good approximation for the description of the electronic properties of these materials. Furthermore, the band gap can be tuned either by the variation of the lattice parameter or by the substitution of the Z element.

O 26.5 Tue 15:15 MA 004

**Keldysh nonequilibrium Green's function vs. Feshbach projection operator approach for plasmon-assisted photoemission** — •Yaroslav Pavlyukh, Michael Schüler, and Jamal Berakdar — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

A unified theoretical treatment of the single and double electron emission is achieved by using the Feshbach projection method. In this formalism the final target's state fixes the projection operator which subsequently determines the effective Hamiltonian and the optical potential for emitted electrons. The method of non-equilibrium Green's functions is a complementary approach which also allows to treat such processes diagrammatically. We explicitly establish a correspondence between these two approaches and illustrate the diagrammatic technique by calculations of the two-electron emission from $C_{60}$ assisted by the excitation of plasmons.

O 26.6 Tue 15:30 MA 004

**Inclusion of thermal lattice vibrations and spin fluctuations within transport calculations** — •Sergiy Mankovsky, Kristina Chadova, Diemo Ködderitzsch, Svitlana Polesya, and Hubert Ebert — Dept. Chemie/Physikalische Chemie, Universität München, Butenandtstr. 5-13, D-81377 München, Deutschland

We present an approach for the calculation of response quantities, e.g. Gilbert damping and electrical conductivity, accounting for temperature induced effects of lattice vibrations and spin fluctuations. The approach is based on the alloy analogy model with thermal vibrations and spin fluctuations modeled by random atomic displacements or magnetic moments deviations, respectively. We discuss various models to deal with spin fluctuations, determining their impact on the temperature dependent behaviour of conductivity and Gilbert damping parameter. We demonstrate the non-additivity of the separate contributions to the conductivity. The results of the calculations are compared to experimental data demonstrating a rather good agreement for the systems under consideration.

# O 27: Nanostructures: Low Dimensions

Time: Tuesday 14:00–16:15 Location: MA 005

O 27.1 Tue 14:00 MA 005

**Characterizing the Ring Neighborhoods of Amorphous 2D Silica** — •Kristen Burson, Christin Büchner, Stefanie Stuckenholz, Markus Heyde, and Hans-Joachim Freund — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Novel two-dimensional (2D) materials have garnered significant scientific interest due to their potential technological applications. For new 2D materials, it is important to consider not only crystalline materials, such as graphene and hexagonal BN, but also amorphous materials. For amorphous materials, a detailed understanding of the complex structure is necessary. Here we present a study of 2D amorphous bilayer silica. The atomic structure has been determined by nc-AFM and STM imaging with atomic resolution, revealing a network of different ring sizes [1]. For any given ring, the sizes of the neighboring rings can be characterized. Characteristic arrangements of rings within the amorphous structure have been identified and their relative prevalence has been quantified. Typical ring arrangements, such as the Stone-Waals defect, are compared with other atomic scale, molecular scale, and macro-scale 2D amorphous systems [2]. Notably, similar 2D ring arrangements are observed across systems with diverse length scales. Results indicate that geometric strain plays an important role in determining ring cluster configurations within 2D amorphous network structures.

[1]Lichtenstein, L.; Heyde, M.; Freund, H.-J. Phys. Rev. Lett. 2012, 109, 106101 [2]Büchner, C. et al. Z. Phys. Chem. 2014, 288(4-5), 587

O 27.2 Tue 14:15 MA 005

**Structural and electronic properties of Ir nanowires on Ge(100)** — •René Heimbuch, Iris Slootheer, and Harold Zandvliet — Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente

Iridium (Ir) nanowires show structural and electronic properties that are potentially of large interest for nano-electronic applications. Here we present detailed studies on the structural evolution of the surface and the growth of Ir nanowires on Ge(100). Using Scanning Tunneling Microscopy at low temperatures, we probed the wires and mapped the electronic landscape on and around the atomic chains. The wires show electronic properties that are very distinctive from the surrounding. A strong metallic character of the Ir nanowires promotes the Ir/Ge(100) system to a potential candidate for exotic low dimensional electronic effects.

O 27.3 Tue 14:30 MA 005

**Reversible and self-organized formation of periodic 1D cobalt nanostructures** — •Pascal Ferstl[1], Marina Schuler[1], Lutz Hammer[1], Klaus Heinz[1], M.Alexander Schneider[1], Florian Mittendorfer[2], Josef Redinger[2], M. Alif Arman[3], Edvin Lundgren[3], and Jan Knudsen[3,4] — [1]Lst. für Festkörperphysik, FAU Erlangen-Nürnberg — [2]Inst. für Angewandte Physik and Center for Computational Materials Science, TU Wien — [3]Division of Synchrotron Radiation Research, Lund University — [4]The MAX IV Laboratory

By alternate oxidation and reduction of 1/3 ML of cobalt deposited on the unreconstructed Ir(100) surface two different quasi one-dimensional nanostructures can be formed and reversibly transformed into each other: An oxygen-rich and an oxygen-free phase, which both show a well ordered single domain 3×1 periodicity.

In this study we present the atomic structure of these two phases revealed by means of quantitative LEED, STM, HRXPS and DFT calculations. The oxygen-free 3×1 phase is an ordered $Ir_2Co$ surface alloy, where every third iridium row of the outermost layer is substituted by a cobalt row. Adsorption of oxygen transforms the latter into a metal-oxide hybrid system with $CoO_2$ stoichiometry. In this structure the Co rows are drastically lifted above the first Ir layer so that there are no more direct Co-Ir bonds. The clean Co-Ir alloy phase can be restored again by reducing the $CoO_2$ phase in hydrogen at only 80°C.

O 27.4 Tue 14:45 MA 005

**Surface self-assembly of $Fe_4$ single molecule magnets** — Philipp Erler[1], Nicole Barth[1], Peter Schmitt[2], •Luca Gragnaniello[1], and Mikhail Fonin[1] — [1]Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany — [2]Fachbereich Chemie, Universität Konstanz, 78457 Konstanz, Germany

Here, we present a successful fabrication of self-organized nanoislands of $Fe_4(dpm)_6L_2$ ($Fe_4$) single molecule magnet (SMM), by using *h*-BN/Rh(111) as template. $Fe_4$ clusters are a promising class of molecules whose magnetic properties have recently raised great interest, due to their capability to retain their SMM behavior when chemically grafted on a gold substrate [1]. However, $Fe_4$ brittleness limits their thermal stability, hindering direct evaporation of the molecules in ultra-high vacuum (UHV) in most cases [2] and, consequently, a thorough investigation via scanning tunneling microscopy and spectroscopy (STM/STS). We overcome this problem by using electrospray as a gentle deposition method in UHV. The structural and electronic properties of sub-monolayers and individual molecules were studied by means of low temperature STM/STS. Despite the complexity of their structure, highly ordered arrays of $Fe_4$ molecules on the *h*-BN substrate can be obtained, therefore providing a promising playground to explore their electronic and magnetic properties in a well-defined configuration.

[1] M. Mannini *et al.*, Nature Mater. **8**, 194 (2009); M. Mannini *et al.*, Nature 468, 417 (2010). [2] Allowed only by a specific $Fe_4$ derivative (see L. Margheriti *et al.*, Small **5**, 1460 (2009).

O 27.5 Tue 15:00 MA 005

**PtFe and IrFe atomic bilayers on Ir(111) investigated by STM** — •Maximilian Meyer, André Kubetzka, Kirsten von Bergmann, and Roland Wiesendanger — Department of Physics, University of Hamburg, Germany

Non-magnetic capping layers are a means to passivate chemically reactive magnetic films and they also allow to tailor specific magnetic properties by modifying the interface [1,2].

Here we use scanning tunneling microscopy (STM) to investigate the growth of Pt and Ir on an atomic layer of Fe on Ir(111) which exhibits an atomic-scale magnetic skyrmion lattice [3].

We will discuss differences and similarities of these two systems and show the influence of the substrate temperature onto the film growth.

In the low coverage regime we observe atomic layer islands of both fcc and hcp stacking and for Pt we find a tendency for 2nd atomic layer nucleation on Fe/Ir(111). For Pt/Fe/Ir(111) the smoothest films were achieved at intermediate temperatures where the atom mobility is increased and alloying has not yet set in.

[1] N. Romming *et al.*, Science **341**, 636 (2013)
[2] B. Dupé *et al.*, Nature Comm. **5**, 4030 (2014)
[3] S. Heinze *et al.*, Nature Physics **7**, 713 (2011)

O 27.6 Tue 15:15 MA 005

**1D-$WO_3$ nanochannel structures used for efficient $H_2$-sensing** — •Ole Pfoch[1], Marco Altomare[1], and Patrik Schmuki[1,2] — [1]Department of Material Science and Engineering, WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany — [2]Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia

1D nanostructures of vertically aligned channels of amorphous $WO_3$ up to ca. 4 $\mu$m length were grown by means of self-organizing electrochemical anodisation. By preliminary screening experiments, the anodisation conditions were optimized so to obtain highly ordered nanochannels with pore diameter of ca. 10 nm. With a proper thermal treatment the anodic $WO_3$ can be converted into crystalline structures. SEM, EDX, XRD, XPS, TEM and SAED are used to further investigate the physical-chemical properties of the $WO_3$ layers. Since $WO_3$ is known to show a rapid response to reducing gases such as $H_2$ and nanostructures are promising candidates for fabricating gas sensors due to their high surface area, gas sensing experiments are performed. Thereby the structures are found to exhibit outstanding gas-sensing abilities such as a fast response at low temperatures (80-120°C) even down to concentrations as low as 0.5 ppm.

O 27.7 Tue 15:30 MA 005

**A joint *first principles* and Kelvin probe force microscopy study of stepped silicon surfaces with unprecedented resolution** — •Stefan Wippermann[1], Carmen Pérez León[2], Holger Drees[2], Michael Marz[2], and Regina Hoffmann-Vogel[2] — [1]Max-Planck-Institut für Eisenforschung, D-40237 Düsseldorf, Ger-

many — [2]Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany

Stepped well-ordered surfaces are important nanotemplates for the fabrication of one-dimensional nanostructures with intriguing electronic properties. The vicinal Si(7710) surface is a popular model system of this kind. It contains (7x7) reconstructed areas equivalent to the well characterized and understood Si(111)-(7x7) surface. Thereby this system essentially contains its own calibration, providing an ideal testbed for surface characterization techniques and understanding in depth the rich morphology of the structural features present in this system.

Here we present a joint experimental and theoretical investigation of the structural properties of the vicinal Si(7710) surface. We carried out Kelvin probe force microscopy (KPFM) measurements with unprecedented atomic resolution, and *first principles* calculations of the local work function as a function of the lateral position of the tip above the surface. These calculations allowed us to interpret the experimental KPFM data in terms of specific structural features and electronic properties of surface states, such as e. g. defects, dangling bond angles and occupations of dangling bonds. R. H.-V. acknowledges ERC starting grant NANOCONTACTS No. ERC 2009-Stg 239838.

O 27.8 Tue 15:45 MA 005

**Computing Equilibrium Shapes of Wurtzite Crystals: The Example of GaN** — •Hong Li[1,2], Lutz Geelhaar[2], Henning Riechert[2], and Claudia Draxl[1] — [1]Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin, Germany — [2]Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

Crystal morphologies are important for the design and functionality of devices based on low-dimensional nanomaterials. The equilibrium crystal shape (ECS) is a key quantity in this context. It is determined by surface energies, which are hard to access experimentally but can generally be well predicted by first-principles methods. Unfortunately, this is not necessarily so for polar and semipolar surfaces of wurtzite crystals. By extending the concept of Wulff construction, we demonstrate that the ECSs can nevertheless be obtained for this class of materials. For the example of GaN, we identify different crystal shapes depending on the chemical potential. It is shown that the crystal exhibits a rod-like shape along the polar c axis, with top and bottom geometries depending on the chemical potential, while the side walls are formed by both types of nonpolar surfaces. Our results can well explain the experimentally observed nanowire shapes. Beyond that, it opens a perspective to gain insight into morphologies of the entire class of wurtzite materials.

O 27.9 Tue 16:00 MA 005

**Near-field Optical Imaging of (6,5)SWCNT/PFO-BPy Conjugates** — •Xian Shi[1], Imge Namal[2], Tobias Hertel[2], and Achim Hartschuh[1] — [1]Department Chemie & CeNS, LMU München, Germany — [2]Institut für Physikalische und Theoretische Chemie, JMU Würzburg, Germany

PFO-BPy wrapped single-wall carbon nanotubes (SWCNTs) are promising candidates for optoelectronic and solar cell applications [1]. We utilized tip-enhanced near-field microscopy (TENOM) [2] with nanometer resolution and signal enhancement to investigate the photoluminescence (PL) and Raman scattering of (6,5) SWCNT/PFO-BPy conjugates. PL images reveal the spatial homogeneity of both emission intensity and energy along individual nanotubes. Raman images indicate their local structural properties. This set of images provides detailed information on several key phenomena influencing the excited state properties of SWCNTs including the interaction with the environment, nanotube-nanotube coupling, exciton mobility and defect density. We compared the results obtained for PFO-BPy wrapped carbon nanotubes with other materials and different sample treatments.

Financial support from the European Project POCAONTAS (FP7-PEOPLE-2012-ITN-316633) is gratefully acknowledged.

[1] G. J. Brady et al. ACS nano 8, 11614-11621, 2014.

[2] N. Mauser and A. Hartschuh, Chem. Soc. Rev 43, 1248-1262, 2014.

## O 28: Moire and Graphene Stacking

Time: Tuesday 14:00–16:00 Location: MA 041

O 28.1 Tue 14:00 MA 041

**Periodic Overlayers and Moiré Patterns: a unified theoretical treatment.** — •Klaus Hermann — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin (Germany)

Complex overlayer structures at single crystal surfaces have been observed where long-range order, expressed by additional approximate surface periodicity with very large unit cells, was found. Examples are Pb(111)-$C_{60}$ near $(\sqrt{403}/7 \times \sqrt{403}/7)R22.8^\circ$ [1], Ag(111)-3S near $(\sqrt{7}\times\sqrt{7})R19.1^\circ$ [2], or graphene at different hexagonal metal surfaces, such as Ir(111) [3]. This phenomenon can be characterized by spatial interference resulting in 2-dimensionally periodic Moiré patterns. We have generalized a previously proposed mathematical formalism [4] of determining such Moiré patterns based on concepts of higher-order coincidence (HOC) lattices. The extended formalism provides simple mathematical relations allowing to compute 2-dimensional Moiré lattices of any order in their dependence on layer rotation and scaling with respect to a given HOC lattice structure. The formalism will be illustrated by example systems observed in experiment. [1] H.L. Li, K.J. Franke, J.I. Pascual, L.W. Bruch, R.D. Diehl, Phys. Rev. B **80** (2009) 085415. [2] M. Yu, D.P. Woodruff, C.J. Satterley, R.G. Joes, and V.R. Dhanak, J. Phys. Chem. **111** (2007) 3152. [3] E. Loginova, S. Nie, K. Thürmer, N.C. Bartelt, and K.F. McCarthy , Phys. Rev. B **80** (2009) 085430. [4] K. Hermann, J. Phys.: Condensed Matter 24 (2012) 314210.

O 28.2 Tue 14:15 MA 041

**Semi-classical method for matrix valued Hamiltonians** — •Michael Vogl, Sam Shallcross, and Oleg Pankratov — Lehrstuhl für Theoretische Festkörperphysik Staudtstr. 7-B2 91058 Erlangen

Semi-classical theories are interesting for their insight into the borderland phenomena embracing quantum and classical physics such as quantum chaos, as well as for providing a non-perturbative scheme for treating complex quantum problems. The plethora of complex graphene-based systems, such as the twist graphene bilayer consisting of two mutually rotated carbon layers, or the AB stacked bilayer with soliton faults (partial dislocations), are systems for which a semi-classical treatment should be very useful. However, the usual semi-classical schemes become prohibitively cumbersome for the matrix valued Hamiltonians inherent to the graphene-based systems. We provide a scheme that allows for a clear route to the semi-classical treatment of such systems, as well as a very efficient numerical scheme.[1] As an example of this procedure we consider the semi-classical treatment of a line partial dislocation in bilayer graphene.

[1] M. Vogl, Semi-classics for Matrix Hamiltonians, Master thesis, Erlangen, 2014.

O 28.3 Tue 14:30 MA 041

**Scanning Probe Microscopy Study of Moiré Patterns on Rotated Graphene Layer on Highly Oriented Pyrolytic Graphite** — •Dilek Yildiz[1,2], Şener Şen[3], Marcin Kisiel[1], Oğuz Gülseren[3], Ernst Meyer[1], and Oğuzhan Gürlü[2] — [1]University of Basel, Basel, Switzerland — [2]Istanbul Technical University, Istanbul, Turkey — [3]Bilkent University, Ankara, Turkey

Highly Oriented Pyrolytic Graphite (HOPG) has weak van der Waals interaction between its layers so they can be cleaved easily and fresh (0001) graphite surfaces can be obtained. As another result of this weak interaction, the topmost graphene layer can be rotated with respect to the rest of the crystal and super periodic structures called as moiré patterns are formed. Such moiré patterns were extensively studied by Scanning Tunneling Microscopy (STM) and Spectroscopy (STS). In this study, we investigate the morphological and electronic properties of moiré patterns on HOPG by using STM and STS under ambient conditions. Apparent corrugation changes of different moiré patterns were studied as a function of the bias voltage. We studied the electronic properties of moiré patterns with respect to their periodicities. Van Hove singularities were observed on moiré patterns in STS data and their origin were clarified by means of ab initio calculations. Observation of moiré patterns by Atomic Force Microscopy

(AFM) is yet to be reported on HOPG surfaces. In our recent studies we are interested in the frictional properties of varying moiré patterns on HOPG. Our particular interest is to observe the frictional response of the moiré patterns to the tip perturbation by use of pendulum geometry AFM.

O 28.4 Tue 14:45 MA 041

**Low energy theory of the graphene twist bilayer** — •Dominik Weckbecker, Sam Shallcross, and Oleg Pankratov — Lehrstuhl für Theoretische Festkörperphysik, Staudtstraße 7, D-91058 Erlangen, Germany

Two mutually rotated layers of graphene exhibit an electronic structure that depends profoundly on the rotation angle of the two layers. At large angles the layers essentially decouple while, in contrast, for small rotation angles strong coupling leads to a dramatically different electronic spectrum: one finds localization on the moire lattice and a significant reduction of the Fermi velocity near the Dirac point [1]. This richness of electronic structure has however proven difficult to capture within an unified low energy Dirac-Weyl picture; while theories exist for the large and small angle regimes there is at present no consistent theory valid at all twist angles [2,3]. We remedy this by deriving a low energy theory which is based on the observation of an emergent momentum coupling scale [1] valid at all angles, which we show to be in excellent agreement with numerical tight-binding calculations. We further explore the rich small angle limit finding a vanishing of the zero mode and a rich gallery of Fermi surfaces. At large angles the theory recovers the effective low energy Hamiltonians previously derived on symmetry grounds [3].

[1] S. Shallcross et al., Phys. Rev. B 87, 245403, 2013.
[2] R. Bistritzer et al., PNAS 108(30):12233-12237, 2011.
[3] E. J. Mele et al., J. Phys. D: Appl. Phys. 45 154004, 2012.

O 28.5 Tue 15:00 MA 041

**What are the possible moiré patterns of graphene on hexagonally packed surfaces? - Universal solution for hexagonally packed coincidence lattices, derived by a geometric construction** — •Patrick Zeller[1] and Sebastian Günther[2] — [1]Department Chemie, LMU, Butenandtstr. 5-13, D-81377 München — [2]Chemie Department, TUM, Lichtenbergstr. 4, D-85748 Garching

We performed a systematic investigation of two coinciding lattices and their spatial beating frequencies that lead to the formation of moiré patterns. A mathematical model was developed and applied for the case of a hexagonally arranged adsorbate layer on a hexagonal support lattice. In particular, it describes the moiré patterns observed for graphene (g) grown on hexagonally arranged transition metal surfaces, systems that serve as promising synthesis routes for the formation of this highly wanted material. We use a geometric construction that derives analytic expressions for first and higher order beating frequencies occurring for arbitrarily oriented g on an underlying substrate lattice. By solving the corresponding equations, we can predict the size and orientation of the resulting moiré patterns. Adding the constraints for commensurability delivers further solvable analytic equations that predict, whether or not first or higher order commensurable phases occur. We explicitly treat the case for first, second and third order commensurable phases. The universality of our approach is tested by comparing our data with moiré patterns that are experimentally observed for g-Ir(111) and g-Pt(111). The derived general properties of such patterns may be used to critically discuss reported moiré unit cells.

O 28.6 Tue 15:15 MA 041

**Observation of Natural X-Ray Birefringence of Graphene** — •Christine Jansing[1], Marc F. Tesch[1,2], Markus Gilbert[1], Andreas Gaupp[1], Hans-Christoph Mertins[1], Andrey Sokolov[2], Dong Hee Shin[3], Suk-Ho Choi[3], Heiko Timmers[4], Dominik Legut[5], and Peter M. Oppeneer[6] — [1]Münster University of Applied Sciences, Stegerwaldstr. 39, D-48565 Steinfurt — [2]HZB, Albert Einstein Str. 15, D-12489 Berlin — [3]Research School of Physics and Engineering, Department of Electronic Materials Engineering, Australian National University, Canberra, ACT 0200, Australia — [4]School of Physical, Environmental and Mathematical Sciences, University of New South Wales Canberra, PO Box 7916, Canberra BC 2610, Australia — [5]Nanotechnology Centre, Ostrava, Czech Republic — [6]Depart. of Physics, Uppsala Uni., Box 530, S-751 21 Uppsala, Sweden

We present the first experimental results that demonstrate the x-ray natural birefringence and the natural linear dichroism (XNLD) of graphene and compare these to our ab-initio calculations. The effects have been detected at the C 1s edge of a graphene monolayer on Cu using polarization spectroscopy in reflection with linearly polarized radiation at the UE56-2-PGM2 beamline at BESSY II. Upon reflection the polarization plane rotates showing an unusually large rotation value of 33° at the $\pi^*$-states near 285 eV. Additionally the polarization of the light changes from linear to circular with a maximum value of Pcirc = 0.95. The new results for a monolayer graphene are compared with those obtained for highly-ordered pyrolitic graphite (HOPG).

O 28.7 Tue 15:30 MA 041

**Reversible sublattice symmetry breaking in monolayer graphene nanomembranes using tip induced pseudomagnetic fields** — •Alexander Georgi[1], Peter Nemes-Incze[1], Ramon Carillo-Bastos[2], Daiara Faria[2], Marco Pratzer[1], Ludger Wirtz[3], Nancy Sandler[2], and Markus Morgenstern[1] — [1]2.Physikalisches Institut B RWTH Aachen University — [2]Department of Physics and Astronomy, Nanoscale and Quantum Phenomena Institute, Ohio University — [3]Physics and Materials Science Research Unit, University of Luxembourg

Strain engineering in graphene might lead to a new generation of electromechanical devices, in particular due to its tunable pseudomagnetic field being a property of the unique sublattice degree of freedom within the honeycomb lattice. However, possibilities to tune the pseudomagnetic field on the nanoscale have not been realized so far. Here, we show that the forces of the tip of a scanning tunneling microscope can be used to switch local fields on and off, by applying strain, as visible by a relative change of the local density of states of the two sublattices up to 30 %. Comparison with tight binding simulations reveals that this contrast corresponds to a local pseudomagnetic field of up to 500 T.

We carefully rule out other possibilities for the apparent sublattice symmetry breaking such as buckling, a local Peierls transition, different lifting forces of the tip above different sublattices, or the correlation of electric and pseudomagnetic fields. Moreover, we show that model calculations of the van-der Waals forces between tip and graphene reproduce the observed effects quantitatively within 50 %.

O 28.8 Tue 15:45 MA 041

**Electronic Conductivity of Twisted Bilayer Graphene** — •Nicolas Ray, Sam Shallcross, and Oleg Pankratov — Lehrstuhl für theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7 B2, 91058 Erlangen, Germany

The electronic structure of a graphene twist bilayer in the small angle limit is characterized, for states near the Dirac point, by electron localization on the moire lattice and by a significant suppression of the band velocities [1]. This should lead to significant (and rotation angle dependent) changes of the bilayer conductivity. We explore this question within the low energy theory of the electron spectrum, and employing the linearized Boltzmann equation for the transport calculations [2]. We examine the scattering probabilities and the conductivity as functions of the twist angle, the doping level and the temperature. Our results show a dramatic decrease of the conductivity of a weakly doped bilayer with decreasing twist angle.

[1] S. Shallcross *et al.*, Phys. Rev. B **87**, 245403 (2013); [2] E. Mariani *et al.*, Phys. Rev. B **86**, 165448 (2012).

# O 29: Near-Field Microscopy

Time: Tuesday 14:00–16:00 Location: MA 042

O 29.1 Tue 14:00 MA 042

**$\lambda/30$ Lateral Resolution in Subsurface Imaging with an Infrared Near-Field Microscope** — •Lena Jung, Benedikt Hauer, and Thomas Taubner — I. Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany

In scattering-type scanning near-field optical microscopy (s-SNOM), optical near-fields at the apex of a sharp illuminated tip are used for an investigation of the optical properties of the sample material with high spatial resolution. Since near-fields penetrate into a dielectric sample, non-destructive imaging of subsurface structures under thin layers of dielectrics is possible [1]. This capability provides a useful tool in the field of nanotechnologies, since nano-electronic devices are often covered by thin dielectric capping layers such as e.g. $SiO_2$ or $Si_3N_4$.

The visibility of gold nanoparticles under a $Si_3N_4$-membrane in dependence of its thickness is investigated as well as the lateral resolution and signal contrast for different sizes of particles. A comparison to transmission electron microscopy (TEM) images of the same sample region enables a direct correlation between the nanostructures and the optical signals. The experimental results are confirmed by model calculations.

A spectroscopic investigation reveals a significant change in the lateral resolution due to the actual value of the dielectric function. Achievable is a resolution down to $\lambda/30$ for mid-infrared light. We observe minima at specific wavelengths and correlate these to the optical properties of the capping material and the so called superlensing effect.

[1] Taubner et al., Opt. Express 13, 8893 (2005).

O 29.2 Tue 14:15 MA 042

**New Directions in Tip-Enhanced Near-Field Optical Microscopy** — •Julia Janik, Nina Mauser, and Achim Hartschuh — Department Chemie and CeNS, LMU München, Germany

The characterisation of nanostructures with high spatial resolution and detection sensitivity can be achieved by tip-enhanced near-field optical microscopy (TENOM)[1]. We report on our efforts to extend this method into further directions. One direction is the application of tip-enhancement to photovoltaic and light-emitting devices as suggested in [2]. We obtained the first high-resolution photocurrent images of carbon nanotube devices using a metal tip to locally enhance optical-to-electrical transduction [3]. We show that the efficiency of the reversed process leading to electroluminescence can be increased as well. We also implemented tip-enhanced near-field optical microscopy at low temperatures (˜5 K) and present a new microscope design based on a solid immersion lens configuration providing very high collection angles and efficiencies.

We acknowledge Financial support by DFG, NIM and the ERC (New- NanoSpec).

[1] N. Mauser, A. Hartschuh, Tip-enhanced near-field optical microscopy, Chem. Soc. Rev. 43, 1248 (2014).

[2] P. Bharadwaj, B. Deutsch, L. Novotny, Optical Antennas, Adv. Opt. Photon. 1, 438 (2009).

[3] N. Mauser et al., Antenna-Enhanced Optoelectronic Probing of Carbon Nanotubes, Nano. Lett. 14, 3773 (2014).

O 29.3 Tue 14:30 MA 042

**Excitation power dependence in tip-enhanced Raman spectroscopy** — •Tobia Mancabelli, Xian Shi, and Achim Hartschuh — Department Chemie & CENS, Ludwig-Maximilians-University, Munich, Germany

Tip Enhanced Raman Spectroscopy (TERS) exploits the enhanced electric field in the proximity of an optical antenna to achieve nanometer spatial resolution and high detection sensitivity [1]. A recent report indicates a contribution of nonlinear Raman scattering in the case of extremely strong enhancement achieved within the nanogap formed by a silver tip on a silver substrate [2]. Recently, a new mechanism contributing to surface-enhanced Raman scattering based on dynamical backaction has been proposed [3]. We conducted power-dependent confocal and tip-enhanced measurements of the Raman G-band intensity of single carbon nanotubes deposited on different substrates to reveal possible contribution from stimulated Raman scattering and dynamical backaction. Financial support by the ERC (NEWNANOSPEC) and the DFG through the Nanosystems Initiative Munich (NIM) is gratefully acknowledged. [1] MAUSER N., HARTSCHUH A.; CHEM. SOC. REV.; 43, 1248, 2014. [2] ZAHNG R. ET AL.; NATURE 82, 498, 2013. [3] ROELLI P. ET AL.; ArXiv: 1407.1518v1 (2014).

O 29.4 Tue 14:45 MA 042

**Gap mode formation in metallic, nanofocusing SNOM tapers** — •Simon F. Becker[1], Martin Esmann[1], Kyungwan Yoo[1,3], Petra Gross[1,2], Ralf Vogelgesang[1], Namkyoo Park[3], and Christoph Lienau[1] — [1]Carl von Ossietzky Universität, 26111 Oldenburg, Germany — [2]Universität Osnabrück, 49076 Osnabrück, Germany — [3]Seoul National University, Seoul, Korea

Surface plasmon polaritons (SPPs) propagating on metallic tapers get nanofocused at the apex. This largely reduces unwanted background contributions in apertureless scanning near-field optical microscopy (SNOM) [1,2] and provides direct access to broadband nanospectroscopy.

Here, we analyze the near-field formation at the apex of single crystalline gold tapers by using them as SNOM probes [3]. We investigate the imaging mechanism in scattering geometry and in the Fourier domain. The experimental results are compared to detailed finite element method (FEM) simulations. In particular, we find strong evidence for the formation of a gap mode between probe and sample, both in the experiment and the simulation. The results indicate that this spectrally broadband interaction is extremely short-ranged and has the potential to enhance the spectroscopic imaging resolution down to the single nanometer regime.

[1] M.I. Stockman, PRL 93, 137404 (2004); [2] S. Schmidt et al., ACS Nano 6, 6040 (2012); [3] M. Esmann et al., BJ Nano 4, 603 (2013).

O 29.5 Tue 15:00 MA 042

**Broadband nanospectroscopy with metallic, nanofocusing SNOM tapers** — •Martin Esmann[1], Simon F. Becker[1], Heiko Kollmann[1], Petra Gross[1,2], Ralf Vogelgesang[1], and Christoph Lienau[1] — [1]Carl von Ossietzky Universität, 26111 Oldenburg, Germany — [2]Universität Osnabrück, 49076 Osnabrück, Germany

Broadband extinction spectroscopy with nanoscale lateral resolution demands methods with low background signals. To this end, a very promising approach is the concept of adiabatic nanofocusing in metallic nanotapers[1,2]. Surface plasmon polaritons (SPPs) are excited on a grating coupler and result in strongly confined near-fields at the taper apex.

Here, we use single crystalline gold tapers as scanning near-field optical microscopy (SNOM) probes[3] in combination with broadband white-light excitation. We test this approach by imaging the spectrally dependent near-field enhancement over a planar gold film. On this basis, we perform extinction spectroscopy on individual nanoantennas with a spectral bandwidth of several hundreds of nanometers. The very high lateral resolution of our approach allows us to spectrally image the mode profiles of such individual nanostructures. In combination with ultrashort pulses this method can be straightforwardly extended to the investigation of coherences in quantum and biological systems.

[1] M.I. Stockman, PRL 93, 137404 (2004); [2] S. Schmidt et al., ACS Nano 6, 6040 (2012); [3] M. Esmann et al., BJ Nano 4, 603 (2013).

O 29.6 Tue 15:15 MA 042

**Analysis of light depolarization in near-field apertureless optical techniques** — •Evgeniya Sheremet, Vladimir Kolchuzhin, Raul D. Rodriguez, Jan Mehner, Dietrich R.T. Zahn, and Michael Hietschold — Technische Universität Chemnitz, Chemnitz, Germany

Apertureless near-field methods mostly rely on localized surface plasmons generated at the apex of gold or silver tips under illumination. This allows the spatial resolution of near-field optical microscopy and spectroscopies to be decreased from hundreds of nanometers to the sub-10 nm scale. The near-field has a different polarization from that of the incident field due to the presence of the tip. This can lead to loss of information about inherent selection rules of the sample, or used to our benefit for separating the near-field signal from the far-field contribution. Here, we analyze the polarization of the enhanced field on the tip apex using finite element method. The simulations are performed for tips with apex radii from 10 to 50 nm in free space placed above dielectric or metallic surfaces, or without substrate. We find that a gold tip placed above a gold substrate efficiently rotates the incident field of any polarization along the tip axis. The same tip in air shows a homogeneous distribution of the field components polarized along different directions thus depolarizing the incident field regardless of its polarization. The simulations also show a drastic improvement in spatial resolution for a tip above a gold substrate as compared to the tip in air. These results demonstrate the importance of the substrate nature in near-field optical techniques.

O 29.7 Tue 15:30 MA 042

**Low-temperature scattering scanning near-field optical microscopy** — •Jonathan Döring, Kehr Susanne C., and Eng Lukas M. — IAPP, Technische Universität Dresden

We present a fully operating low-temperature scattering scanning near-field optical microscope (LT-s-SNOM) with access to a tunable free-electron laser (FEL) source. The light scattered off an AFM tip strongly depends on the tip-sample near-field interaction, and thus enables mapping of optical properties with a resolution several orders of magnitude below the diffraction limit. The FEL provides spectrally narrow laser radiation in the regime from 4 to $250\,\mu m$ at a high power density. By the novel and unique combination of LT-s-SNOM and FEL, optical properties of materials can be measured at specific wavelengths as well as at temperatures down to $4\,K$. Our device is therefore perfectly suited for investigating phase transitions of sample materials featuring phonon resonances in the mid-to-far-infrared regime.

We present measurements of ferroelectric phase transitions of barium titanate (BTO). We use this unique setup to investigate the two ferroelectric phase transitions of barium titanate single crystals below room temperature at $253\,K$ and $173\,K$. The first constitutes a structural phase transition from tetragonal to orthorhombic, which reflects in both a different domain arrangement and significant phonon resonance shifts, as probed near-field optically [1]. The second transition changes the pattern to rhombohedral, again reflected in both altered micrographs and spectra.

[1] Döring et al., Appl. Phys. Lett. 105, 053109 (2014)

O 29.8 Tue 15:45 MA 042

**Adapting ultra-broadband Synchrotron Radiation Sources for nano-FTIR Spectroscopy** — •Peter Hermann[1], Arne Hoehl[1], Bernd Kästner[1], Piotr Patoka[2], Georg Ulrich[2], Jörg Feikes[3], Markus Ries[3], Tobias Goetsch[3], Godehard Wüstefeld[3], Burkhard Beckhoff[1], Eckart Rühl[2], and Gerhard Ulm[1] — [1]Physikalisch-Technische Bundesanstalt (PTB), Abbestraße 2-12, 10587 Berlin — [2]Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin — [3]Helmholtz-Zentrum Berlin (HZB), Albert-Einstein-Straße 15, 12489 Berlin

Near-field techniques such as infrared scanning near-field optical microscopy and nano-FTIR spectroscopy enable imaging and spectroscopic characterization of samples at the nanoscale. While for near-field imaging typically monochromatic light sources are required to map the chemical composition of the sample surface, near-field infrared spectroscopy requires sources with a broad emission spectrum. Successful nano-FTIR experiments utilizing ultra-broadband synchrotron radiation have been recently demonstrated by several groups. In order to exploit the full potential of this approach we report on the adaption of storage ring optics at the Metrology Light Source (MLS) reducing the size of the electron bunches in order to improve the spatial coherence of synchrotron radiation. In combination with appropriate spectral filters the sensitivity of synchrotron-based near-field spectroscopy can be increased significantly, thus enabling also the spectroscopic characterization of thin organic layers.

## O 30: Inorganic/Organic Interfaces: Towards Application

Time: Tuesday 14:00–16:00 Location: MA 043

O 30.1 Tue 14:00 MA 043

**Increased light emission from organic light emitting diodes by surface plasmon polariton modification** — •Cornelius Fuchs[1], Paul-Anton Will[1], Martin Wieczorek[1], Malte C. Gather[2], Simone Hofmann[1], Sebastian Reineke[1], Karl Leo[1], and Reinhard Scholz[1] — [1]Technische Universität Dresden, Institut für Angewandte Photophysik, George-Bähr Str. 1, 01069 Dresden — [2]University of St. Andrews, SUPA, School of Physics and Astronomy, North Haugh, St. Andrews, Scotland, UK, KY16 9SS

We demonstrate enhanced external quantum efficiency (EQE) from monochrome top-emitting light emitting diodes (OLEDs). The EQE is increased by about 20 % compared to an optimized reference device. The enhancement is achieved by modifying the refractive index of the hole transport layer (HTL) material. The reference HTL possesses a refractive index of 1.77, averaged over the emission spectrum of the emitter material, whereas the improved device uses a HTL with a lower refractive index of 1.52. Both devices are optimized for maximized first order outcoupling efficiency. Due to the low refractive index of the HTL, the dispersion relation of the surface plasmon polariton (SPP) excited at the opaque metal bottom electrode shifts to smaller in-plane wavenumbers compared to the reference HTL. The shift decreases the power lost into evanescent excitations. Hence, the outcoupling efficiency of the OLED is increased, leading to the enhanced EQE. The proposed method is found to be applicable to emitter materials possesing isotropic as well as oriented distribution of the transition dipole moments.

O 30.2 Tue 14:15 MA 043

**Charge Transport through Carbon Nanomembrane Molecular Junctions** — •Paul Penner[1], Xianghui Zhang[1], Emanuel Marschewski[1], Florian Behler[2], Polina Angelova[1], André Beyer[1], Jens Christoffers[2], and Armin Gölzhäuser[1] — [1]Fakultät für Physik, Universität Bielefeld, Bielefeld, Germany — [2]Institut für Chemie, Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany

Self-assembled monolayers (SAMs) of phenylthiol (PT), biphenylthiol (BPT), p-terphenylthiol (TPT) and p-quaterphenylthiol (QPT) formed on polycrystalline Au(111) are irradiated with low energy electrons and convert to carbon nanomembranes (CNMs). Molecular junctions incorporating pristine and cross-linked self-assembled monolayers (SAMs) from thiolphenyl homologues are fabricated and investigated. A two-terminal setup composed of a $Ga_2O_3$/EGaIn top electrode and the Au substrate on which SAMs are prepared as a bottom electrode was used to characterize the molecular junctions. A comparison of charge transport characteristics reveals a decrease of conductance of CNM-based junctions by one order of magnitude, as well as a conversion of asymmetric junctions with SAMs into symmetric junctions with CNMs, which could be attributed to the decoupling of CNMs from the Au substrate and the partial loss of aromaticity of CNMs after irradiation. Transition voltage (TV) spectroscopy was also employed to investigate both types of junctions. We observe the length-dependent behavior of TV in both systems and a reduction of TV of CNM-based junctions in comparison to SAM-based junctions.

O 30.3 Tue 14:30 MA 043

**Fabrication of (supra)molecularly precise 2D material device elements** — •Sarah Wieghold[2], Juan Li[1], Maximilian Krause[2], Patrick Simon[1,3], Jose Garrido[1,3], Yuri Avlasevich[4], Chen Li[4], Klaus Müllen[4], Ueli Heiz[2], Johannes Barth[1], Carlos-Andres Palma[1], and Friedrich Esch[2] — [1]Physik-Department, Technische Universität München, 85748 Garching, Germany — [2]Chemie-Department, Technische Universität München, 85748 Garching, Germany — [3]Walter Schottky Institut, Technische Universität München, 85748 Garching, Germany — [4]Max Planck Institute for Polymer Research, 55128 Mainz, Germany

The recent spotlight on highly crystalline natural-occurring and synthetic two-dimensional materials (2DMs) stands as a unique opportunity to accelerate atomically-precise technology. Here we explore the fabrication and characterization of 2D material devices of supramolecular networks with graphene attaining molecular precise disposition of all elements at interfaces. We present the first technologically relevant, photovoltaic response of a by-design artificial 2DM consisting of a bicomponent supramolecular network on transparent, graphene-passivated H-C(100) diamond [1] and employing a gallium droplet as a counter electrode. Our results pave the way toward atomically precise (opto)electronic technology.

[1] Li, J. et al., Three-dimensional bicomponent supramolecular nanoporous self-assembly on a hybrid all-carbon atomically flat and transparent platform, Nano Letters 2014, 14, 4486.

O 30.4 Tue 14:45 MA 043

### Reactive interaction of (sub-) monolayers and multilayers of the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide with co-adsorbed lithium on Cu(111)

— •Florian Buchner[1,2], Maral Bozorgchenani[1,2], Benedikt Uhl[1,2], Hanieh Farkhondeh[1,2], and R. Jürgen Behm[1,2] — [1]Helmholtz Institute Ulm, 89081 Ulm, Germany — [2]Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany

The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][TFSA] is a promising candidate for the improvement of rechargeable Li-ion batteries. In this model study the reactive interaction of (sub-) monolayers and multilayers of [BMP][TFSA] with lithium (Li) was investigated on Cu(111) by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIRS) under ultrahigh vacuum conditions. Upon co-deposition of Li to [BMP][TFSA] multilayers at 80 K we mainly identified changes in the chemical state of the [TFSA] anion and changes in absorption of anion related mid-IR bands. The co-deposition of Li to [BMP][TFSA] (sub-) monolayers verified the decomposition of [TFSA], independently on the order of deposition. After annealing to 300 K, most of the carbon of the anion and the cation desorbs; at 450 K LiF and $Li_2S$ decomposition products dominate. Addition of very small amounts of Li to [BMP][TFSA] resulted in intriguing changes in the STM images which are most likely due to a surface mediated coordination of Li to [TFSA].

O 30.5 Tue 15:00 MA 043

### Ultrathin Ionic Liquid Films on HOPG and on Ni(111)-supported graphene

— •Florian Rietzler[1], Jens Nagengast[2], Hans-Peter Steinrück[1], and Florian Maier[1] — [1]Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — [2]Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Profound knowledge of the interfaces between ionic liquids (ILs) and carbonaceous surfaces is highly relevant in catalysis and electrochemistry. In this work, ultrathin films of the IL 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([C1C1Im][Tf2N]) were prepared under clean ultra high vacuum conditions by means of physical vapor deposition, and were analyzed by angle resolved XPS (ARXPS). The films were deposited onto highly oriented pyrolytic graphite (HOPG) as well-defined reference system, and onto nickel-supported graphene surfaces. Using ARXPS detailed information on the growth mode and on the molecular orientation of the IL is accessible.

For all investigated systems, clear evidence for three-dimensional growth was found. However, film morphology strongly depends on the nature of the substrate. In particular, the interaction of the IL with supported graphene seems to be stronger than with HOPG.

The results will be compared to ultrathin IL films deposited on well-defined metal surfaces such as Ni(111) and Au(111).

O 30.6 Tue 15:15 MA 043

### Stability of thin layers of the ionic liquid [BMP][TFSA] on a rutile $TiO_2$(110) surface and co-deposition of Li

— •Benedikt Uhl[1,2], Maral Hekmatfar[1,2], Florian Buchner[1,2], Dorothea Alwast[1,2], and R. Jürgen Behm[1,2] — [1]Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — [2]Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany

Ionic liquids (IL) have attracted high interest because of their special chemical and physical properties; among others, the application in electrolytes of Li-ion batteries is a promising concept. To gain a better understanding of the fundamental molecular processes at the electrode|electrolyte interface, the interaction of n-butyl-n-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide [BMP][TFSA] with rutile $TiO_2$(110) was investigated by X-ray photoelectron spectroscopy (XPS) in grazing emission and scanning tunneling microscopy (STM) under UHV conditions at temperatures between 80 K - 630 K. [BMP][TFSA] on $TiO_2$(110) is stable and does not show decomposition up to around 470 K. Addition of Li, either before or after [BMP][TFSA] deposition, leads to a reaction of Li with the $TiO_2$ substrate and formation of a new $Ti^{3+}$ species in the near surface region together with a new oxygen species. Thereby the [BMP][TFSA] stays intact, however, all its signals shift by roughly 1 eV to higher binding energies, which is most likely due to interactions with the new $Ti^{3+}$ species in the substrate. Most important, the thermal stability of the [BMP][TFSA] is not affected by the Li-incorporation.

O 30.7 Tue 15:30 MA 043

### Adsorption of organic molecules on a water-covered Fe(100) surface from first-principles

— •Gregor Feldbauer[1,2], Pedro Bedolla[2], Michael Wolloch[2], Peter Mohn[1], Josef Redinger[1], and András Vernes[1,2] — [1]Institute of Applied Physics, Vienna University of Technology, Vienna, Austria — [2]Austrian Center of Competence for Tribology, Wiener Neustadt, Austria

Biofuels, especially ethanol mixed with standard gasoline or diesel, have become an important part of the worldwide motor fuel consumption. [1] Hence, the interaction of organic molecules constituting such biofuels with metallic surfaces is of high technological interest. In a combustion engine apart from organic molecules of the pure fuel there are always other chemical constituents, which may change the interfacial properties of the metallic surface. Water or acids contained in fuel lubricity additives and trace contaminants are prominent examples. In this contribution, the adsorption of ethanol, isooctane and acetic acid on a bare and a water-covered bcc Fe(100) surface is investigated within the framework of density functional theory including van der Waals interactions. In particular, the impact of a water mono-layer on the adsorption energies, equilibrium configurations and electronic charge distributions is discussed. It is shown that the effect of the water layer strongly depends on the type of bond between the molecule and the surface. In addition, the possibility of a dissociative adsorption of the acetic acid and the formation of molecular hydrogen is studied.

[1] IEA, Tracking Clean Energy Progress 2013; International Energy Agency, Paris, 2013

O 30.8 Tue 15:45 MA 043

### Modeling of air exposed titanium dioxide

— Wenke Friedrichs, Norman Geist, Dennis Sandvoss, and •Walter Langel — Institut für Biochemie, Universität Greifswald, 17489 Greifswald

Adhesion of biomolecules to inorganic surfaces is of condsiderable interest for medical applications. We report a classical molecular dynamics study of peptides on titanium dioxide. Previous work refers to clean hydroxylated surfaces mimicking UHV-preparation. Air exposed Ti is not only passivated and partially hydroxylated but also covered by a hydrocarbon film making it more hydrophobic than a polar metal oxide. A computational model for this contamination must be based on volatile organic compounds in atmosphere, which screen the hydrophilic surface and are poorly soluble in water films on it. We report simulations of pentanol layers of various mass coverage on a variety of TiO2-surfaces. Physisorbed layers are stable, and their contact angles match experimental data. * On the clean hydroxylated surfaces most peptides easily adsorb in the simulation due to polar groups. In contrast to other work we can trace hindering of adsorption by the hydrocarbons working as a microscopic wax.Only partly hydrophobic species penetrate the contamination and attach due to polar groups, and this behavior seems to be correlated with the partition coefficient of the peptide. This result should have impact on several applications of titanium dioxide.

# O 31: Tribology

Time: Tuesday 14:00–15:45 Location: MA 144

O 31.1 Tue 14:00 MA 144

**Influence of Temperature on Contact Ageing of Nano-Asperities** — •Matthias Vorholzer, Dirk Dietzel, Michael Feldmann, and André Schirmeisen — Institute of Applied Physics, University of Giessen, Germany

In recent years research in nanotribology has advanced at an increasing pace. But although a lot of fundamental insight into various tribological processes has been gained, the problem of nanoscale contact ageing still remains largely unexplored. Recently, single-asperity slide-hold-slide experiments have been conducted with an AFM at room temperature under ambient conditions to directly investigate the evolution of static friction with time [1]. The results were explained based on a model that describes the formation of chemical bonds between the surfaces [2]. Thermal activation should thus play a major role in the temperature dependence of the ageing processes, which have been analyzed in this work under UHV conditions for temperatures ranging from 15K to 350K.

Our results confirm logarithmic increase of static friction over time for all temperatures. However, the distinct temperature dependence cannot be explained by purely thermally activated processes, which suggests that additional processes like viscoelastic contact area variations need to be considered.

[1] Li et al., Nature 480, 233-235 (2012) [2] Liu et al. PRL 109, 186102 (2012)

O 31.2 Tue 14:15 MA 144

**Stochastic stick-slip friction on oxide thin films** — •Andra D. Craciun, Jean-Louis Gallani, and Mircea V. Rastei — Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS, Université de Strasbourg, F-67034 Strasbourg, France

Most of sliding surfaces in micro- and nano-mechanical devices are covered by native oxides [1]. Little is known however about nanoscale friction on these surfaces [2,3]. Here, we report on lateral forces needed to move a nanoscale asperity on various oxide thin films, as studied by an atomic force microscope operating in vacuum and at different temperatures. Force-distance traces unveil erratic stick-slip movements separated by several nanometers. The variations of friction force with normal load demonstrate dispersive adhesive interactions at interface. We modeled our findings by considering a Lennard-Jones-like interaction potential, which accounts for changes in the effective contact area. The model captures the formation and fluctuation of stick-slip phases and provides guidelines for predicting transitions from stick-slip to continuous sliding.

[1] See proceedings of IEEE 27th annual international conference on MEMS San Francisco, California (2014). [2] A. Schirmeisen, L. Jansen, H. Holscher, H. Fuchs, Appl. Phys. Lett. 88, 123108 (2006). [3] M. Lessel, P. Loskill, F. Hausen, N. Gosvami, R. Bennewitz, K. Jacobs, Phys. Rev. Lett. 111, 035502 (2013).

O 31.3 Tue 14:30 MA 144

**Impact of temperature variation on nanoscale adhesion forces** — •Mircea. V. Rastei, Maxime Kein-Wierez, and Alexandre Pinon — Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS, Université de Strasbourg, F-67034 Strasbourg, France

Nanoscale adhesion is a key parameter in formation and stability of many nanomaterials. Without forming chemical bonds, van der Waals interactions induce an attractive potential which establish an equilibrium bond distance between two close contacting bodies. Here, we present a combined atomic force microscopy and theoretical study on how temperature influences the adhesion force triggered by van de Waals interactions. Similar to the case of atomic-scale lateral friction forces [1,2], we found that adhesion follows a distribution whose density function is an asymmetric bell-shaped curve. By increasing temperature the asymmetry increases whereas the most probable adhesion force value decreases. We checked various forms of interaction potentials within the reaction rate theory and evaluate several parameters governing adhesion at the nanoscale. [1] Y. Sang, M. Dubé, and M. Grant, Phys. Rev. Lett. 87, 174301 (2001). [2] A. Schirmeisen, L. Jansen, and H. Fuchs, Phys. Rev. B 71, 245403 (2005).

O 31.4 Tue 14:45 MA 144

**Dynamic shear force microscopy of liquids in nanometer confinement** — •Marc-Dominik Krass[1,2], Nitya Nand Gosvami[3], Om Prakash Khatri[4], Robert W. Carpick[3], and Roland Bennewitz[1,2] — [1]INM-Leibniz Institute for New Materials, Nanotribology Group, Saarbrücken, Germany — [2]Department of Physics, Saarland University, Saarbrücken, Germany — [3]Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia 19104, USA — [4]CSIR-Indian Institute of Petroleum, Chemical Science Division, Mohkampur Dehradun 248005, India

We present a new method to measure shear forces of liquids in nanometer confinement. A torsionally oscillating atomic force microscope probe (AFM) is approached to the surface. Direct torsional actuation is achieved by a micrometer-scale magnetic bead attached to the back side of the cantilever which experiences a torque by an alternating magnetic field generated by an integrated solenoid.

Dynamic measurements are conducted in a simple liquid (hexadecane) as well as in halogen-free ionic liquids ([trioctylhexylammonium][bis(salicylato)borate]). The experimental data shows changes in the dynamic signals which correlate with jumps in normal force reflecting molecular layering of the liquid. The changes in amplitude and phase of the lateral tip oscillation indicate respective changes of shear dissipation in the confined liquids.

O 31.5 Tue 15:00 MA 144

**Puckering stick-slip friction induced by a sliding nanoscale contact on graphite** — •Mircea V. Rastei, Benoit Heinrich, Pedro Guzman, and Jean-Louis Gallani — Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS, Université de Strasbourg, F-67034 Strasbourg, France

We report on the experimental observation of puckering-induced nanoscale friction at a graphite surface [1,2]. Using an atomic force microscope operating in vacuum, we show that puckering effect induces nanoscale stick-slip processes originating from periodic deformations of the contact region followed by thermally activated relaxations. These processes are found to depend on the stiffness difference between the crystal axes, and on other tunable parameters such as sliding velocity. The angle between the sliding direction and the stiff crystallographic axis determines the periodicity of the slip events defining domains of various friction properties. We show that each domain presents a particular logarithmic dependence of friction with speed, indicating thermally assisted sliding regimes implying different potential barriers. The difference is proposed to arise from the way the tip interacts with the ridge of the puckered region, which in turn depends on local structural defects. The experimental data are interpreted using the rate theory, with specific potential barriers for each frictional domain. [1] M.V. Rastei, B. Heinrich and J.L. Gallani, Phys. Rev. Lett. 111, 084301 (2013) [2] M.V. Rastei, P. Guzman, J.L Gallani, Phys. Rev. B 90, 041409(R) (2014)

O 31.6 Tue 15:15 MA 144

**Contact Ageing observed during Stick Slip Movement of Antimony Nanoparticles** — Michael Feldmann, •Dirk Dietzel, and Andre Schirmeisen — Justus Liebig University, Giessen, Germany

Contact ageing is an essential process to understand macro-scale friction dynamics and is typically related to an increasing contact area of asperities. It is less clear, however, if nanoscale asperities of constant size are also capable of ageing. Only recently, such contact ageing was demonstrated for antimony nanoparticles sliding on HOPG [1]. From temperature and velocity dependent measurements, a thermally activated contact ageing of the interface was deduced, while, at the same time, an increase of contact area can be ruled out. Additional measurements with a high data acquisition rate have now revealed that particle movement follows a stick slip pattern as it is common in friction force microscopy. By regarding the slip events as recurring contact renewal, the age of the contact can directly be related to the stick phases. This allows for a very direct assessment of contact ageing and a logarithmic increase of friction with the age of contact is found.

[1] Feldmann, Dietzel, Fuchs, Schirmeisen, Phys. Rev. Lett. 112, 155503 (2014)

O 31.7 Tue 15:30 MA 144

**Friction boosted by spontaneous epitaxial rotations** —

•Davide Mandelli[1], Andrea Vanossi[1,2], Nicola Manini[1,2,3], and Erio Tosatti[1,2,4] — [1]SISSA, Trieste, Italy — [2]CNR-IOM Democritos, Trieste, Italy — [3]Universita degli Studi di Milano, Milano, Italy — [4]ICTP, Trieste, Italy

It is well known in surface science that incommensurate adsorbed monolayers undergo a spontaneous, energy-lowering epitaxial rotation from aligned to misaligned relative to a periodic substrate. We show first of all that a model 2D colloidal monolayer in an optical lattice, of recent importance as a frictional model, also develops in full equilibrium a small rotation angle, easy to detect in the Moire pattern. The colloidal monolayer misalignment is then shown by extensive sliding simulations to increase the dynamic friction by a considerable factor over the aligned case. More generally, this example suggests that spontaneous rotations are rather ubiquitous and should not be ignored in all tribological phenomena between mismatched lattices.

This work was mainly supported by the ERC Advanced Grant 320796-MODPHYSFRICT, and partly by SINERGIA contract CRSII2 136287, by PRIN/COFIN contract 2010LLKJBX 004, by COST Action MP1303.

## O 32: Surface Magnetism and Spin Phenomena

Time: Tuesday 18:15–21:00 Location: Poster A

O 32.1 Tue 18:15 Poster A

### Single molecule spintronics with spin carriers of 2p, 3d or 4f electrons

— •yajie zhang and kai wu — College of Chemistry and Molecular Engineering, Peking University, Beijing, China

A revolution in electronics is with the contemporary evolution of the two novel disciplines of spintronics and molecular electronics. A fundamental link between these two fields can be established using organic magnetic materials. Using a low-temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), we are able to study the single molecules under ultrahigh vacuum conditions at 4.2 /0.4 K. In this talk, we measured the magnetic properties of retinoic acid molecules, FePc and DyPc2 adsorbed on metal surface with corresponding spin carries of 2s, 3p, and 4f electrons. Unlike the pre-existing metal ion in FePc or DyPc2, retinoic acid molecules can be switched reversibly to a special state by placing the tip over the neck of the bulky heads at an appropriate sample voltage. The generation of a stable cationic radical makes the molecule have an unpaired electron. The dI/dV spectrum confirms the appearance of spin in switched states. In addition, we proposed that the two Pc ligands in the same double-decker DyPc2 molecules molecule rotate by 45 degrees against each other, which can be directly deduced from the STM imaging.

O 32.2 Tue 18:15 Poster A

### Spin-resolved electron transmission through chiral films on metal surfaces

— •Matthias Kettner[1], Benjamin Göhler[1], Debabrata Mishra[2], Georg F. Hanne[2], Ron Naaman[2], and Helmut Zacharias[1] — [1]Physikalisches Institut, Universität Münster, Germany — [2]Department of Chemical Physics, Weizmann Institute, Rehovot, Isreal

The increasing interest in sources for spin polarized electrons for spintronic applications leads to new approaches, including interaction of electrons with chiral molecules. Experiments on self-assembled monolayers of DNA indicated a spin-filtering behavior of the molecules [1]. In our experiments the samples, kept at room temperature, are irradiated with 213nm laser radiation to generate photoelectrons from metal substrates covered with various chiral thin films. These electrons transmit the chiral film and are analyzed by a Mott polarimeter. It can be shown that due to the interaction of the photoelectrons within the films electrons are spin-filtered. Longitudinal spin polarizations up to 57% can be measured in case of double stranded DNA even by irradiation with linearly polarized light [2]. Experiments with other chiral molecules, namely membrane proteins and self-assembled monolayers of $\alpha$-helical polypeptides show similar electron spin filtering properties [3]. Furthermore a dependence of the spin polarization on the length of the molecules is measured.

[1] S.G. Ray et al., PRL 96, 036101 (2006)
[2] B. Göhler et al., Science 331, 894 (2011)
[3] D. Mishra et al., PNAS 110, 14872 (2013)

O 32.3 Tue 18:15 Poster A

### Spin-polarized surface electronic structure of Ta(110) and W(110): Similar, yet different

— •Bernd Engelkamp[1], Hossein Mirhosseini[2], Henry Wortelen[1], Anke Schmidt[1], Jürgen Henk[3], and Markus Donath[1] — [1]Physikalisches Institut, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany — [2]Institut für Anorganische Chemie und Analytische Chemie, 55122 Mainz, Germany — [3]Institut für Physik, Martin Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

For Ta(110) and W(110), a very similar surface electronic structure is expected. One remarkable feature on W(110) is a spin-polarized, Dirac-cone-like occupied surface state with a spin texture, which is reminiscent of topological surface states [1], [2]. Due to the lack of one electron in tantalum compared with tungsten this surface state is expected above the Fermi level for Ta(110).

In this poster, we present a spin- and angle-resolved inverse photoemission study of Ta(110) in combination with spectral-density calculations. Surprisingly, we could not identify a Dirac-cone-like surface state on Ta(110), but instead a spin-split unoccupied surface state. The similarities and differences between the surface electronic structure of W(110) and Ta(110) will be discussed.

[1] K Miyamoto *et al.* Phys. Rev. Lett. **108**, 066808 (2012)
[2] H Mirhosseini *et al.* New J. Phys. **15**, 033019 (2013)

O 32.4 Tue 18:15 Poster A

### Construction and realization of a 1K spin-polarized scanning tunneling microscope operable in a high magnetic field

— Andreas Sonntag[1], Jan Hermenau[1], •Nadine Hauptmann[2], and Alexander Ako Khajetoorians[1,2] — [1]Institute of Applied Physics, Jungiusstrasse 9A, 20355 Hamburg, Germany. — [2]Institute for Molecules and Materials, Radboud Universiteit, 6500 GL Nijmegen, The Netherlands

Low-temperature scanning probe microscopy is a powerful method to explore the means of atomic-scale magnetism. In particular, this method has the potential of studying non-collinear magnetic structures on the cutting edge of magnetic material research, such as skyrmions [1], which are promising candidates for future application in data-storing and information-processing devices [2]. We present the design and setup of a home-built scanning tunneling microscope working at 1K based on a JT-stage with 4He, operating in a 9T out-of-plane magnetic field. The system is optimized for long hold times (∼7 days), and capable of spin-polarized measurements based on a robust tip/sample exchange mechanism. Additionally, the system features two additional chambers for preparation of magnetic material on both tip and sample.

[1] S. Heinze, K. von Bergmann, M. Menzel, J. Brede, A. Kubetzka, et al., Nature Phys. 7, 713 (2011). [2] J. Sampaio, V. Cros, S. Rohart, A. Thiaville, and A. Fert, Nature Nanotech., 8, 839 (2013).

O 32.5 Tue 18:15 Poster A

### Tuning the Magnetic Anisotropy and the Coupling to the Surface in Fe-Octaethylporphyrin-Cl Complexes on Au(111)

— •Olof Peters, Benjamin W. Heinrich, Xianwen Chen, Christian Lotze, and Katharina J. Franke — Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Magnetism in single transition metal atoms is determined by small details in their atomic scale environment. Variations in the ligand field of metal organic complexes can change the molecule's spin state and its zero field splitting. Here, we report the controllable manipulation of a molecule's spin state and magnetic anisotropy by changing its ligand field with the tip of a scanning tunneling microscope.

As a model system we use Fe-octaethylporphyrin-Cl (FeOEP-Cl) complexes adsorbed on a Au(111) surface to study the influences of a Au tip approaching to the molecule's Fe center. Via inelastic electron tunneling spectroscopy we probe spin excitations and observe an increase in the zero-field splitting as the tip-molecule distance decreases. In addition a signature of Kondo screening appears, indicating a different coupling of the molecule to the surface. B-field dependent measurements reveal the expected splitting of the Kondo resonance. We ascribe our results to a modification of the crystal field leading to a shift in the d-level energies.

O 32.6 Tue 18:15 Poster A

**Surface states on Fe(110) - exploring their spin, decay rates, and magnetic linear dichroism** — Beatrice Andres, •Marko Wietstruk, and Martin Weinelt — Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Investigating iron (Fe) may seem old-fashioned but still it exhibits an exotic electronic band structure regarding it's spin dependence. The large exchange splitting combined with hybridization of *s*, *p*, and *d* states results in totally different conditions for the formation of majority and minority surface-states [1]. In contrast to the well-known bulk band structure, very few studies on surface states have been performed. Some show quasiparticle renormalization in the surface states due to electron-magnon coupling [2,3].

We study the surface band structure on Fe/W(110) in a spin- and time-resolved one- and two-photon-photoemission experiment. On the one hand, we directly probe the occupied electronic structure with the fourth harmonic (6 eV) of a Ti:Sa laser. On the other hand, we use the fundamental (1.65 eV) and third harmonic (5 eV) to probe unoccupied image-potential states and investigate their spin-dependent decay rates. We find two occupied minority surface features crossing the Fermi level at $\approx 0.1\,\text{Å}^{-1}$ in $\overline{\Gamma}$-$\overline{\mathrm{H}}$ direction. These two minority features show a magnetic-linear-dichroic contrast (MLD) of opposite sign indicating different symmetries.

[1] Jürgen Braun, *Phys. Rev. B* **65**, 184412 (2002)
[2] Jörg Schäfer, *Phys. Rev. Lett.* **92**, 097205 (2004)
[3] Jörg Schäfer, *Phys. Rev. B* **72**, 155115 (2005)

O 32.7 Tue 18:15 Poster A

**Tunneling processes into localized subgap states in superconductors** — •Michael Ruby[1], Falko Pientka[1,2], Yang Peng[1,2], Benjamin W. Heinrich[1], Felix v. Oppen[1,2], and Katharina J. Franke[1] — [1]Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Dahlem Center for Complex Quantum Systems, Freie Universität Berlin, 14195 Berlin, Germany

The Yu-Shiba-Rusinov states bound by magnetic impurities in conventional s-wave superconductors are a simple model system for probing the competition between superconducting and magnetic correlations. Shiba states can be observed in scanning tunneling spectroscopy (STS) as a pair of resonances at positive and negative bias voltages in the superconducting gap. These resonances have been interpreted in terms of single-electron tunneling into the localized sub-gap states. This requires relaxation mechanisms that depopulate the state after an initial tunneling event. Recently, theory suggests that the current can also be carried by Andreev processes which resonantly transfer a Cooper pair into the superconductor.

We performed high-resolution STS experiments on single adatom Shiba states on the superconductor Pb, and provide evidence for the existence of two transport regimes. The single-electron processes dominate at large tip-sample distances and small tunneling currents, whereas Andreev processes become important at stronger tunneling. Our conclusions are based on a careful comparison of experiment and theory.

O 32.8 Tue 18:15 Poster A

**The magnetic properties of $\mathrm{CoH}_n$ complexes on *h*-BN/Rh(111)** — •Matthias Muenks[1], Peter Jacobson[1], Tobias Herden[1], Gennadii Laskin[1], Oleg Brovko[2], Markus Ternes[1], and Klaus Kern[1,3] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]Max Planck Institute of Microstructure Physics, Halle, Germany — [3]École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Transition metal adatoms on decoupling layers, such as *h*-BN/Rh(111), have peaked interest because they provide a testbed for magnetic properties at the single atomic scale. Intriguing features such as a high magnetic anisotropy of Co adatoms on MgO [1] or the controlled ionization of Co adatoms on graphene [2] are among these exciting results. Here we use a combined STM/AFM working at 1.2 K and magnetic fields up to 14 T to investigate $\mathrm{CoH}_n$ complexes that adsorb on the highly corrugated *h*-BN/Rh(111) Moiré [3] [4]. We found that $\mathrm{CoH}_2$ shows a Kondo resonance characteristic for a spin-1/2 system, whereas CoH molecules have a clear spin-1 signature. For these spin-1 systems we present experimental proof of the correlation between the magnetic anisotropy energy and the coupling strength to the substrate. The result is supported by theoretical calculations.

[1] I. G. Rau *et al.*, Science 344 (6187), pp. 988-992 (2014) [2] V. W. Brar *et al.*, Nature Physics 7 , pp. 43-47 (2011) [3] T. Herden *et al.*, Nano Letters 14 (6), pp. 3623-3627 (2014) [4] F. D. Natterer *et al.*, PRL 109, pp. 066101 (2012)

## O 33: Graphene

Time: Tuesday 18:15–21:00 Location: Poster A

O 33.1 Tue 18:15 Poster A

**Facile Electrochemical Transfer of Single Crystal Epitaxial Graphene from Ir(111)** — Line Koefoed[2], •Antonija Grubišić Čabo[1], Mikkel Kongsfelt[2], Søren Ulstrup[1], Andrew Cassidy[1], Patrick R. Whelan[3], Marco Bianchi[1], Maciej Dendzik[1], Filippo Pizzocchero[3], Bjarke Jørgensen[4], Peter Bøggild[3], Liv Hornekaer[1], Philip Hofmann[1], Steen U. Pedersen[2], and Kim Daasbjerg[2] — [1]Department of Physics and Astronomy and Interdisciplinary Nanoscience Center, University of Aarhus, Ny Munkegade 120, 8000 Aarhus C, Denmark — [2]Department of Chemistry and Interdisciplinary Nanoscience Center, University of Aarhus, Langelandsgade 140, 8000 Aarhus C, Denmark — [3]Department of Micro- and Nanotechnology, Technical University of Denmark, 2800 Kongens Lyngby, Denmark — [4]Newtec A/S, Staermosegårdsvej 18, 5230 Odense M, Denmark

We present an electrochemical method for the transfer of large-area, high-quality single crystalline graphene from Ir(111) to $\mathrm{SiO_2}$/Si under ambient conditions. The method is based on intercalation of tetraoctylammonium ions between the graphene layer and the Ir surface. This simple technique allows transfer of graphene single crystals having the same size as the substrate they are grown on (diameter ≈ 8 mm). In addition, the substrate can be re-used for further growth cycles. A detailed Raman map analysis of the transferred graphene reveals that the initial characteristics and imprints left on the sheet of graphene in terms of strain and wrinkles from the growth process remain after transfer.

O 33.2 Tue 18:15 Poster A

**The influence of the subtrate roughness on the electronic properties of sidewall graphene nanoribbons** — •Johannes Aprojanz, Jens Baringhaus, Julia Wiegand, Michael Oestreich, and Christoph Tegenkamp — Institut für Festkörperphysik, Leibniz Universität Hannover, Germany

Graphene nanoribbons (GNR), epitaxially grown on the sidewalls of silicon carbide (SiC) mesa structures, have shown exceptional transport properties such as ballistic conduction within a single channel and electronic mean free paths of up to 15 $\mu$m [1]. We present a detailed study of the growth process of sidewall GNR using scanning probe and electron microscopy as well as Raman spectroscopy. Focussing on the influence of the substrate roughness, the density of terrace steps and the step height can be precisely controlled by a resistive "face-to-face" heating treatment The local electronic properties are investigated by means of a 4-tip STM. The roughness of the SiC and of the mesa sidewalls is identified as detrimental to the electronic performance of sidewall GNR. The mean free path of the ribbons is shown to be directly dependent on the substrate terrace width. For a high density of terrace steps, a transition from ballistic to one dimensional diffusive transport is observed. In addition, Raman spectra show a selective graphene growth on the mesa sidewalls with a I(D)/I(G) ration below 0.1, which indicates high quality graphene nanostructures.

[1] Baringhaus et al., Nature **506**, 349 (2014)

O 33.3 Tue 18:15 Poster A

**Towards the growth of double-layer graphene by conversion of molecular monolayers** — •Christof Neumann[1], Gerardo Algara-Siller[2], Daniel Emmrich[1], Marta Trelka[1], Ute Kaiser[2], and Andrey Turchanin[1] — [1]Faculty of Physics, University of Bielefeld, 33615 Bielefeld — [2]Electron Microscopy Group of Materials Science, University of Ulm, 89081 Ulm

Graphene double-layers are desired for implementation of novel electronic and optoelectronic devices as well as for applications in nanofiltration and energy storage. Despite the recent great success in production of single-layer graphene sheets, viable routes to produce graphene double-layers have not been yet established. Here, we present a molecular approach towards graphene double-layers based on the temperature-induced conversion of cross-linked self-assembled monolayers of 1,1',4',1"-terphenyl-4-thiol (TPT) on Cu(111) and polycrystalline copper foils. We characterize this transformation by complementary experimental techniques including X-ray photoelectron and Raman spectroscopy, low energy electron diffraction, helium ion and scanning tunneling microscopy. To determine the structure of suspended graphene nanomembranes we employ high resolution transmission electron microscopy and selected area electron diffraction.

O 33.4 Tue 18:15 Poster A

**Magnetotransport of epitaxial Graphene with single ion-implanted Boron, Nitrogen and Carbon atoms** — Philip Willke[1], •Anna Sinterhauf[1], Sangeeta Thakur[3], Julian A. Amani[2], Thomas Kotzott[1], Steffen Weikert[2], Kalobaran Maiti[3], Hans Hofsäss[2], and Martin Wenderoth[1] — [1]IV. Physikalisches Institut, Universität Göttingen, Germany — [2]II. Physikalisches Institut, Universität Göttingen, Germany — [3]Department of Condensed Matter Physics and Materials' Science, TIFR, Mumbai, India

Using magnetotransport (MR) experiments we investigate the transport properties of SiC-Graphene in combination with low-energy ion implantation. Here, we demonstrate the incorporation of single boron, nitrogen and carbon atoms for which the microscopic structure has been additionally studied by scanning tunneling microscopy [1]. The ion-implanted samples exhibit a higher resistance and a lower mobility than undoped samples. Additionally, we find a positive MR for undoped samples switching to a negative MR for doped samples at high magnetic fields, especially for $^{11}B^+$- and $^{12}C^+$-ions. We explain this behavior with the additional presence of localized scattering centers which we describe in the context of weak localization theory. This work was supported by DFG priority program 1459 "Graphene".

[1] P. Willke et al., Appl. Phys. Lett. 105, 111605 (2014)

O 33.5 Tue 18:15 Poster A

**Local properties of graphene nanoribbons with well-controlled structural variations** — •Christian Härtinger, Fabian Queck, and Jascha Repp — Institute of Experimental and Applied Physics, University of Regensburg, D-93040 Regensburg

Atomically well-defined graphene nanoribbons can be grown by bottom-up on-surface chemistry [1], which allows for a detailed analysis by scanning probe microscopy and spectroscopy methods. This synthesis can be even extended to grow graphene nanoribbon heterostructures with a local variation of doping [2]. Here, instead we implement local structural variations of a nanoribbon on an Au(111) substrate by introducing suitable precursor molecules in the synthesis process. The influences of these structural variations on the local electronic properties are studied at low temperatures of 5 K by means of scanning probe microscopy and spectroscopy.

[1] Cai et al., Nature 466, 470-473 (2010)

[2] Cai et al., Nature nanotechnology 9, 896-900 (2014)

O 33.6 Tue 18:15 Poster A

**Electronic and transport properties of graphene nanoribbons on Ni(111)** — •Bernhard Kretz[1] and Aran Garcia-Lekue[1,2] — [1]Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastian, Spain — [2]IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

It is well known that graphene holds a great potential for electronic applications. The graphene-Ni system is an interesting case where the interaction with the ferromagnetic substrate gives rise to a number of remarkable phenomena.[1] In particular, the spin-dependent scattering of electrons at the edges of graphene islands on Ni(111) makes this system very interesting for spintronic devices.[2] Besides, the electron scattering is found to be dependent on the detailed edge structure of the graphene islands, which can exhibit unreconstructed or Stone-Wales reconstructed zigzag edge conformations.[3] In this work, we study the influence of the edge structure on the transport properties across graphene-Ni junctions. We consider graphene nanoribbons on Ni(111) with an unreconstructed and a Stone-Wales reconstructed zigzag edge, both of which are unpassivated, and we use density functional theory (DFT) calculations using the SIESTA and TranSIESTA codes.

[1]V. M. Karpan et al., Phys. Rev. Lett. 99, 176602 (2007); M. Weser et al., APL 96, 012504 (2010)

[2] A. Garcia-Lekue et al., PRL 112, 066802 (2014)

[3] A. Garcia-Lekue et al., submitted

O 33.7 Tue 18:15 Poster A

**Self-assembled PTCDI monolayers for band gap engineering using organic solid/solid wetting deposition** — •Oliver Gretz[1,2] and Frank Trixler[1,2,3] — [1]Technische Universität München, School of Education, München, Germany — [2]Zentrum Neue Technologien, Deutsches Museum, München, Germany — [3]Department für Geo- und Umweltwissenschaften & Center for NanoScience, Sektion Kristallographie, Ludwig-Maximilians-Universität München, Germany

Graphene based semiconductors could be fabricated by inducing a band gap at the Dirac point in the graphene band structure. According to theoretical investigations perylene-3,4,9,10-tetra-carboxylic-diimide (PTCDI) is a promising organic semiconductor to open up a band gap in graphene by monomolecular physisorption. However the self-assembly of PTCDI monolayers on graphite could only be shown by epitaxial growth in ultra-high vacuum, yet.

Organic Solid/Solid Wetting Deposition (OSWD) is a process which enables the deposition of insoluble molecules such as organic semiconductors on substrate surfaces under ambient conditions. Here we show first results with PTCDI using OSWD, obtained via scanning tunneling microscopy, which are crucial for tuning the band structure of graphene.

O 33.8 Tue 18:15 Poster A

**Interaction between polycrystalline copper substrate and graphene during atmospheric Chemical Vapor Deposition** — •Umut Kamber, Cem Kincal, Hakki Tunç Çiftçi, Berk Zengin, Dilek Yildiz, and Oğuzhan Gürlü — Istanbul Technical University, Istanbul, Turkey

Due to its inevitable potential to be used in wide scale electronics applications, research on high quality, large area, single sheet graphene production became an intense field. For this purpose Chemical Vapor Deposition (CVD) was presented as the most efficient method. In order to obtain defect-free CVD grown graphene sheets, understanding the interaction between graphene and substrate surface is crucial. We observed that graphene can grow over different Cu facets in a continuous film, as reported earlier. Graphene films are depressed near the step-edges of the substrate and moiré patterns occur on some of the atomically flat terraces. Formation of the moiré patterns on only some of the Cu facets indicate differences between the interaction of graphene with different Cu facets. Formation of the graphene on the Cu surface clearly affects the mobility of the Cu atoms on the relevant facet at high temperature. Moreover, we observed that if the copper surfaces are covered by bulk carbon without forming graphene, copper surface crystallizes more properly than graphene covered one. Thus, we claim that formation of graphene effects the crystallization of copper surface, which generates a growth feedback affecting the quality of the graphene film grown.

O 33.9 Tue 18:15 Poster A

**Thickness, roughness and electronic structure characterisation of graphene using soft x-ray reflection spectroscopy** — •Christine Jansing[1], Hud Wahab[2], Marc F. Tesch[1,3], Markus Gilbert[1], Andreas Gaupp[1], Andrey Sokolov[3], Dong Hee Shin[4], Suk-Ho Choi[4], Hans-Christoph Mertins[1], Heiko Timmers[2], Dominik Legut[5], and Peter M. Oppeneer[6] — [1]Münster Uni. of Applied Sciences, D-48565 Steinfurt — [2]School of Physical, Environmental and Mathematical Sciences, Uni. of New South Wales Canberra, Canberra, Australia — [3]HZB, D-12489 Berlin — [4]Dep. of Appl. Physics, College of Appl. Science, Kyung Hee Uni., Yongin 446-701, Korea — [5]Nanotechnology Centre, Ostrava, Czech Republic — [6]Depart. of Physics, Uppsala Uni., Uppsala, Sweden

X-ray reflection spectroscopy has been performed on graphene layers supported by different substrates across the C 1s absorption edge. Results confirm that the chemical vapour deposition onto copper foil has produced graphene of monolayer coverage. Graphene, deposited under the same conditions, transferred with a PMMA carrier to other substrate materials, has been measured to be significantly thicker. The interface- and the surface-roughness of the graphene layers have been determined. Structure in the measured reflection spectra can be correlated with ab-initio electronic band structure calculations and assigned to C 1s electron excitations. For the graphene layers transferred to a SiO2 substrate a feature is present that indicates excitation at an energy that is 1.8 eV less than the energy associated with the $\pi^*$ orbital. This finding is consistent with NEXAFS observations.

O 33.10 Tue 18:15 Poster A

**Preparation of Graphene using the confinement controlled sublimation method** — •Cornelis Hilscher, Ulf Berges, Dominique Handschak, Christoph Keutner, Lothar Brosda, Philipp Espeter, and Carsten Westphal — Experimentelle Physik I, TU Dortmund

Graphene is one of the most promising novel materials. Due to rapid, out of equilibrium growth at 1200 °C in ultra high vacuum successfull production of high quality graphene, suitable for electronic applications, still causes many problems. There are some possible solutions like using argon or an enclosure to overcome these issues.

In this work the confinement controlled sublimation method [1] will be used to grow graphene on SiC(0001)-6H. The silicon carbide (SiC) is surrounded by a graphite enclosure with a small pinhole. Thus, the sublimating silicon stays in the enclosure causing a high silicon vapor pressure during the preparation process. Accordingly, the silicon's sublimation rate is decreased significantly, which leads to a 300 °C increase of the graphene formation temperature. Hence, the growth proceeds near to thermodynamic equilibrium and the graphene layer takes much longer to form. So very homogeneous graphene is expected.

Commissioning and characterization of the preparation chamber is still in progress and includes optimization of parameters like background pressure, heating time and heating temperature.

[1] de Heer, W. A. et al (2011): *Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide.* In: PNAS, **108**, 41, 16900–16905

O 33.11 Tue 18:15 Poster A

**Polarization doping of graphene on silicon carbide** — Samir Mammadov[1], Jürgen Ristein[2], Roland J. Koch[1], Markus Ostler[1], Christain Raidel[1], Martina Wanke[1], Remigijus Vasiliauskas[3], Rositza Yakimova[3], and •Thomas Seyller[1] — [1]Institut für Physik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany — [2]Lehrstuhl für Laserphysik, FAU Erlangen-Nürnberg, Erwin-Rommel-Str. 1, D-91058 Erlangen, Germany — [3]Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden

Being an atomically thin layer, graphene has no bulk. Hence, the charge carier density is influenced by its environment, especially the substrate. While epitaxial graphene on SiC(0001) is n-type doped due to charge transfer from interface states [1], quasi-freestanding graphene (QFG) on H-terminated SiC(0001) is p-type doped [2]. This was explained by the spontaneous polarization of the hexagonal SiC substrate [3]. As a test, we have carried out angle-reolved photoelectron spectroscopy of QFG on H-terminated 3C-SiC(111), 6H-SiC(0001), and 4H-SiC(0001). Using semi-insulating and n-type substrates we shed light on the contributions to the charge carrier density in QFG caused by the spontaneous polarization of the substrate, and the band alignment between the substrate and the graphene layer. In this way we provide quantitative support for the polarization doping model.

[1] S. Kopylov et al., Appl. Phys. Lett. 97 (2010) 112109. [2] F. Speck et al., Appl. Phys. Lett. 99 (2011) 122106. [3] J. Ristein et al., Phys. Rev. Lett. 108 (2012) 246104.

O 33.12 Tue 18:15 Poster A

**Phonon Dispersion of Bilayer Graphene on 6H-SiC(0001)** — •Sindy Franz, Christian Heidrich, Roland J. Koch, and Thomas Seyller — Institut für Physik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany

Electron phonon coupling in graphene leads to characteristic changes in the phonon dispersion as well as a renormalization of the band structure. In the phonon dispersion it results in the well-known Kohn anomalies at the center of the Brillouin zone as well as the K-point. Using high-resolution electron energy loss spectroscopy (HREELS) in off-specular scattering geometry we investigate the phonon dispersion of epitaxial bilayer graphene on silicon carbide. In order to interpret our results, we compare them to previous measurements of monolayer graphene and of the buffer layer.

O 33.13 Tue 18:15 Poster A

**Phonon-Plasmon-Coupling in Bilayer Graphene on 6H-SiC(0001)** — •Christian Heidrich, Sindy Franz, Roland Koch, and Thomas Seyller — Institut für Physik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany

Understanding the interaction between phonons and charge carriers of graphene is of high relevance from a fundamental as well as from an application point of view. Here we report on a study of bilayer epitaxial graphene on SiC(0001) using high resolution electron energy-loss spectroscopy (HREELS). This surface sensitive method is useful for the investigation of phonon vibrations, plasmon excitations, and the coupling of both. It is also possible to study the dispersion of these phenomena over the whole Brillouin zone by varying the scattering geometry. Changing the primary beam energy on the other hand enables measuring those dispersion relations very close to the center of the Brillouin zone. Here we employ the latter to study the coupling of graphene's free charge carrier plasmon to phonons in the substrate as well as graphene itself in the dipole scattering regime. Using dielectric theory calculations, we simulated our measurements and the dispersion relation for the coupled phonon plasmon modes to compare with the experiment.

O 33.14 Tue 18:15 Poster A

**Symmetry broken states of high mobility graphene on boron nitride devices suited for combined transport and STM experiments** — •Felix Jekat, Tjorven Johnsen, Nils Freitag, Peter Nemes-Incze, and Markus Morgenstern — II. Physikalisches Institut B, RWTH Aachen, Otto-Blumenthal-Straße, 52074 Aachen

Monolayer graphene is an ideal candidate to combine STM and transport measurements in the Quantum Hall regime. Such measurements require samples in which the exposed graphene surface is clean of processing residues and show high mobility. Here we present magnetotransport measurements of a monolayer graphene on boron nitride prepared by a process which fulfills the above requirements. The sample temperature is as low as 280 mK at a magnetic field of up to 10 T. The presented device shows a field effect mobility of $50,000\,\frac{\mathrm{cm}^2}{\mathrm{Vs}}$. We observe full degeneracy splitting, at a magnetic field of 6 T in the zeroth and first Landau Level within the hole regime and the insulating phase in the zeroth Landau level. In the electron regime, only two fold degeneracy splitting is present. Temperature dependent measurements were conducted to determine the activation gaps of the broken symmetry states revealing gaps up to 80 K.

O 33.15 Tue 18:15 Poster A

**Preparation of high mobility graphene samples for combined transport and STM experiments** — •Tjorven Johnsen, Felix Jekat, Nils Freitag, Peter Nemes-Incze, and Markus Morgenstern — II. Physikalisches Institut B, RWTH Aachen, Otto-Blumenthal-Straße, 52074 Aachen

Graphene on boron nitride provides the possibility to measure high mobility two dimensional electron systems by scanning tunneling microscopy. For this kind of measurement clean surfaces are crucial leading to the requirement that the exposed graphene surface has to be clean of processing residues. Adapting a dry transfer method presented by Kretinin et al. [1] for graphene transfer on boron nitride and employing shadow mask evaporation we are able to produce ultra clean graphene surfaces. A graphene flake is placed on a boron nitride flake exfoliated on $\mathrm{SiO_2/Si}$ chip serving as the back gate. Charge carrier concentration can thus be controlled during the experiment. The graphene flake ($30\times30\,\mu$m, bubble free area of $10\times10\,\mu$m) is contacted by 50 nm gold contacts defined by shadow mask evaporation. Homemade glass fibers [2] and TEM grids are utilized as shadow masks with alignment precision down to $2\,\mu$m. Four probe transport measurements exhibit high mobility ($50,000\,\frac{\mathrm{cm}^2}{\mathrm{Vs}}$) and symmetry breaking in Quantum Hall Effect at 0.3 K. We also report on the less successful contacting by microsoldering [3].

[1]A. V. Kretinin et al., NanoLett.14, 3270 (2014)
[2]N. Staley et al., Appl. Phys. Lett. 90, 143518 (2007)
[3]V. Geringer et al., Appl. Phys. Lett. 96, 082114 (2010)

O 33.16 Tue 18:15 Poster A

**Polarization-dependent radiation patterns of Raman scattering from Graphene** — •Harald Budde, Nicolas Coca Lopez, Xian Shi, and Achim Hartschuh — Department Chemie and CeNS, LMU München, Germany

Raman Scattering Spectroscopy is a powerful technique for studying graphene and other sp2 carbon materials [1]. We combined Raman Spectroscopy with back focal plane (BFP) imaging, a method used to visualize the angular distribution of emitted or scattered light. As an example BFP imaging allows to determine the orientation of single dipolar emitters [2, 3].

Graphene's Raman radiation pattern can be described as the incoherent sum of two orthogonal point dipole emitters despite its extended two-dimensional structure. Parameter-free model calculations using previously reported Raman polarization data are in excellent agreement with the observed radiation patterns of both G and 2D band. We show that the observed polarization ratio of the 2D band and the 2D/G intensity ratio depend on the numerical aperture of the microscope objective used. Finally, the detection efficiency in microscopic Raman measurements is extracted from calculated patterns and is in agreement with the experimental data.

[1] A. Ferrari, D. Basko, Nat. Nanotech. 8, 235-246, 2013.

[2] M. Lieb, J. Zavislan, L. Novotny, J. Opt. Soc. Am. B 21, 1210-1215, 2004.

[3] N. Hartmann, G. Piredda, J. Berthelot, G. Colas des Francs, A. Bouhelier, A. Hartschuh, Nano Lett. 12, 177-181, 2012.

O 33.17 Tue 18:15 Poster A

**Innovative protocols for the epitaxial growth of graphene and boron nitride on Ag(111)** — •Manuela Garnica, Felix Bischoff, Yuanqin He, Jacob Ducke, Martin Schwarz, Johannes V. Barth, and Willi Auwärter — Physik Department E20, Technische Universität München, Germany.

In recent years, the research of graphene and other 2D materials has spurred tremendous expectations for potential technological applications. In particular, the chemical vapour deposition (CVD) technique has been shown to be an effective method to grow large-areas of graphene and h-BN on highly reactive metals [1]. However, the low reactivity of nobel metals makes the synthesis of 2D materials using the standard CVD techniques cumbersome [2]. In this work, we explore different growth methods of graphene and h-BN layers on Ag(111) substrates. We combine novel and well-established protocols like CVD, E-Beam evaporation or ion gun assisted deposition. The characterization of the structural properties of these layers was achieved by atomic-scale scanning probe microscopy (STM/AFM). We report the observation of different domain length, edges and defects for the resulting layers. Furthermore, we explore with subnanometer resolution the electronic properties and local surface potential of the layers by means of scanning tunneling spectroscopy.

[1] M. Batzill, Surf. Sci. Rep. 67 (2012), p. 83

[2] B. Kiraly et al. Nat. Commun. 4 (2013) 2804; F. Müller et al. Phys. Rev. B 82, (2010) p. 113406; Martinez-Galera et al, Nano Lett 11, (2011) p3576

O 33.18 Tue 18:15 Poster A

**Transition of image-potential states from free-standing graphene to the graphene/metal interface** — •Nico Armbrust, Jens Güdde, and Ulrich Höfer — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg

We present a theoretical study of the formation of image-potential states on a graphene layer at varying distance to a metal surface. For this purpose we have constructed an analytical one-dimensional model-potential on the basis of the two-band model for the metal and a parametrized potential that reproduces the double Rydberg-like series of even and odd image-potential states of free-standing graphene. This enables us to calculate energies and wavefunctions of the combined system for arbitrary distances between graphene and the metal surface by solving the one-dimensional Schrödinger-equation numerically. For large distances, the image-potential states are typically located at the graphene sheet since its work function is lower than that of most metals. We show, how this double series of free-standing graphene evolves into a single series of the semi-infinite graphene/metal system when a flat graphene layer approaches the metal surface. Our model can quantitatively reproduce experimental data on graphene/Ir(111) and graphene/Ru(0001) which strongly differ in the interaction strength and therefore the binding distance. In particular, the model can explain the different binding energy and lifetime of the first ($n = 1$) image-potential state in the valley and hill areas of the moiré superlattice of graphene/Ru(0001).

O 33.19 Tue 18:15 Poster A

**Structural defects on swift heavy ion irradiated graphitic surfaces** — •Cem Kincal[1], Dilek Yildiz[1], Deniz Aşan Acar[1], Clara Grygiel[2], Cornelis J. van der Beek[3], and Oğuzhan Gürlü[1] — [1]Istanbul Technical University, Istanbul, Turkey — [2]Université de Caen, Caen , France — [3]Ecole Polytechnique, Palaiseau, France

Hillock like structures on Highly Oriented Pyrolytic Graphite (HOPG) surfaces due to perpendicular swift heavy ion (SHI) irradiation were previously reported. Our results showed that structures that form on HOPG surfaces due to uranium SHI irradiation in perpendicular geometry have a variety of shapes and sizes rather than just being hillock like. Most of such defects were observed to be distributed on a line rather than being localized to a single point. On the other hand, SHI irradiation of moiré zones on HOPG surfaces under grazing incidence did neither show destruction of the graphene layer generating the moiré pattern, nor any unzipping of the graphene as shown to happen on SHI irradiation of graphene crystals on dielectric substrates. Rather the defects forming as a result of grazing incidence irradiation were comet like both on pristine HOPG samples as well as on moiré domains. Moreover, our irradiation experiments on different graphitic samples showed variations in the structures of the induced defects on the surfaces depending on the crystal quality. Comparison of perpendicular irradiation defects on HOPG terraces to the ones on the moiré domains showed considerable differences.

O 33.20 Tue 18:15 Poster A

**Water chemistry beneath graphene: Formation and breathing of a super-dense OH-H2O phase under graphene** — Elin Grånäs[1], •Ulrike A. Schröder[2], Mohammad A. Arman[1], Mie Andersen[3], Timm Gerber[2], Karina Schulte[4], Jesper N. Andersen[1,4], Thomas Michely[2], Bjørk Hammer[3], and Jan Knudsen[1,4] — [1]Division of Synchrotron Radiation Research, Lund University, Sweden — [2]II. Physikalisches Institut, Universität zu Köln, Germany — [3]Interdisciplinary Nanoscience Center and Department of Physics and Astronomy, Aarhus University, Denmark — [4]MAX IV Laboratory, Lund University, Sweden

Placing catalysts in confined environments, e.g. carbon nanotubes, is a powerful method to modify their activity or selectivity. Unfortunately, atomic level understanding of the confinement effects is hindered by the complexity of these materials.

We use Ir(111)-supported graphene (Gr) flakes to study room temperature reduction of atomic oxygen in a confined 2D nano-reactor with X-ray photoelectron spectroscopy and scanning tunneling microscopy. The Gr cover can be used to trap OH-H2O phases that otherwise would desorb directly. Our study of these Gr-stabilized phases and their response to oxygen and hydrogen exposure reveals 2D breathing of a O-OH-H2O phase as O-atoms are dissolved into the structure (expansion) and subsequently converted to OH and H2O (contraction). Using density functional theory calculations combined with a genetic search algorithm, the structure and stability of the trapped OH-H2O structures were determined.

# O 34: Metal Substrates: Structure, Epitaxy and Growth

Time: Tuesday 18:15–21:00 Location: Poster A

O 34.1 Tue 18:15 Poster A

**Emissivity of polished tungsten surfaces as a function of temperature, detection angle and wavelength** — •Mate Puljiz, Sara Wanjelik, and Mathias Getzlaff — Institute of Applied Physics, University of Düsseldorf

The temperature of heated metallic surfaces in UHV chambers is usually measured by infrared pyrometry. Since metals cannot be regarded as black bodies, the material-dependent emissivity must be known in order to obtain accurate temperature data.

In this contribution, we report on the emissivity of a smooth polished tungsten surface with respect to its dependence on temperature, detection angle and wavelength. For this purpose, a temperature measurement using a W/Re thermocouple being in contact with the sample as reference was carried out simultaneously with a pyrometric measurement of the spectral radiance at wavelengths of 0.96 and 1.6 $\mu$m in a temperature range from 523 to 2473K. The sample was mounted rotatably in order to allow measurements for different detection angles. Subsequently, the emissivity was calculated using the measured data according to Planck's law. The results show a distinct angular dependence of the emissivity.

O 34.2 Tue 18:15 Poster A

**Large potential steps at weakly interacting metal-insulator interfaces** — •Menno Bokdam[1,2], Geert Brocks[1], and Paul J. Kelly[1] — [1]Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, Computational Materials Science, Enschede, The Netherlands — [2]Faculty of Physics, University of Vienna, Computational Materials Physics, Vienna, Austria

Potential steps exceeding 1 eV are regularly formed at metal|insulator interfaces, even when the interaction between the materials at the interface is weak physisorption. From first-principles calculations on metal|*h*-BN interfaces we show that these potential steps are only indirectly sensitive to the interface bonding through the dependence of the binding energy curves on the van der Waals interaction. Exchange repulsion forms the main contribution to the interface potential step in the weakly interacting regime, which we show with a simple model based upon a symmetrized product of metal and *h*-BN wave functions. In the strongly interacting regime, the interface potential step is reduced by chemical bonding.

O 34.3 Tue 18:15 Poster A

**STM study of the preparation of superconducting Ta(110) surfaces** — Thomas Eelbo, •Vladimir Zdravkov, and Roland Wiesendanger — Department of Physics, Scanning Probe Methods Group, University of Hamburg, Jungiusstr. 11a, D-20355 Hamburg, Germany

Exciting physics is expected on superconductor-ferromagnet interfaces [1]. Scanning tunneling microscopy/spectroscopy (STM/STS) has an great potential to study such systems due to it's lateral, energy and spin resolution capabilities. However, extreme sensitivity of STM/STS to surface contaminations requires a clean sample for reliable experiments. We explore possibilities to obtain clean and homogeneous Ta(110) surfaces which are characterized by STM/STS, by low-energy electron diffraction, and by Auger spectroscopy. In an early stage of the preparation we identify a surface reconstruction which is attributed to oxygen contaminants, favored by oxygen's high solubility and diffusivity within the Ta bulk crystal. We remove the oxygen from the surface by repeated cycles of high-temperature annealing in ultrahigh vacuum and Ar ion sputtering. Using this approach we succeeded in the preparation of surfaces with an effective contaminant-coverage of less than 5%.

[1] Stevan Nadj-Perge et al. , Science 346, 602(2014)

O 34.4 Tue 18:15 Poster A

**Gold on Rhenium(10-10): A Combined STM and LEED Study** — •Sebastian Schwede and Klaus Christmann — Inst. f. Chemie u. Biochemie FU Berlin

In complementing previous LEED and MEED experiments [1] we have performed an STM and LEED study on the growth of Au films on a Re(10-10) surface. While deposition at 300 K hardly leads to ordered growth, subsequent annealing to 850 K produces rectangular single-crystalline bilayer (BL) islands oriented parallel to the main crystal axes, with a size-dependent surface structure: islands with lengths between ca. 20 - 50 A exhibit a pseudomorphic (1x1) structure, while larger islands can no longer compensate the elastic strain caused by the lattice misfit and form (1xn) surface phases with n = 3, 4, 5. The Au diffusion seems to run via an intermediate precursor state located at and above the Au island edges. Films with Au coverages > 2 BL show a stable (1x8) structure that persists up to surprisingly high coverages of 30 BL. The STM images suggest a unique structural motif for all (1xn) phases that consists, in [0001] direction, of a bilayer line assembly with (n-1) Au bottom rows and (n-2) top rows, followed by an empty (vacant) row, a single Au row and another vacant row. In [1-210] direction the structure matches the Re - Re lattice spacing. [1] C. Pauls and K. Christmann J. Phys.: Condens. Matter 21 (2009) 134012

O 34.5 Tue 18:15 Poster A

**Study of atomic layer deposition with scanning tunneling microscopy** — •Zied Rouissi, Massimo Tallarida, and Dieter Schmeisser — Department of Applied Physics and Sensors,Brandenburg University of Technology, 03046 Cottbus, Germany

We present a work concerning the study of the initial steps of atomic layer deposition (ALD) with scanning tunneling microscopy (STM). We focus on the role of the substrates which has been often neglected.However, the detailed knowledge of precursor-substrate reactions is important for the understanding of how ALD proceeds. We report on the reaction of the Al-precursor, trimethyl-Al (TMA), on nanostructured surfaces such as Ag nanoclusters and nanostripes prepared by thermal evaporation on HOPG. We characterized the surface before and after one TMA adsorption pulse at room temperature, observing that the morphology of step edges changes after TMA creating a new terraces with a width of 7-10 nm, translated in the direction of the TMA deposition. This shows that, in case of a regular stepped surface, the substrate morphology would keep the same regularity with the translation in a direction privileged by the precursor absorption.

O 34.6 Tue 18:15 Poster A

**Thermodynamics of Deposition Flux dependent Intrinsic Film Stress** — Amirmehdi Saedi and •Marcel Rost — Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

The growth of polycrystalline films at temperatures above ˜0.2 of the melting temperature is accompanied by compressive stress development after film closure. Mysteriously, a significant part of this stress has a reversible nature: it disappears when the deposition is stopped and re-emerges upon resumption. It has been suggested that the variation of the surface chemical potential upon starting/stopping of the deposition may cause adatoms to diffuse in/out of the grain boundaries leading to the development/relaxation of the intrinsic compressive film stress. However, film growth involves a myriad of atomic processes such that the mystery is not yet solved and new mechanisms and ideas are still published frequently. Here we represent an analytical derivation, in which we address the variation of the chemical potential of the surface, the grain boundaries, and the film, that fully explains the magnitude of the reversible compressive stress using pure thermodynamic arguments. The tremendous stress levels observed in the experiments can indeed be explained by the flux induced density variations in the extremely dilute adatom gas on the surface.

O 34.7 Tue 18:15 Poster A

**Temperature-dependent surface structure of *in-situ* cleaved $TlNi_2Se_2$ investigated by STM** — •Martin Schmitt[1], Tobias Mauerer[1], Paolo Sessi[1], Hangdong Wang[2], Qianhui Mao[2], Minghu Fang[2], and Matthias Bode[1] — [1]Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — [2]Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

Recently, the Ni-chalcogenide $TlNi_2Se_2$ has been identified as a heavy-fermion multiband superconductor with a critical temperature $T_C = 3.7\,K$ [1]. We have investigated the temperature-dependent surface structure of *in-situ* cleaved $TlNi_2Se_2$ by means of low- and variable-temperature scanning tunneling microscopy. The cleaving process leads to large atomically flat (001) surfaces with typical terrace width that exceed 100 nm. These terraces are separated by step edges which—in the vast majority of cases—are multiples of the Tl–Tl layer spacing, $d_{\mathrm{Tl-Tl}} = c/2 = 6.72\,\text{Å}$. Our results indicate that the $\mathrm{TlNi_2Se_2}$ surface structure at $T \leq 120\,\mathrm{K}$ critically depends on the sample temperature during the cleaving process. Low-temperature cleavage leads to a surface which is dominated by a square-shaped $(\sqrt{2} \times \sqrt{2})$ superstructure and coexisting stripes of a $(2 \times 1)$ structure. In contrast, samples cleaved at room temperature exhibit a more irregular "wormlike" superstructure. Temperature-dependent STM data show an irreversible transition from the former to the latter at a temperature above of about 130 K upon heating.

[1] Hangdong Wang *et al.*, Phys. Rev. Lett.**111**, 207001 (2013).

O 34.8 Tue 18:15 Poster A

**Structural sensitivity of medium energy intensity data in a LEED analysis** — •Lutz Hammer, Pascal Ferstl, and M.Alexander Schneider — Solid State Physics, FAU Erlangen-Nürnberg

The crystallographic analysis of complex surface structures involves the quantitative determination of many structural parameters and hence requires a large experimental data base. For a full-dynamical LEED intensity analysis this means that either data sets taken at various angles of incidence have to be used or the energy range of the normal-incidence analysis has to be extended to significantly higher values. We investigated the implications of the second approach by comparing the structural sensitivity of low (50 - 300 eV) and high energy data sets (550 - 800 eV) obtained for different ordered phases of an oxidized or reduced cobalt submonolayer on Ir(100). As expected, the high energy data show a better sensitivity to structural details within deeply buried layers due to the larger penetration depth of the electron wave field. Although the relative scattering contribution of the surface layer is reduced, the the sensitivity towards structural changes at the very surface hardly diminishes. This compensation is caused by the smaller electron wave length at higher energies that provides an increased spatial resolution. The extension of the energy range thus also improves the reliability of the LEED analysis and may lead in favourite cases to structural uncertainties down to a single picometer.

O 34.9 Tue 18:15 Poster A

**Oxygen interaction with Rhenium(10-10): A combined LEED and STM study** — •Sebastian Schwede[1], Jörg Lenz[2], and Klaus Christmann[1] — [1]Inst. f. Chemie u. Biochemie FU Berlin — [2]Mantis Deposition GmbH. Mainz

A previous LEED and ARUPS study on the interaction of oxygen with a Re(10-10) surface [1] revealed a series of ordered oxygen phases, among others a c(2x4), a (1x5), a (1x4), and a (1x3) saturation phase. We have reinvestigated this system by means of scanning tunneling microscopy and focused on the growth mechanism and the surface morphology of the O-induced structures. The c(2x4) phase with an oxygen coverage of 0.25 contains one O atom that is located in the hcp site of the unreconstructed Re unit mesh, while a massive oxygen-driven surface reconstruction sets in as the (1xn) phases form for O coverages > 0.5. The (1x3)-2O saturation structure at a coverage of 0.67 can best be explained on the basis of a double-missing row reconstruction as proposed in recent DFT calculations [2]. [1] J. Lenz et al., Surf. Sci. 269/270 (1992) 410 [2] P. Kaghazchi and T. Jacob, Phys. Rev. B81 (2010) 075431

O 34.10 Tue 18:15 Poster A

**Effect of Sr on the microstructure and properties of Mg-6Al alloy** — •Tayebeh Nayeri and Sina Sadreddini — Department of Materials Science and Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran.

In this study, microstructures and properties of the Mg*Al alloy with strontium addition are studied. After the addition of strontium, structure analysis was performed to investigate phase evaluation. The potentiostate were also carried out in 3.5% Nacl solution with the results showing that the effect of adding strontium element to magnesium-aluminum alloys on corrosion behavior of this metal was strongly dependent on microstructure of the final alloy (e.g. grain size, type, intermetallic compounds, etc.).The major second phase included Al4Sr and Al2Sr, but the amount and morphology of these compounds was different in the alloys. The results indicated a reduction in the amount of Mg17 Al12 phase and corrosion rate as well as a rise in the resistance to cavitations.

O 34.11 Tue 18:15 Poster A

**Initial stage of small molecular adsorption on Li metal: a DFT study** — •Martin Callsen and Ikutaro Hamada — Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

Reliable and efficient storage of energy in secondary batteries is the key for the advance of mobile communication and future electricity driven mobility technologies. Therefore research dedicated to the increase of the power density and the life time of Li based secondary batteries has recently gained a priority status. In order to design new and improved combinations of electrode and electrolyte materials, a comprehensive knowledge of the chemistry of Li is required. We will present density functional theory (DFT) calculations on the initial stage of adsorption of small molecules on low index Li surfaces in order to shed light on the reactivity of the Li electrode with electrolyte fragments.

## O 35: Nanostructures at Surfaces

Time: Tuesday 18:15–21:00 Location: Poster A

O 35.1 Tue 18:15 Poster A

**Reactivity of Pt nanocluster arrays** — •Karin Gotterbarm, Florian Späth, Udo Bauer, Carina Bronnbauer, Oliver Höfert, Hans-Peter Steinrück, and Christian Papp — Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Graphene-supported nanocluster arrays are intriguing systems for the investigation of catalytic processes. We report on the reactivity of Pt nanoparticles deposited on graphene/Rh(111). High resolution XPS was employed to investigate the interaction with CO and $\mathrm{SO_2}$ as well as the oxidation of CO. Three CO-induced species are observed in the C 1s core level spectra. These are assigned to CO adsorbed in on-top and bridge terrace sites and step sites in comparison with single crystal data. The step sites are occupied first during adsorption and show the highest desorption temperature, indicating that these are the most stable adsorption sites for CO. The oxidation of CO follows roughly pseudo first order kinetics. The activation energy determined from an Arrhenius analysis was found to be smaller than for stepped platinum crystals. The adsorption and reaction of $\mathrm{SO_2}$ is monitored by measuring the S 2p core level, showing several $\mathrm{SO}_x$ ($x$ = 1 - 3) species as intermediates and sulfur as final product on the surface.

This work was supported by SFB 953 "Synthetic Carbon Allotropes".

O 35.2 Tue 18:15 Poster A

**Deposition of small clusters on oxide films and investigation of their mobility** — •Raphael Floegel[1], Christoph Schröder[1], Dominik Wolter[1], Matthias Bohlen[1], Conrad Becker[2], and Heinz Hövel[1] — [1]Fakultät Physik / DELTA, Technische Universität Dortmund, Germany — [2]Aix-Marseille Université, CINaM, Marseille, France

Metal oxides have many applications (catalysis, microelectronics etc.). $\mathrm{Al_2O_3}$ oxide films produced by oxidation of $\mathrm{Ni_3Al}$(111) can be used as a template for cluster growth. [1] They are characterised with Low-Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM).

Oxide films are also favourable for the study of deposited clusters because on the one hand the clusters are only marginally influenced by the substrate surface. On the other hand thin oxide films can still be characterised with STM. By the deposition of small mass selected clusters on the produced oxide films a systematic investigation of their mobility and coalescence depending on their size can be performed.

[1] S. Degen, C. Becker and K. Wandelt, Faraday Discuss., **125**, 343-356 (2004).

O 35.3 Tue 18:15 Poster A

**FeNi nanoparticle preparation and deposition on W(110)** —

•Hendrik Bettermann, Matthias Werner, and Mathias Getzlaff — Institute of Applied Physics, University of Duesseldorf

Deposited clusters and nanoparticles are rather interesting objects not only from a fundamental point of view but also for technological applications due to their electronic and magnetic properties which show a strong dependence on particle size. Interactions between nanoparticles and substrate during and after deposition have an important influence on particle properties.

Our contribution is focused on Fe/Ni alloy nanoparticles of up to 5 nm in diameter.

We report on our initial results of a newly installed magnetron sputter aggregation source. Particles are mass/charge filtered in a quadrupole mass selector and deposited on a W(110) substrate. Size and structural properties are investigated by means of scanning tunneling microscopy (STM) under UHV conditions. We compare these results with those of larger nanoparticles of similar composition.

O 35.4 Tue 18:15 Poster A

**Fabrication and characterization of silicon nanoparticles embedded in amorphous atomic layer deposited Al2O3** — •Klemens Ilse[1], Johannes Ziegler[1], Alexander Sprafke[1], and Ralf Wehrspohn[1,2] — [1]Department of Physics, Martin-Luther University Halle-Wittenberg, Halle (Saale), 06120, Germany — [2]Fraunhofer Institute for Mechanics of Materials IWM, Halle (Saale), 06120, Germany

Due to their promising material properties and opportunities for integration into silicon planar technologies, silicon nanoparticles are subject of high interest for next-generation applications in microelectronics, photonics, photovoltaic, or nanobiotech industries. Common silicon nanoparticle fabrication techniques, such as ion implantation, magnetron sputtering or the superlattice approach include annealing steps with temperatures above 1000°C to enable formation and crystallisation of silicon nanoparticles. Typically, the obtained silicon nanocrystals are embedded in a matrix consisting of silicon dioxide or silicon nitride.

In this work, silicon nanoparticles were fabricated by low-pressure non-thermal plasma-processes and embedded in amorphous aluminium oxide produced by atomic layer deposition (ALD). Both processes were performed in a single reactor without any vacuum break in between and in a low temperature regime.

Here, characterization results concerning the crystallinity, photoluminescence, material composition, and particle size of the embedded silicon nanoparticles are presented and discussed.

O 35.5 Tue 18:15 Poster A

**Mass selected metal clusters on rare gas films: comparison with free beam data** — •Christoph Schröder[1], Natalie Miroslawski[1], Dominik Wolter[1], Matthias Bohlen[1], Bernd von Issendorff[2], and Heinz Hövel[1] — [1]Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund — [2]Albert-Ludwigs-Universität Freiburg, Physikalisches Institut, 79104 Freiburg

Mass-selected metal clusters were deposited on rare gas layers in order to investigate the electronic structure of the nanoparticles influenced by the surface. The electron states are analyzed with ultraviolet photoelectron spectroscopy (UPS), using a monochomatic argon discharge lamp with a photon energy of $h\nu$=11.6 eV. As a reference we use UPS spectra of clusters measured in a free beam [1,2]. Using investigations of $C_{60}$ molecules on rare gas films, the quantitative comparison between the spectra for clusters in a free beam and deposited on rare gas is significantly improved.

[1] O. Kostko, PhD-thesis, Albert-Ludwig-Universität Freiburg (2007).

[2] H. Häkkinen, M. Moseler, O. Kostko, N. Morgner, M. A. Hoffmann and B. v. Issendorff, Phys. Rev. Lett. **93**, 093401 (2004).

O 35.6 Tue 18:15 Poster A

**Temperature dependent shape of deposited FeNi nanoparticles** — •Matthias Werner, Hendrik Bettermann, and Mathias Getzlaff — Institute of Applied Physics, University of Duesseldorf

Most of the properties of nanoparticles significantly depend on their size. For alloy systems the stoichiometry also plays an important role. In this contribution we report on the temperature dependent shape of size-selected deposited FeNi nanoparticles. This investigation is carried out by STM.

Fe50Ni50 Nanoparticles are produced by an arc cluster ion source (ACIS) and mass-filtered by an electrostatic quadrupole. The particles with diameters from 5 to 15 nm are deposited under UHV and soft-landing conditions on a W(110) surface. They are tempered in situ by a resistive heater integrated in the manipulator. The heating process is varied in intensity and time. Melting point and variations close to it are observed to depend on the clusters' diameter. The influence of the anisotropy of the W(110) surface is also taken into consideration.

O 35.7 Tue 18:15 Poster A

**Production and deposition of mass-selected iron clusters on $MoS_2$ investigated with AFM** — •Matthias Bohlen, Christoph Schröder, Dominik Wolter, and Heinz Hövel — Fakultät Physik/DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany

In order to deposit iron clusters on various surfaces, we used a magnetron-sputter gas aggregation cluster source [1] and a semi-continuous time-of-flight mass selector [2]. For iron clusters the simulation of suitable target geometry was important. We deposited $Fe_{2000\,\pm\,36}$ clusters with different coverages, from 1 % to 20 % of a cluster-monolayer, on different samples. Using a cleaved surface of a $MoS_2$ crystal, atomically flat on microscopic areas but providing some bonding of the clusters, we were able to use atomic force microscopy (AFM) and verify a narrow cluster height distribution. The change of the cluster size due to contact with air is discussed.

[1] H. Haberland, M. Mall, M. Moseler, Y. Qiang, Th. Reiners, Y. Thurner, J. Vac. Sci. Technol. A **12**, 2925 (1994).

[2] B. von Issendorff, R.E. Palmer, Rev. Sci. Instru. **70**, 4497 (1999).

O 35.8 Tue 18:15 Poster A

**3d metal nanoparticles deposited on graphene** — •Wolfram Gilbert, Torsten Veltum, Hendrik Bettermann, and Mathias Getzlaff — Institute of Applied Physics, University of Düsseldorf

In the past few years graphene gained the attention of scientists due to its unique mechanical and electrical properties. In addition to this, fabrication and deposition of nanoparticles on a substrate is of great interest for studies, e.g. as model catalysts. In this contribution we compare the properties of nanoparticles deposited on graphene with those on a 3d metal thin film.

A thin metallic film is epitaxially grown by electron beam evaporation on a W(110) single crystal under ultra-high vacuum conditions. To achieve a structurally ordered monolayer graphene on the ferromagnetic substrate we use chemical vapour deposition with propylene. The structure of this system is characterized in-situ by means of scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED).

The nanoparticles are produced by a continuously working arc cluster ion source (ACIS), mass-selected by an electrostatic quadrupole ($\Delta$m/m=10%) and subsequently deposited on the target surface under soft landing conditions. The structural analysis of the nanoparticles is carried out by STM.

O 35.9 Tue 18:15 Poster A

**Deposition of mass selected clusters produced with the THErmal CLuster Apparatus (THECLA)** — •Andreas Gruhn, Stefanie Roese, Jens-Christian Meyer, David Engemann, and Heinz Hövel — Fakultät Physik / DELTA, TU Dortmund, Germany

The clusters in THECLA are produced in a supersonic nozzle expansion [1][2]. In this case the clusters have a mass distribution and a narrow velocity distribution. A typical cluster consists of $\left(2.5\pm^{2.8}_{1.7}\right)\cdot 10^2$ atoms and has a velocity of $1.3\cdot 10^3\,\frac{m}{s}$. It is a matter of particular interest to have a mass selected cluster beam. In the source the clusters are partially ionized. The ion current is increased by a hot-cathode plasma ionisation [3]. Because of their charge, the cluster ions can be mass selected by deflection in a transverse electric field. The ion current is measured with a moveable Faraday cup. After deposition on substrates, the clusters can be characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The quality of mass selection is determined by comparing the results and the mass spectrum of the source. Based on the measurements and simulations, the ion optics is optimized. The goal is to achieve maximum quality of the mass selection with a sufficient high ion current. This allows more accurate measurements of properties depending on the cluster size.

[1] O. F. Hagena, Z. Phys. D 20, 425 (1991). [2] H. Hövel et al., Phys. Rev. B 48, 18178 (1993). [3] I. M. Goldby et al., Rev. Sci. Instrum. 68, 3327 (1997).

O 35.10 Tue 18:15 Poster A

**Contamination induced defect formation during Chemical Vapor Deposition of graphene and the formation of silicon dendrites** — •Umut Kamber[1], Cem Kincal[1], Bariş Yağci[2], Özgür Birer[2], and Oğuzhan Gürlü[1] — [1]Istanbul Technical University, Istanbul, Turkey — [2]Koç University, Istanbul, Turkey

Chemical Vapor Deposition (CVD) is an effective method used for producing graphene on copper foils. During CVD process Cu foils are heated up to 1200 K in a quartz tube under the flow of a mixture of hydrogen and argon. In order to grow graphene methane is let in to the tube for a short while with a very small flow rate compared to argon or hydrogen. Depending on the temperature during growth, flow rates of each gas, as well as on heating and cooling rates, the quality of graphene is affected. In our work we encountered silicon contamination on some of the sample batches. We have made systematic preparations and measurements in order to understand the reason of such contamination. Depending on the existence of graphene the shapes and sizes of such contaminants were observed to vary. The formation of point like and dendritic silicon-oxide islands on graphene and their manipulation by means of localized etching will be presented.

O 35.11 Tue 18:15 Poster A

**Investigation of the geometric structure of small deposited Au clusters.** — Ivan Baev[1], Torben Beeck[1], •Deniza Chekrygina[1], Stephan Klumpp[1], Michael Martins[1], Stephan Roth[2], Parasmani Rajput[3], Gonzalo Santoro[2], Sarathlal Koyiloth Vayalil[2], and Wilfried Wurth[1,2] — [1]Physics Department, University of Hamburg, D-22761, Hamburg, Germany — [2]DESY, D-22607, Hamburg, Germany — [3]3Atomic & Molecular Physics Division, Bhabha Atomic Research Center, Trombay, 400085, Mumbai, India

The investigation of new materials is nowadays propelled by the possibility to create size selected clusters of any desired materials. With the improvement of new 3rd generation synchrotron sources it should be possible to measure the geometric structure of clusters as small as several atoms in size. So far studies using spectroscopic techniques have focused on electronic and magnetic properties of small deposited metal clusters which could show new promising physical and chemical properties.

In this work we present a development towards disentangling structural effects from pure electronic effects as function of cluster size, with a main goal to investigate the geometry of deposited Au clusters on a Si wafer stabilized with an Al cap layer. In our work we are going to use grazing incidence small angle x-ray scattering (GISAXS) and x-ray absorption spectroscopy (EXAFS) to achieve this goal.

This work is supported by a PIER innovation grant.

O 35.12 Tue 18:15 Poster A

**Scanning photoelectron microscopy of high-temperature-$Cs_xC_{68}$** — •Jürgen Weippert[1], Seyithan Ulas[1], Sharali Malik[2], Matteo Amati[3], Luca Gregoratti[3], Maya Kiskinova[3], and Artur Böttcher[1] — [1]Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany — [2]Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — [3]ESCA microscopy beamline Elettra - Sincrotrone Trieste, ScPA Area Science Park, 34149 Basovizza-Trieste, Italy

Surface morphology of the non-IPR fulleride $Cs_xC_{68}$ grown via codepositing Cs and mass-selected $C_{68}^{+}$ in UHV has been studied by scanning photoelectron microscopy (Escamicroscopy). $Cs_xC_{68}$ survives heating up to $T^* \approx 1000K$ and shows a high thermal stability (related IPR fullerides: decomp. $\approx 800K$). The $C1s$- and $Cs4d$-based images revealed $Cs$-rich islands as striking species surrounded by planar $Cs$-poor areas. The islands are created by thermally activated segregation of $Cs$ atoms emerging from the subsurface region. Whereas $C1s$ and $Cs4d$ XP spectra taken from the $Cs$-poor regions show ionic bonds stabilizing the $Cs_x^{+a}C_{68}^{-b}$ compound the chemical state of the elements constituting the $Cs$-rich islands has no comparable examples in the literature of -$C$-$Cs$ bonds. The islands are photoactive: Initially $Cs4d$ band exhibits four components $(69-81eV)$, and $C1s$ band consists of two components $(281-286eV)$. This structure evolves under illumination $(hv \approx 500eV)$ towards the pattern of ionic -C-Cs bonds.

O 35.13 Tue 18:15 Poster A

**Does the band structure picture hold for Si Nanocrystals of few nm in size?** — Prokop Hapala, •Ante Šiljić, Pavel Jelínek, Pingo Mutombo, Katerina Kusova, and Ivan Pelant — Institute of Physics of the ASCR, v.v.i. Cukrovarnicka 10, Prague 6, Czech Republic

There has been a long-standing discussion on whether or not an electronic band structure concept. i.e. energy-to-wavevector dispersion, can be assigned to zero-dimensional objects such as quantum dots (nanocrystals) (see e.g. [1]). To answer this question, we developed a general method [2], which allows reconstruction of electronic band structure of nanocrystals from ordinary real-space electronic structure calculations. We combine the method with fully relaxed large-scale Density Functional Theory calculations of a realistic Si nanocrystals of up to 3 nm in size with different surface passivations including hydrogen, hydroxyl and methyl groups [3]. To demonstrate character of the band structure of Si nanocrystals, we calculate band dispersion along the Γ-X direction to compare it with a bulk counterpart. Based on this comparison, we conclude that the band structure concept is applicable to silicon nanocrystals with diameter larger than ~2 nm with certain limitations. In addition we will discuss impact of polarized surface hydroxyl groups or geometric distortion on momentum space selection rules important for light emission.

[1] M. S. Hybertsen, Phys. Rev. Lett. 72, 1514 (1994)
[2] P. Hapala, et al., Phys. Rev. B 87, 195420 (2013)
[3] K. Kůsová et al., ACS Nano 4, 4495 (2010)

O 35.14 Tue 18:15 Poster A

**SiOx nanoparticles generation in the gas phase by pulsed DC magnetron sputtering** — •Oleksandr Polonskyi, Egle Vasiliauskaite, Thomas Strunskus, and Franz Faupel — Institute for Materials Science, Chair for Multicomponent Materials, Christian-Albrechts University at Kiel, Kaiserstr. 2, 24143 Kiel, Germany

Nanoparticles and their composites have received an increasing attention in the last few decades due to their unique chemical, physical, mechanical, electrical, and optical properties, which provide hosts of potential applications in modern technology. Si-based nanomaterials are in particular interest. In this work we utilize such called gas aggregation cluster sources (GAS), based on the magnetron sputtering, for fabrication of SiOx nanoparticles. We observed that a low concentration of oxygen is necessary to admix for the cluster formation process. It was shown that a gas aggregation source based on pulsed reactive DC magnetron sputtering gives rise to a high increase in deposition rate of nanoparticles compared to continuous operation. The focus of the contribution is on nanoparticles size control and cluster growth and transport mechanism in the GAS. The influence of experimental conditions (Ar pressure/flow, discharge parameters, oxygen admixture) on nanoparticles size was investigated. The prepared nanoparticles were characterized with regard to chemical composition, morphology and optical properties.

O 35.15 Tue 18:15 Poster A

**Teaching the growth of nanostructures and Ostwald ripening in a master course chemistry** — •Jan Philipp Meyburg and Detlef Diesing — Universität Duisburg-Essen

Growth of nanostructures and processes as ageing and ripening of grown nanostructures are fundamental for the understanding of processes in catalysis, for instance. The authors show a computer experiment based on a kinetic Monte Carlo simulation. The computer experiment describes both phenomena, growth and ripening applied to the homoepitaxial growth of silver on a Ag(111) surface. Using DFT data for the activation energy of diffusion and lateral pair interaction energies the computer experiment simulates the island formation during the nanostructure growth in the regime of low coverages $\theta \approx 0.1$. If the adsorption processes are switched off, the dendritic to hexagonal shapes of the nanostructures change to larger sphere like structures due to sole surface diffusion as typical for Ostwald ripening. A selection of the first student results is shown. These results are compared with STM experiments [1,2] for growth and ripening on (111) surfaces. [1] E. Cox et al. Phys. Rev. B, 71:115414, 2005 [2] K. Morgenstern et al., Phys. Rev. Lett., 76:2113, 1996.

O 35.16 Tue 18:15 Poster A

**Hydrogenation of doped silicon clusters** — •Christine Bülow[1], Vicente Zamudio-Bayer[1], Arkadiusz Lawicki[1], Georg Leistner[1], Konstantin Hirsch[1], Bernd von Issendorff[2], and Tobias Lau[1] — [1]Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — [2]Physikalisches Institut, Universität Freiburg, Freiburg, Germany

Silicon is the most widely used semiconductor for various applications. Due to the demand of miniaturization of electronic devices there has been a high interest to study silicon nanoparticles. Small 3d-transition-metal doped silicon clusters show a distinct behavior of their magnetic properties: While in exohedrally doped species the dopant exhibits almost atomic spin magnetic moments, endohedrally doped silicon clusters loose the spin polarization of the metal dopant atom. This quenching is coordination driven and several theoretical investigations predict that hydrogen passivation can restore the magnetic moment of the dopant. Additionally, hydrogen passivation stabilises the clusters.

In this work we present two different methods to produce free hydrogen passivated silicon clusters in the gas phase using a magnetron sputtering source. Hydrogenation is either done by introducing hydrogen into the plasma of the magnetron or by physio- or chemisorption in a collision cell. The cluster composition is analysed in a time-of-flight mass spectrometer. We discuss the mass spectra of these two different preparation methods.

O 35.17 Tue 18:15 Poster A

**Protein-Assisted Assembly of Nanoparticles on Nanoparticles: Toward Plasmonic Nanoclusters** — •Roland Höller, Andreas Fery, and Munish Chanana — Department of Physical Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany

Metallic core-satellite nanoclusters are highly interesting for their potential applications in the fields of surface-enhanced Raman spectroscopy (SERS), light harvesting, and optical metamaterials due to their ability to support localized surface plasmons and thus allowing to manipulate electromagnetic fields at the nanoscale.[1] Many strategies have been developed to assemble colloidal plasmonic nanoparticles into metal-metal core-satellite nanoclusters using small alpha-omega end-functionalized molecular linkers, viruses, and DNA.[2] However, most of these approaches for nanocluster fabrication are either limited to 2D structures on substrates or arduous and expensive in synthesis. In this work, we present a novel protein-assisted nanoparticle assembly method, which is simple, inexpensive and upscalable, yielding highly stable and well-defined plasmonic core-satellite nanoclusters with small interparticle distances. The morphology of the nanoclusters was characterized using TEM and SEM. The optical properties were studied at the ensemble level and single cluster level by means of UV-Vis spectroscopy and dark-field optical microscopy and spectroscopy.

[1] Fan et al., Science 2010, 328, 1135.

[2] a) Gandra et al., Nano Letters 2012, 12, 2645; b) Li et al., Small 2012, 8, 3832; c) Sebba et al., Nano Letters 2008, 8, 1803.

O 35.18 Tue 18:15 Poster A

**Interaction of Palladium with Ultrathin Ionic Liquid films** — •Benjamin May, Florian Rietzler, Hans-Peter Steinrück, and Florian Maier — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Profound knowledge of the interfaces between ionic liquids (ILs) and catalytically active transition metals is highly relevant in heterogeneous catalysis. In particular in SCILL (Solid Catalyst with Ionic Liquid Layer) systems, the IL layer allows modifying reactions by influencing solubility of reactants and/or selectivity of the catalyst (co-catalytic effect).[1]

X-ray photoelectron spectroscopy (XPS) was used in this study to obtain basic information on the interactions between an ionic liquid (IL) and palladium atoms and nanoparticles. To do this ultrathin films of the IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate were prepared on an Au(111) surface via IL physical vapor deposition[2] at different substrate temperatures. Pd was then thermally evaporated onto these frozen and liquid IL films. Interactions of IL and Pd as well as changes in IL film morphology were monitored by XPS.

This work was supported by the Cluster of Excellence Engineering of Advanced Materials.

[1] U. Kernchen et al., Chem. Eng. Technol. 2007, 30, 985-994.

[2] T. Cremer et al., Langmuir 2011, 27, 3662-3671.

## O 36: Plasmonics and Nanooptics

Time: Tuesday 18:15–21:00 Location: Poster A

O 36.1 Tue 18:15 Poster A

**Optical-tuning of surface phonon polaritons with a phase-change material** — •Xiaosheng Yang, Peining Li, Tobias Mass, Angela De Rose, Ann-Katrin Michel, and Thomas Taubner — I. Institute of Physics (IA), RWTH Aachen University, Germany

As an alternative to metallic surface plasmon polaritons (SPPs), surface phonon polaritons (SPhPs) on polar dielectric crystals provide many opportunities in infrared and terahertz nanophotonic applications [1]. For example, localized SPhP modes have been experimentally demonstrated to show high quality factors on periodic nanopillar arrays (40-135) and single circular microcavities (around 60) [2][3]. However, such effects within SPhP structures can only be tunable by varying the size of nanostructure and resonances are fixed once fabricated. Here, we perform theoretical studies of active tuning of SPhPs by changing the phase of germanium antimony telluride (GST) thin film. Initial experiments are made with thermally and optically induced GST phase change [4][5].

[1] J. Caldwell et al., Nanophotonics (doi:10.1515/nanoph-2014-0003) (2014); [2] J. Caldwell et al., Nano Lett. 13, 3690-3697 (2013); [3] T. Wang et al., Nano Lett. 13, 5051-5055 (2013); [4] A. Michel et al., Nano Lett. 13, 3470-3475 (2013); [5] A. Michel et al., ACS Photonics 1 (9), 833-839 (2014).

O 36.2 Tue 18:15 Poster A

**Phase-change induced switching of a SiC superlens** — •Johannes Reindl, Peinning Li, Lena Jung, and Thomas Taubner — Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany

Conventional optics can only resolve structures larger than half of the used lightsource's wavelengths. The utilization of the superlensing phenomenon enables an improved extraction of near-field information and thus beats the diffraction limit[1-2]. Nearly a decade ago the functionality of SiC as a superlens in infrared optics was shown [3]. But it suffers, like all phonon-polariton based superlenses, from its predetermined, non-changeable structural properties. The use of Phase-Change Materials, materials that can be switched reversibly between a stable crystalline and amorphous state, would expand the existing application by circumventing the monochromatic nature of this kind of superlens. Therefore, theoretical calculations of a switchable superlens and initial experimental measurements with s-SNOM are done on a layer-system consisting of SiC and germanium antimony teluride (GST).

[1] Pendry, Phys. Rev. Letters 85, 3966 (2000)

[2] Fang et al., Science 308, 534 (2005)

[2] Taubner et al., Science 313, 1595 (2006)

O 36.3 Tue 18:15 Poster A

**Sensitivity engineering in direct contact Au@Pd nanosandwich hydrogen sensors** — •Nikolai Strohfeldt, Jun Zhao, Andreas Tittl, and Harald Giessen — 4. Physikalisches Institut, Universität Stuttgart

We demonstrate a hydrogen sensing scheme, using complex hybrid plasmonic nanostructures, with stacked gold and palladium nanodisks. So far plasmonics mostly focusses on studying influences of lateral coupling on hybrid plasmonic structures. However, for industry products it would be more feasible to use stacked nanostructures that can be fabricated in one step. We, for the first time, study the influence of stacking order and geometry, experimentally and numerically, to find an optimal arrangement for a hydrogen sensor device. With the best sensing geometry - a stack of gold as lower and palladium as upper disk - we obtain spectral shifts as large as 30 nm at about 4 vol.% $H_2$, which is a strong improvement compared to previous indirect designs. Our samples yield large absorption and scattering signals and are fabricated by low-cost hole-mask colloidal lithography and therefore yield sample sizes over areas of 1 $cm^2$.

O 36.4 Tue 18:15 Poster A

**Nano-photonic computations of light propagation and absorption in nano-structured hybrid solar cells** — •Thomas Kiel[1], Thomas Pfadler[2], Martin Stärk[2], Julia F. M. Werra[1], Christian Matyssek[1], Johannes Boneberg[2], Lukas Schmidt-Mende[2], and Kurt Busch[1,3] — [1]Humboldt-Universität zu Berlin, Institut für Physik, AG Theoretische Optik & Photonik, D-12489 Berlin, Germany — [2]Universität Konstanz, D-78457 Konstanz, Germany — [3]Max-Born-Institut, D-12489 Berlin, Germany

Nano-structured multilayer organic-inorganic solar cells are promising candidates for enhanced efficiency due to additional absorption features as compared to unstructured solar cells. We consider a common inverted solar cell material setup with a periodically nano-structured $TiO_2$ grating, covered by a P3HT-PCBM blend as the active material and followed by PEDOT-PSS, which are enclosed by ITO and silver contacts. In this setup resonant absorption enhancement outside of the main optical absorption band of P3HT-PCBM is observed experimentally.

We perform numerical calculations solving Maxwells equations using the Discontinuous-Galerkin Time-Domain Method to provide explanations of the experimentally observed behavior. Specifically, in order to obtain deeper insight into the mechanisms involved we compute spatially resolved absorption profiles and investigate the influence of the $TiO_2$ grating periodicity, which we compare to the experimental data.

O 36.5 Tue 18:15 Poster A

**plasmonic based low emission coatings** — Mehdi Keshavarz Hedayati, •Moheb Abdelaziz, and Mady Elbahri — Nanochemistry and Nanoengineering, Institute for Materials Science, Faculty of Engineering, Christian-Albrechts-Universität zu Kiel, Kiel, Germany

High energy consumption in the current century makes development of new efficient energy saving materials inevitable. One of the highly used energy saving material are "low emission coatings" (also known as low-e coating) which are generally fabricated by transparent conductors. In such a approach, the transmission of visible light is relatively high while the near infrared transmission is negligible. However, the typical transparent conductors are made of indium tin oxide which is a costly compound and hence the need of cheaper replacing system is critical. In this work, we make use the high reflection of metallic film in IR frequency to our benefit to develop a new highly efficient low-e material. There, a composite out of metal-dielectric which sustain plasmon resonance is used to suppress the reflection of thin metal film in visible while keeping the reflection at NIR very high. In that sense, the resulting structure is highly transparent in visible whereas it block the light passage at NIR (by reflection). Therefore the heat can be maintained in the house if such a film is being used as the windows coating in cold area (e.g. Germany). The simple fabrication of this two layers coating turn it a reasonable alternative for next generation of low-e materials.

O 36.6 Tue 18:15 Poster A

**Development and construction of an aperturless Scanning Nearfield Optical Microscope** — •Jonas Albert, Matthias Brandstätter, and Markus Lippitz — Experimentalphysik III, Universität Bayreuth

We are interested in mapping optical fields of nanoobjects such as plasmonic structures. For that purpose we built an aperturless Scanning Nearfield Optical Microscope (aSNOM), to combine spatial resolution of an AFM with optical information. In a first step we built an "open" AFM with optical access to the tip,while still keeping a high stability of the system in sight. Our AFM shows vertical sub-nanometer resolution with the possibility to illuminate sample and tip from the side and the bottom. In a second step the optical near field detection system is installed. With an Michelson-type interferometric detection we gain signal amplification plus optical phase information. For background suppression a cross-polarization scheme is implemented to get optimal signal-to-noise ratio.

O 36.7 Tue 18:15 Poster A

**Phase-tagged PEEM for localized surface plasmons** — •Soo Hoon Chew[1], Sebastian Nobis[1], Alexander Gliserin[1], Peter Geisler[2], Michael Förster[3], Yingying Yang[4], Seungchul Kim[5], Jürgen Schmidt[1], Matthias Kübel[1], Peter Hommelhoff[3], Bert Hecht[2] und Ulf Kleineberg[1] — [1]Faculty of Physics, Ludwig Maximilian University of Munich, 85748 Garching, Germany — [2]Institute of Physics, University of Würzburg, 97074 Würzburg, Germany — [3]Department of Physics, University of Erlangen-Nuremberg, 91058 Erlangen, Germany — [4]Institute of Semiconductors, Beijing 100083, P. R. China — [5]Max Planck Center for Attosecond Science, Pohang, 790-784, South Korea

Strong carrier-envelope phase (CEP) effects have been shown to be crucial in controlling electron motion recently in solids. As a further step, it is also very interesting to extend the CEP control on novel photonic devices. We have developed the single-shot phase-tagged time-of-flight photoelectron emission microscope (ToF-PEEM) with the aim to study localized surface plasmons in tailored plasmonic nanostructures. First, we use a CEP-sensitive nanotip to test the proof of principle of our setup. We also show some theoretical calculations of CEP effects on bowtie and dipole nanostructures with various gap sizes. The next experiments will be performed on single-crystalline gold nanostructures with ultralow surface roughness based on the theoretical prediction. The phase-tagged ToF-PEEM setup provides a versatile tool for both spatial-resolved and energy-resolved studies of attosecond control of electrons in tailored plasmonic nanostructures.

O 36.8 Tue 18:15 Poster A

**Long range coupling within an ensemble of quantum dots by plasmonic nanostructures** — •Laura Meissner[1], Christian Dicken[1], Michael Jetter[2], and Markus Lippitz[1] — [1]Experimentalphysik III, Universität Bayreuth, 95440 Bayreuth, Germany — [2]Institut für Halbleiteroptik und Funktionelle Grenzflächen, Universität Stuttgart,70569 Stuttgart, Germany

The dipole-dipole interaction between quantum emitters leads to well known effects such Dicke super-radiance of J aggregates. In a solid-state system, this interaction is weak due to its short range nature and the inhomogeneity of the ensemble. We investigate how a long-range surface plasmon can help to couple an ensemble of quantum dots. In a first approach, we combine high-density InP quantum dots with a two-dimensional surface plasmon forming at a gold layer. In this poster, we compare luminescence intensities and lifetimes as well as spatial emission patterns for different coupling geometries.

O 36.9 Tue 18:15 Poster A

**STM induced light emission from pristine and adsorbate covered surfaces** — •Ebru Ekici, Maren C. Cottin, Rolf Möller, and Christian A. Bobisch — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

In scanning tunneling microscopy (STM) mostly elastic tunneling occurs, however, also a very small percentage of inelastic tunneling takes place. This may lead to a local excitation at the tip-sample junction and the following relaxation may be accompanied e.g. by emission of photons [1]. The spectral analysis of the emitted light from the tunneling junction in the STM experiment carries information about the involved radiative decay channels, e.g. within adsorbed organic molecules [2]. Here, we studied the STM induced light emission from (noble metal) substrates which are partially covered with the archetype organic molecules 3,4,9,10-tetracarboxylic dianhydride (PTCDA), copper-phthalocyanine (CuPc) and $C_{60}$. Spectra of the integral photon yield as a function of the tunneling energy and spatially resolved photon maps for the pristine and molecule covered surfaces will be discussed. Further perspectives for manipulating the light emission properties by adsorbate layers will be presented.

[1] G. Hoffmann, T. Maroutian, and R. Berndt, Phys. Rev. Lett. 93, 076102 (2004)

[2] C. Chen, P. Chu, C. A. Bobisch, D. L. Mills, and W. Ho, Phys. Rev. Lett. 105, 217402 (2010)

O 36.10 Tue 18:15 Poster A

**Pump-probe infrared near-field nanospectroscopy on germanium and silicon** — •Frederik Kuschewski[1], S.C. Kehr[1], B. Green[2], S. Kovalev[2], M. Gensch[2], and L.M. Eng[1] — [1]Institut für Angewandte Photophysik, TU Dresden, 01062 Dresden, Germany — [2]Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany

Scattering-type scanning near-field optical microscopy (s-SNOM) is a versatile method to map the optical properties on the nanoscale. In combination with novel pulsed THz radiation sources, ultra-short dynamics can be observed in materials of very high interest (e.g. graphene). However, these experiments use very high repetition rates. Here, we introduce a technique to detect minute pump effects in the near-field signal, capable of processing low pumping repetition rates and, hence, allowing for measurements of biological samples.

In s-SNOM, the optical is exctracted via the method of higher-harmonic demodulation, which is extended to a novel side-band technique that allows for the pure measurement of pump-induced effects. In a pilot experiment, we investigated pure Si, Ge and a SiGe thin-film sample under excitation by a Nd:YAG ps laser while near-field probing was carried out by a cw $CO_2$ laser or by the tunable free-electron laser FELBE at the Helmholtz-Zentrum Dresden-Rossendorf.

All three samples show a time-variable pump-effect in the near-field when being probed at ∼10 μm wavelength. Moreover, image scans proof the resolution far beyond the diffraction limit. The experiment provides a definite proof of the applicability of our approach for investigating ultra fast phenomena in the near-field.

O 36.11 Tue 18:15 Poster A

**Imaging ring resonator plasmons using photoemission electron microscopy** — •Deirdre Kilbane, Anna-Katharina Mahro, Pascal Melchior, Cristian González, Michael Hartelt, Philip Thielen, Markus Rollinger, Stefan Mathias, and Martin Aeschlimann — Physics Department and Research Centre OPTIMAS, University of Kaiserslautern, Germany

Understanding fundamental interactions of light and matter e.g. the dynamic response of a metal to incident light is essential for designing plasmonic devices such as biosensors. Ring resonators are ideal biosensors since the binding of a biomolecule alters the near-field response causing detectable changes in the resonance wavelength and intensity. Typically far-field optical detection techniques are used to determine the spectral properties of these nanoantennas. However the near field response is determined on a length scale that is intrinsically smaller than the optical diffraction limit. We therefore use electrons instead of photons for imaging the near-field distribution. We characterize arrays of ring resonators by combining photoemission electron microscopy (PEEM) with a tuneable excitation source, an optical parametric oscillator (OPO). These ultrahigh spatially and spectrally resolved measurements reveal resonance conditions for different ring radii and depths.

O 36.12 Tue 18:15 Poster A

**Micro-scale Imaging Ellipsometry on Single-crystalline Gold Flakes for Plasmonic Applications** — •Peter Richter[1], Ovidiu D. Gordan[1], Muhammad Y. Bashouti[2], Björn Hoffmann[2], Thorsten Feichtner[2], Ahmed M. Salaheldin[3], Mirza Mačković[4], Christel Dieker[4], Erdmann Spiecker[4], Silke Christiansen[2,5], and Dietrich R. T. Zahn[1] — [1]Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz — [2]Max Planck Institute for the Science of Light, D-91058 Erlangen — [3]Universität Erlangen-Nürnberg, Institute of Particle Technology, D-91058 Erlangen — [4]Universität Erlangen-Nürnberg, Center for Nanoanalysis and Electron Microscopy (CENEM), D-91058 Erlangen — [5]Helmholtz Centre Berlin for Materials and Energy, D-14109 Berlin

Micro-scale single-crystalline gold flakes were drop casted onto a silicon surface intended to be used as substrate material for the fabrication of nanostructured plasmonic devices. Using an Accurion nanofilm ep4 imaging ellipsometer with a 1 μm lateral resolution, we demonstrate that spectroscopic micro-ellipsometry measurements on the gold flakes are prominently suitable to investigate their crystal and surface quality. The spectra were acquired under a 50x microscope objective in a spectral range from 1.55 to 3.25 eV at multiple angles of incidence. The ellipsometric parameters $\Psi$ and $\Delta$ were extracted only from a small region of interest positioned in the middle of the gold flake. An optical model was applied to assure the Kramers-Kronig consistency of the experimental data and to deliver reliable results for the dielectric function, which agrees well with previous literature reports.

O 36.13 Tue 18:15 Poster A

**Coupling of an organic cyanine dye with a plasmonic structure** — •Jessica Koller[1], Thorsten Schumacher[1], Christian Dicken[1], Daniela Wolf[1], Anna Köhler[2], and Markus Lippitz[1] — [1]Experimentalphysik III, Universität Bayreuth — [2]Experimentalphysik II, Universität Bayreuth, Germany

By placing a multichromophoric system nearby a metal surface the optical properties of the system can be modified due to the interaction between the surface plasmon polariton and the molecular states. This can lead to an emission enhancement and energy transfer between different emitters on the surface.

In this context we want to examine the optical properties of a hybrid plasmon-emitter-system consisting of an organic cyanine dye and different plasmonic structures by means of spatially resolved fluorescence spectroscopy. Therefor we use a J-aggregate forming TDBC dye which shows a sharp resonance in absorbance and luminescence for high dye concentrations. At this juncture we start with the analysis of thin TDBC-PVA-films with different dye concentrations and present TDBC luminescence spectra and measurements of photostability. Additionally, a method to reduce photoactived bleaching by oxygen is tested as well as first results for the coupling of TDBC with plasmonic structures are given and compared to numerical simulations.

O 36.14 Tue 18:15 Poster A

**Optical emission and absorption characteristics of graphene on copper in a tunnel junction** — •Hakki Tunç Çiftçi, Berk Zengin, Umut Kamber, Cem Kincal, Dilek Yildiz, and Oğuzhan Gürlü — Istanbul Technical University, Istanbul, Turkey

Graphene has a huge potential for applications in optoelectronic devices due to its relatively small but efficient absorption of photons in a broad range of energies. Still the structural properties of graphene needs to be investigated at the atomic scale in order to expand the applicability of this novel material further in the optics, plasmonics and other related fields. Photon Scanning Tunneling Microscopy (pSTM) is a very useful tool for the purposes of studying structural properties at the atomic level as well as optical properties of graphene with very high, simultaneous, spatial information. In this work Chemical Vapor Deposition (CVD) grown graphene on copper was investigated with ambient pSTM. We studied the photon emission properties of STM among tip and graphene/Cu junction as well as the structural response of the surface due to different optical excitations. Bias voltage dependent characteristic of the tunnel junction under different illuminations were also investigated both on flat terraces and on moiré zones forming on the graphene/Cu system.

O 36.15 Tue 18:15 Poster A

**On the Importance of the Plasmonic Near-Field Spectrum for SEIRA** — •Jochen Vogt[1], Christian Huck[1], Frank Neubrech[1,2], Andrea Toma[3], David Gerbert[1], and Annemarie Pucci[1] — [1]Kirchhoff-Institute for Physics, Heidelberg University, Germany — [2]4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany — [3]Istituto Italiano di Tecnologia, Genova, Italy

The near-field characteristics of plasmonic infrared (IR) nanoantennas are of great importance for molecular sensing, e.g., with surface-enhanced IR absorption (SEIRA). Recent studies investigated the spatial extend [1], lateral distribution, and Angstrom-scale surface-distance dependence [2]. In addition, the spectral near-field information is crucial to design optimum nanostructures for vibrational sensing. The red shift between the plasmonic near- and far-field intensity peaks that has to be considered in the design was theoretically described and then experimentally confirmed using scanning near-field optical microscopy [3] and, as shown in this contribution, by IR micro-spectroscopy. We investigated vibrational SEIRA signals of a thin molecular layer on IR nanoantenna substrates. Varying the spectral tuning of plasmonic resonance and molecular vibrations, we find the maximum SEIRA in accordance with the predicted near- and far-field resonance energy shift. Furthermore, depending on the detuning, we observe the enhanced vibrational signals as asymmetric lines that are described by the Fano model. [1] Neubrech et al., ACS Nano 2014 [2] Bochterle et al., ACS Nano 2012 [3] Alonso-Gonzalez et al., PRL 2013

O 36.16 Tue 18:15 Poster A

**IR Microscopy: Spectra-Structure Correlations in Plasmonic Metamaterials and Hybrid Surfaces** — •Timur Shaykhutdinov, Thomas W. H. Oates, Andreas Furchner, and Karsten Hinrichs — Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Department Berlin, Schwarzschildstraße 8, 12489 Berlin, Germany

Anisotropic plasmonic metamaterials, organic-inorganic hybrid surfaces, and thin organic films and interfaces are of high importance for applications in the field of nanotechnology and in the design of structure-resolving biosensors, photonic and optoelectronic devices. A fundamental requirement to this end is a detailed characterization of their structural properties and fundamental interactions, which induce and control their unique macroscopic optical response.

For a comprehensive understanding of structure- and heterogeneity-induced effects of these novel materials in the fingerprint region, both far- and near-field optical measurement concepts with high sensitivity and lateral resolution are required. Current methods include generalized ellipsometric IR microscopy (developed at the ISAS Berlin) and nanoscale IR microscopy based on photothermal induced resonance (PTIR), a technique also referred to as AFM-IR.

In combination with new measurement concepts, optical calculations (e.g. using rigorous coupled-wave analysis (RCWA), finite-difference time-domain method (FDTD)) of both the electromagnetic far- and near-fields are essential to avoid incorrect spectral assignments and unphysical conclusions.

O 36.17 Tue 18:15 Poster A

**Simulations of s-SNOM Systems** — •Lisa Ortmann, A. Hille, S.C. Kehr, and L.M. Eng — Institut für Angewandte Physik, George-Bähr-Straße 1, 01069 Dresden

Scattering scanning near-field optical microscopy (s-SNOM) utilizes scattering of electromagnetic waves by a sharp probe that is coupled via near-field interaction to the sample of interest. For small tip-sample distances, the near-field optical resolution and contrast clearly depend on the tip radius and the different sample properties only. Such a scenario may be easily modelled by the analytical dipole-approximation. Nevertheless, this simplified model suffers from limitations such as neglected retardation or the non-point-like tip, and thus is inappropriate to be applied to more complex systems including e.g. anisotropic substrates or structured samples. Hence, a full numerical description is needed to gain a deeper understanding of experimental results.

We present here simulations of the tip-sample interaction in a typical s-SNOM configuration. Our systems consist of a perfect electrically conducting sphere as the scattering and scanning tip, and various samples ranging from perfect electric conductors over typical dielectrics to anisotropic substrates. All calculations are performed using a classical finite element method (COMSOL).

O 36.18 Tue 18:15 Poster A

**Bistable nano-plasma formation and EUV light generation in plasmonic nanostructures** — •Frederik Busse, Murat Sivis, and Claus Ropers — IV. Physical Institute, University of Göttingen, Göttingen, Germany

The enhancement of light in plasmonic nanostructures offers new means to study highly nonlinear optical phenomena using ultrashort low-energy laser pulses at MHz repetition rates. Specifically, the excitation of noble gas atoms in resonant bow-tie antennas and tapered hollow waveguides facilitates nanostructure-based extreme-ultraviolet (EUV) light generation at local intensities above 10 TW/cm$^2$. Contrary to initial reports [1, 2] which indicate the feasibility of plasmon-enhanced coherent high-harmonic generation, it was recently shown that incoherent fluorescence stemming from multiphoton and strong-field excitation dominates the EUV light generation process under such conditions [3, 4].

Here, we present a study of gas plasma processes in tapered hollow waveguides which can lead to a pronounced intensity-hysteresis in the fluorescence signal. In addition to the spectral analysis of the fluorescent EUV radiation, we measure intensity- and pressure-dependent electron and ion yields which give further insights into the ionization mechanisms.

[1] S. Kim *et al.*, Nature **453**, 757(2008),
[2] I.-Y. Park *et al.*, Nat. Photon. **5**, 677 (2011).
[3] M. Sivis *et al.*, Nature **485**, E1 (2012).
[4] M. Sivis and C. Ropers, Phys. Rev. Lett. **111**, 085001 (2013).

O 36.19 Tue 18:15 Poster A

**Calculation of photothermal heating in DNA-gold nanoparticle networks due to irradiation with laser light** — Malte Linn, •Alexander Nedilko, and Gero von Plessen — Institute of Physics (IA), RWTH Aachen, Germany

Molecule metal-nanoparticle hybrid systems, such as DNA-gold nanoparticle (AuNP) networks, have attracted great interest because of their unique optical properties and their versatile chemical functionalities. Since DNA dehybridization is temperature-sensitive, the DNA-AuNP networks can be dissociated by thermal and photothermal heating. In this work, we calculate the temperature increase in DNA-AuNP networks induced by irradiation with c.w. laser light. To this end, we use generalized Mie theory to calculate the optical power absorbed by the individual nanoparticles in AuNP aggregates in water. By inserting the absorbed powers into finite-element calculations, the temporal and spatial changes of the temperature distribution within the AuNP aggregates and in their vicinity are computed. The maximal temperature in the AuNP aggregate is found to grow with aggregate size due to heat accumulation. While the irradiated AuNPs serve as heat sources, their individual temperature increases are only a few percent higher than those of the water regions between them, resulting in a relatively smooth temperature distribution in each aggregate.

O 36.20 Tue 18:15 Poster A

**Real space imaging of nanotip plasmons using electron energy-loss spectroscopy** — •Benjamin Schröder[1], Sergey Yalunin[1], Thorsten Weber[2,3], Murat Sivis[1], Felix von Cube[2,3], Thomas Kiel[4], Christian Matyssek[4], Stephan Irsen[3], Kurt Busch[4], Claus Ropers[1], and Stefan Linden[2] — [1]IV. Physical Institute, University of Göttingen, Germany — [2]Physikalisches Institut, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany — [3]Research center caesar, center of advanced european studies and research, Bonn, Germany — [4]Institut für Physik, Humbold-Universität zu Berlin, Germany

The excitation of surface plasmon polaritons (SPPs) on metallic nanotips results in a plasmonic confinement and enhancement of electromagnetic fields at the apex. This field concentration provides for novel means of imaging and spectroscopy. One key aspect for the understanding and optimization of such a plasmonic structure is the dispersive evolution of propagating SPPs. In this contribution, we present a study of SPP excitation on a gold tip by using a scanning transmission electron microscope in combination with electron energy-loss spectroscopy. This technique allows for a spatially and spectrally resolved mapping of standing wave patterns on the nanotip's shaft. The data clearly shows a wavelength compression towards the apex and also indicates a significant contribution of higher azimuthal modes with increasing radii. We provide a fully retarded theoretical analysis of the adiabatic phenomenon based on a modal expansion. The numerical results demonstrate an excellent agreement with the data.

O 36.21 Tue 18:15 Poster A

**Simulation of the second harmonic response from hybrid plasmonic nanoantennas** — •Yevgen Grynko[1], Jens Foerstner[1], Heiko Linnenbank[2], and Stefan Linden[2] — [1]University of Paderborn, Paderborn, Germany — [2]University of Bonn, Bonn, Germany

Experimental spectroscopy of hybrid metallic/dielectric nanogap-antennas shows twofold enchancement of the SHG signal in comparison to pure metallic nanoantennas. Here, we study numerically their linear optical properties and the origin of the SHG emitted from such structures. We use the Discontinous Galerkin Time domain method and Maxwell-Vlasov hydrodynamic approach to describe the nonlinear flow of the free electron gas in a metal [1].

[1] S. Linden, F. B. P. Niesler, J. Förstner, Y. Grynko, T. Meier, and M. Wegener, Collective Effects in Second-Harmonic Generation from Split-Ring-Resonator Arrays, Phys. Rev. Lett. 109, 015502, 2012.

O 36.22 Tue 18:15 Poster A

**Comparing the emission quenching of electric dipole and magnetic dipole transitions near metal nanoparticles of different shapes** — •Deepu Kumar[1], Dmitry Chigrin[1], Florian Hallermann[1], Alexander Sprafke[2], and Gero von Plessen[1] — [1]RWTH Aachen University, 52074 Aachen, Germany — [2]$\mu$MD Group, Institute of Physics, Martin-Luther University Halle-Wittenberg, 06120 Halle, Germany

Near-field coupling to metal nanoparticles (MNPs) can lead to an enhancement of excitation and emission rates of molecular or ionic emitters placed in the vicinity of the particle. Magnetic dipole (MD) transitions are usually neglected in the treatment of such coupling due to their lower radiative rates as compared to electric dipole (ED) transitions. However, MD transitions appreciably contribute to some of the intra-4f transitions in rare-earth ions such as trivalent erbium (Er$^{3+}$). We use Mie theory and the finite element method (FEM) to study the excitation and decay rates of purely ED and purely MD transitions in the close vicinity of MNPs of different shapes, such as spheres, ellipsoids and split rings acting as nanoantennas. We compare the emission quenching of ED and MD transitions in the extreme near-field regime, i.e. the close vicinity of the surface of the MNPs.

O 36.23 Tue 18:15 Poster A

**Tip-Enhanced and Confocal Scanning Photocurrent Microscopy on Graphene.** — •Nicolas Coca Lopez, Tobia Mancabelli, Harald Budde, and Achim Hartschuh — Department Chemie and CeNS, LMU München, Germany.

Scanning photocurrent microscopy (SPCM) is a powerful tool to investigate the electronic properties of nanoscale devices such as carbon nanotube- or graphene-based field-effect transistors [1, 2]. However, due to the diffraction limit of propagating light, most SPCM measurements on graphene reported so far have been restricted to a spatial resolution of few hundred nanometers, making it impossible to optically characterize a device on the nanoscale. Tip-enhanced near-field optical microscopy (TENOM) overcomes this limit [3]. Exploiting the strong electromagnetic field enhancement in the vicinity of an illuminated metallic nanoparticle, the absorption, and hence, charge carrier generation in nearby photoactive materials is locally increased [4].

Here, we report on our last advances on the combination of SPCM and TENOM and our results regarding charge carrier generation and transport in graphene.

[1] Freitag, M. et al., Nano Lett. Vol. 7, No. 7, 2007 [2] Müller T. et al., Phys. Rev. B 79, 245430, 2009 [3] Mauser, N. et al., Chem. Soc. Rev., Vol. 43, No. 4, 2014 [4] Rauhut, N. et al., ACS Nano, Vol. 6, No. 7, 2012

O 36.24 Tue 18:15 Poster A

**Spectroscopic ellipsometry of anisotropic metal nanostructures on patterned diblock co-polymer thin film** — •Johannes F. H. Risch Risch[1], Sarathlal Koyiloth Vayalil[1], Gonzalo Santoro[1], Shun Shun[1,2], Bastian Besner[3], Philipp Bremer[3], Dieter Rukser[3], Yuan Yao[4], Ezzeldin Metwalli[4], Peter Müller-Buschbaum[4], Michael A. Rübhausen[3], and Stephan V. Roth[1] — [1]DESY, Notkestr. 85, D-22607 Hamburg — [2]KTH, Teknikringen 56-58, SE-100 44 Stockholm — [3]UHH, INF CFEL APOG, Luruper Chaussee 149, D-22761 Hamburg — [4]TUM, Physik Department LS E13, James-Franck-Str. 1, D-85748 Garching

Hybrid materials play a crucial role in modern advanced material science. Nanostructures can exhibit plasmonic resonances based on the shape, size and ordering, which can be used for example for SERS. Nanostructured gold films were fabricated by oblique angle deposition on a patterned diblock co-polymer thin film. Due to selective wetting behavior hierarchical films were created. Furthermore the gold clusters on top of the polymer film show a shape anisotropy leading to optical birefringence. Using angular resolved spectroscopic ellipsometry we investigate the optical properties of these hybrid films at selected different growth stages below and above the percolation threshold.

# O 37: Scanning Probe Techniques

Time: Tuesday 18:15–21:00 Location: Poster A

O 37.1 Tue 18:15 Poster A

**Construction of a dilution fridge based UHV spin-polarized STM operational in a vector magnetic field** — •Jan Hermenau[1], Andreas Sonntag[1], and Alexander Khajetoorians[2] — [1]Institute of Nanostructure and Solid State Physics, Hamburg University, Hamburg, Germany — [2]Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) and inelastic STS (ISTS), can address single spins at the atomic scale with unprecedented precession. Nevertheless, common cryostat designs for spin-polarized STM sub-Kelvin application are based on 3He liquification, which are limited in base temperature, hold time, and cooling power. To address these limitations for spin-polarized detection, we demonstrate the design and construction of a dilution fridge based UHV spin-polarized microscope operational in a vector magnetic field, capable of atomic spin detection and atomic manipulation. Our design consists of tip/sample exchange at cold temperatures and features extremely low 4He consumption with a long hold time. The easy-to-use compact design is capable of cold material deposition, and it is housed in an ultra-quiet laboratory featuring a 150 isolated foundation and proper acoustical and RF shielding.

O 37.2 Tue 18:15 Poster A

**Development of a Dedicated Lithographic System for Focused Electron Beam Induced Processing (FEBIP)** — •Florian Vollnhals, Fan Tu, Martin Drost, Hans-Peter Steinrück, and Hubertus Marbach — Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058, Erlangen.

Focused Electron Beam Induced Processing (FEBIP) subsumes a number of electron beam based lithographic techniques for the fabrication of nanostructures on surfaces, e.g. Electron Beam Induced Deposition (EBID) or Surface Activation (EBISA). In EBID, for example, a metal-organic precursor is dosed onto a surface and locally decomposed by a highly focused electron beam. Non-volatile fragments form a nanosize deposit while volatile ones are pumped off.[1,2]

These techniques rely on precise spatio-temporal control of the electron beam, to which end a lithographic attachment for an UHV-SEM was developed. The system is based on commercially available DAC hardware and LabVIEW as a programming environment. We will discuss some of the beam control-related challenges that were encountered during FEBIP research using standard EBL systems and present the capabilities of the new setup using examples from EBID and EBISA studies under UHV conditions.

Supported by the DFG via grant MA 4246/2-1, the COST Action CM1301 (CELINA) and by the excellence cluster Engineering of Advanced Materials of the FAU Erlangen-Nürnberg.

[1] W. van Dorp et al., J. Appl. Phys. 104 (2008), 0801301.

[2] H. Marbach, Appl. Phys. A 117 (2014), 987.

O 37.3 Tue 18:15 Poster A

**Development of a compact pulsed laser system for Scanning Tunneling Microscopy** — •Terence Thias, Philipp Kloth, Ole Bunjes, and Martin Wenderoth — IV. physikalisches Instut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

Pulsed laser excitation in STM allows resolving processes on surfaces beyond the bandwidth of the current amplifier. A major challenge of optical excitation in STM is controlling the influence of thermal effects. We implemented a sub-micrometer precise stage that allows the scanning of the focus point of the laser beam along the tip-surface junction - even during tunnel conditions. Thereby we assure to find the spot of maximum excitation in a standardized manner guaranteeing reproducible conditions. To keep the thermal power at the tip constant, standard pump-probe pulses must be transformed into complex laser pulse patterns [1]. We have developed a compact and convenient laser setup that can be added to any STM with optical access to the sample surface. Using an optical modulator with a bandwidth in the gigahertz range and a high frequency function generator, we process a continuous wave laser beam into nanosecond pulses. By generating pulse series exclusively in an electronic way we can easily adapt parameters like pulse width or repetition rate to the demands of the experiment. [1] Terada et al., Nature Photonics, 4(12), 2010.

O 37.4 Tue 18:15 Poster A

**GXSM - a smart & customizeable SPM control** — Percy Zahl[1], •Thorsten Wagner[2], and et al.[3] — [1]Brookhaven National Laboratory Upton, USA — [2]Johannes Kepler University Linz, Austria — [3]http://gxsm.sf.net

The open source and community driven scanning probe microscopy software project GXSM takes the next level to provide a highly and in-operando adaptable scanning probe microscopy (SPM) control system. A highly efficient digital signal processor (DSP) interfaces any SPM to a Linux based PC. Via a gnome based graphical user interface (GUI) standard tasks like scanning can be easily performed. The GUI allows the user also to control highly advanced tasks like mapping and probing/manipulations. Standalone, i.e., without DSP hardware, GXSM can perform image analysis and multidimensional visualization.

GXSM is based on an object oriented (C++) and modular design. Since 15 years this structure was flexible enough to adapt any further development. Plug-ins are available for background correction, data analysis, math feature detection (via the OpenCV library), statistics, scan data im-/export, and Python scripting remote control. In particular, the hardware interface is also based on this plug-in structure allowing to adapt for various DSP hardware.

In this contribution we will report on the recent developments to adapt more flexible to different SPM configurations via a kind of hot-plug signal routing on the DSP level. We will also give a status report on the efforts to migrate GXSM to the latest GTK/Gnome environment.

O 37.5 Tue 18:15 Poster A

**Role of orbital structure in High-resolution STM of molecules** — •Ondřej Krejčí, Prokop Hapala, Martin Ondráček, and Pavel Jelínek — Institute of Physics , Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague, 16253, Czech Republic

Recently, we demonstrated that most features visible in high-resolution

AFM images of molecules can be explained by simple mechanical model considering relaxation of an atomistic particle attached to the tip. On top of this, we introduced a simple model for calculating STM current considering only inter-atomic hoppings between relaxed atomistic particle and molecule [1]. The simple model is able to reproduce the main characteristics of high-resolution STM maps in close distance regime where the relaxation effects prevail. But since it completely neglects an electronic structure of the scanned sample, it fails at far distances where the electronic structure is dominating in the STM current. In this work, we implemented an efficient method for simulation of the high resolution STM images considering the molecular electronic structure and the atomistic particle relaxation as well. The method is able to reproduce observed contrast in both the close distance and the far distance regimes, including the gradual transition between them. It gives solid theoretical background for better understanding of high-resolution STM experiments. [1]Hapala, P. et al., Phys. Rev. B 90, 085421 (2014).

O 37.6 Tue 18:15 Poster A

**Performance of the mK-STM in the new Precision Laboratory** — •Jacob Senkpiel[1], Bertholt Jäck[1], Matthias Eltschka[1], Wolfgang Stiepany[1], Markus Etzkorn[1], Christian R. Ast[1], and Klaus Kern[1,2] — [1]Max-Planck-Institute for Solid State Research, D-70569 Stuttgart — [2]Ècole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

External vibrational and electromagnetic noise can yield a strong influence on the data quality of high precision experiments, like e.g., spectroscopic measurements of a superconducting gap with a scanning tunneling microscope (STM). Especially when pushing the frontier of resolution, these factors become a crucial point to consider. Here, an STM operating at a temperature of 10 mK for which Assig et al. [1] demonstrated an energy resolution of $\Delta E = 11.4 \pm 0.3\,\mu$eV is used for probing the smallest energy scales. The influence of external noise on this system was minimized by moving it from a standard lab environment to a specially designed Precision Laboratory. The performance of the mK-STM due to the optimized vibrational damping and high level electromagnetic shielding are presented.

[1] M. Assig et al., Rev. Sci. Instrum. **84**, 033903 (2013)

O 37.7 Tue 18:15 Poster A

**Scanning Tunneling Microscopy-study of the interplay between light induced effects and tunnel current on the GaAs (110) surface** — Philipp Kloth, •Katharina Kaiser, and Martin Wenderoth — IV. Physikalisches Institut, Georg-August Universität Göttingen, Germany

Using a low temperature Scanning Tunneling Microscope in combination with optical excitation we have studied the effect of the tunnel current on the surface photovoltage at the GaAs (110) surface. Spectroscopic measurements show that light-generated holes at the surface can be addressed by tunneling electrons, opening an additional tunnel channel into valence band states. Current dependent analysis reveals that this additional channel can be saturated. We have performed a detailed analysis of the saturation current as a function of the optical induced carrier density and the applied bias voltage. By changing the tunnel current we can actively switch between the dominant channel being either the optically induced channel or the common channel present under dark conditions. Moreover we show that the annihilation of holes in the valence band via the tunnel current affects the tip induced band bending at the surface.

O 37.8 Tue 18:15 Poster A

**Bidirectional quantitative force gradient microscopy sensors** — •Christopher F. Reiche[1], Julia Körner[1], Silvia Vock[1], Volker Neu[1], Bernd Büchner[1,2], and Thomas Mühl[1] — [1]Leibniz-Institut für Festkörper- und Werkstoffforschung IFW Dresden — [2]Institut für Festkörperphysik, Technische Universität Dresden

Dynamic scanning force microscopy (dSFM) is a versatile high spatial resolution method to study force-related surface properties of many different samples. We present our new approach of bidirectional force gradient microscopy, that includes lateral force microscopy and is compatible with usual dSFM equipment. We also provide methods for the quantitative evaluation of the force gradient data gathered with such a sensor. Furthermore, we discuss a novel approach to greatly enhance the dSFM sensor's sensitivity while still using conventional cantilever deflection detection. This signal amplification concept may also be adapted to many other oscillation based micro- and nanosystems and methods. Finally, we apply this concept to our magnetic force microscopy probes equipped with wear-resistant iron filled carbon nanotube tips, whose monopole-like stray field characteristics make them ideal for easy and reproducible quantitative field gradient measurements [1,2].

[1] F. Wolny, T. Mühl, U. Weissker, K. Lipert, J. Schumann, A. Leonhardt, and B. Büchner, Nanotechnology 21, 435501 (2010)

[2] T. Mühl, J. Körner, S. Philippi, C. F. Reiche, A. Leonhardt, and B. Büchner, Appl. Phys. Lett. 101, 112401 (2012)

O 37.9 Tue 18:15 Poster A

**Study of Nano Particle Friction Forces on Silicon using Atomic Force Microscopy** — •Hannah Lauer, Daniel Geiger, Susanne Rappl, and Othmar Marti — Institute of Experimental Physics, Ulm University

For a variety of applications and industrial processes friction forces of nano particles on substrates are of prime importance. These forces are influenced by humidity, temperature and ageing phenomena of the contact zone. To investigate these parameters, a model system consisting of a planar surface and spherical particles with well known material properties like silicon was introduced. The interaction force between particle and surface was measured by means of atomic force microscopy (AFM).

A measurement procedure was developed that enables the controlled displacement and tracking of particles. Particles were moved in contact mode AFM. The force exerted by the tip is given by the torsion of the cantilever. However, this procedure is restricted to the measurement of one out of two in-plane force components. Therefore, the mean particle-surface interaction force has to be determined by statistical data analysis. The trajectory of the particles was monitored by imaging the sample in tapping mode before and after particle movement.

Experiments in progress with silica particles demonstrate the importance of adhesion. They also indicate that the rest time is an important parameter.

O 37.10 Tue 18:15 Poster A

**Four Tip Scanning Tunneling Potentiometry Facilitating Low Injection Currents** — •Felix Lüpke, Stefan Korte, Vasily Cherepanov, and Bert Voigtländer — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and JARA-Fundamentals of Future Information Technology

We present a multi-tip scanning tunneling potentiometry implementation. While two of the four tips are used to inject a current into a sample, the third tip is scanned across the surface, recording topography and local electrochemical potential quasi-simultaneously by an interrupted feedback loop [1]. The fourth tip is used as a voltage reference probe. Choosing a distance in the $\mu$m range for the injection tips results in the current to be almost exclusively injected into the nanostructure to be studied. As a result, a small amount of current $\sim\mu$A results in a substantial amount of voltage drop $\sim$mV. The small currents needed and the straightforward measurement procedure make this application easy to implement in similar four tip setups with a minimum of hardware adjustments. The capability of the presented setup is demonstrated by experimental results on Si and Bi surfaces.

[1] T. Druga, et al., Rev. Sci. Instrum. 81, 083704 (2010)

O 37.11 Tue 18:15 Poster A

**Scanning Tunneling Microscope for 37T Magnetic Field** — •Jan W. Gerritsen[1], Suruchi Singh[1,2], Wei Tao[2], Bas L. M. Hendriksen[1], Peter C. M. Christianen[2], Ulrich Zeitler[2], and Jan C. Maan[2] — [1]Institute for Molecules and Materials, Radboud University Nijmegen, Netherlands — [2]High Field Magnet Laboratory, Institute for Molecules and Materials, Radboud University Nijmegen, Netherlands

We are adapting [1] and developing a scanning tunneling microscope (STM) that will work in magnetic fields up to 37T [2]. This unique instrument should enable us to image surfaces and nanostructures with very high resolution and to perform local electronic spectroscopy (STS) in hitherto unexploited magnetic field ranges. State-of-the-art STMs in superconducting magnets typically operate up to 15T. Our STM works inside the 32mm bore of a Bitter magnet with fields up to 37T and at liquid helium temperatures (1.4K). The challenge here is to develop an STM for these extreme environments. The 140l/sec cooling water for the magnet and 40kA current in the coil lead to a very bad acoustic and vibration environment for scanning probe microscopes. In our design, materials and vibration isolation for the STM head have been chosen to be compatible with these extreme conditions inside the magnet. I will show the design as well as the performance of the STM at high fields and low temperatures in topographic images and dI/dV spectroscopy experiments.

[1] J.G.A. Dubois et al., Rev. Sci. Instrum. 66, 4146 (1995)
[2] www.ru.nl/hfml/

O 37.12 Tue 18:15 Poster A

**A low-vibration SPM system for the mK-regime** — ●P. Borgens, A. Raccanelli, V. Cherepanov, F.P. Coenen, F.S. Tautz, and R. Temirov — Forschungszentrum Jülich GmbH, Deutschland

We report the progress in development of a mk-STM system cooled by adiabatic demagnetisation refrigeration (ADR). Our system features a 4He cryostat with 1K pot able of reaching 1.2K. The magnetic cooling unit uses a 2-stage ADR pill with the first stage precooling the wiring of the STM to 500mK and the second stage providing cooling to the base temperature of down to 35mK. The 1K pot can be operated by either a mechanical pumping stage or by a high capacity noise-free sorption pump that is able of providing the pumping for up to 100h. The specially developed KoalaDrive STM provides high stability against mechanical vibrations. For further reduction of the noise the entire system is located in a electromagnetically shielded and vibrationally isolated room.

O 37.13 Tue 18:15 Poster A

**3D structure determination of individual molecules by means of Atomic Force Microscopy** — ●Florian Albrecht[1], Coral Herranz-Lancho[2], Niko Pavliček[1,3], Mario Ruben[2], and Jascha Repp[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany — [2]Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany — [3]IBM Research - Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland

Functionalizing the tip of an Atomic Force Microscopy (AFM) with a single CO molecule has been shown to be a powerful tool to determine the geometric structure of individual molecules [1-3]. So far this technique was applied to molecules with only little deviations from a planar shape. We performed AFM measurements in a low temperature combined scanning tunneling and atomic force microscope with functionalized tips. We extract the geometric structure of a non-planar molecule from a 3D data set [4, 5]. Thermal annealing of the sample leads to an on-surface reaction with different products, the identification of which is exploited to support the structure assignment of the 3D molecular structure of the reactant [2].

[1] L. Gross, et al., Science 325, 1110 (2009)
[2] D. G. de Oteyza, et al., Science 340, 1434 (2013)
[3] N. Pavliček, et al., Phys. Rev. Lett. 108, 086101 (2012).
[4] F. Mohn, et al., Appl. Phys. Lett. 99, 53106 (2011)
[5] B. Schuler, et al., Phys. Rev. Lett. 111, 106103 (2013)

O 37.14 Tue 18:15 Poster A

**Influence of higher flexural modes in piezoresponse force microscopy** — ●Valon Lushta[1], Thomas Göddenhenrich[1], Bernhard Roling[2], and André Schirmeisen[1] — [1]Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35392 Gießen — [2]Physikalische Chemie,Philipps-MarburgUniversität Marburg, D-35032 Marburg

Piezoresponse force microscopy, based on contact resonance of the cantilever, is a useful tool for probing the local piezoelectric properties on ferroelectric materials. Dual AC resonance tracking and band excitation techniques have been used to investigate the local deformation and polarization of ferroelectric domains. Measurements are performed at different flexural eigenmodes of the cantilever. The results of local amplitude and phase hysteresis loops reveal, that an excitation of higher flexural modes is less sensitive to a parasitic non localized capacitive force contribution between cantilever and sample surface.

O 37.15 Tue 18:15 Poster A

**Role of the tip in photon emission from Au surfaces in Scanning Tunneling Microscopy** — ●Berk Zengin, Hakki Tunç Çiftçi, and Oğuzhan Gürlü — Istanbul Technical University, Istanbul, Turkey

Photon emission induced by tunnelling current has been studied by means of photon scanning tunnelling microscopy (pSTM) since the advent of STM. Several reports had been published on the proper conditions of photon emission from the tip-Au surface tunnel junction. It has been shown that the tip material and its geometry play a serious role on the emitted photons. Yet, the variations on the Au surface as well as the photon emission maps were mainly related to the surface conditions. Our results show that tip cleanliness is one of the key reasons in the observed topography as well as on the photon maps. Moreover, the tunnelling current induced electromigration is also one of the events that happen at relatively high tunnelling current values. By use of different tips and tip preparation procedures we have shown that on similar thermally evaporated gold films, different results can be obtained by pSTM. Our results show that the results attained with pSTM cannot be interpreted without proper tip calibration.

## O 38: Semiconductor Substrates

Time: Tuesday 18:15–21:00 Location: Poster A

O 38.1 Tue 18:15 Poster A

**Sulfur Dioxide Adsorption in Carbon Nanotube Studied by Molecular simulation and a Simple Analytical Model** — ●Yongbiao Yang, Mahshid Rahimi, Michael Böhm, and Florian Müller-plathe — TU Darmstadt, 64287 Darmstadt, Germany

Sulfur dioxide (SO2) is one of the main toxic gases which can result in acid rain, thus removing SO2 from atmosphere currently becomes an important subject both in industry and in science. Grand-canocical Monte Carlo method and a simple analytical model are used to understand the adsorption of SO2 onto bundles of 3D aligned double-walled carbon nanotubes (DWCNT) of different diameters and different intertube distances at 300 K. At molecular level, SO2 is found to adsorb to CNT with oxygen atoms nearer to CNT wall than sulfur atoms whether for inner or outer adsorption. It is also found condensation happens at a lower pressure compared to bulk case of SO2. For outer adsorption, the adsorption type changes from type I to type IV when intertube distance is increased from 0 nm to 2 nm. This trend is even more remarkable with CNTs of relatively larger diameter. Finally we show that the simulation data of adsorption isotherm can be well discribed by a simple analytical model.

O 38.2 Tue 18:15 Poster A

**Study of the ZnO surface by XSW: elucidating the position of adsorbed oxygens** — ●Antoni Franco-Cañellas[1], Jens Niederhausen[2], Martin Oehzelt[2,3], Tien-Lin Lee[4], Alexander Gerlach[1], Norbert Koch[2,3], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany — [2]Institut für Physik, Humboldt-Universität zu Berlin, Germany — [3]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, BESSY II, 12489 Berlin, Germany — [4]Diamond Light Source, UK

For its promising applications in optoelectronics and sensing devices, zinc oxide (ZnO) has attracted significant attention in the last decades. Of particular interest in this context are devices based on the combination of ZnO with different organic semiconductor materials. It is well known that for these heterostructures the characterization of the interface is of paramount importance to understand and tune the properties of the final device [1]. In this work we focus on the study of the ZnO surface, for different terminations, using the X-ray standing wave technique (XSW) [2] and photoelectron spectroscopy. Particularly, the adsorption site of the hydroxil (OH-) groups is resolved. These results will help to elucidate how the OH-groups affect deposited organic layers. Furthermore, they can provide information on surface-driven phenomena, which are specially important for ZnO nanostructures with high surface-to-volume ratio.

[1] Y. Xu et al. Phys. Rev. Lett., 111 (2013) 226802.
[2] A. Gerlach et al., in The Molecule-Metal Interface (eds N. Koch, N. Ueno and A. T. S. Wee), Wiley-VCH, Weinheim, Germany (2013).

O 38.3 Tue 18:15 Poster A

**First-principles study of covalent and noncovalent functionalization of single-walled carbon nanotubes with diisocyanates** — ●Jakub Goclon[1], Mariana Kozlowska[2], Pawel Rodziewicz[2], and Bernd Meyer[1] — [1]Interdisciplinary Center for Molecular Mate-

rials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg, Germany — [2]Institute of Chemistry, University of Bialystok, Poland

Using density functional theory (DFT) we investigated the covalent and noncovalent functionalization of (6,0) and (10,0) single-walled carbon nanotubes (SWCNTs) with 4,4'-methylene diphenyl diisocyanate (MDI) and toluene-2,4-diisocyanate (TDI) molecules. MDI and TDI are frequently utilized in the production of polyurethanes [1], which can be used in hybrid polymer–CNTs composites and coatings. Such hybrid materials are much more resistant to wear than the pure polymers [2].

The structural and electronic properties of MDI-SWCNT(6,0)/(10,0) and TDI-SWCNT(6,0)/(10,0) were scrutinized. We have also analyzed the changes in the electronic band structure of the SWCNTs caused by the amide bond formation after the covalent and noncovalent functionalization. Additionally, the MDI–MDI and TDI–TDI mutual interactions on the carbon nanotube surface were investigated.

[1] S. A. Madbouly, J. U. Otaigbe, *Prog. Polm. Sci.* **34**, 1283 (2009). [2] H.-J. Song, Z.-Z. Zhang, X.-H. Men, *Eur. Polym. J.* **43**, 4092 (2007).

O 38.4 Tue 18:15 Poster A

**Opening of subsurface dangling bond triplets via atomic manipulation** — Jan Berger[1,2], Evan Spadafora[1], •Pingo Mutombo[1], Pavel Jelinek[1,3], and Martin Švec[1] — [1]Institute of Physics, Academy of Sciences of the Czech republic, Prague, Czech Republic — [2]Czech Technical University, Prague, Czech Republic — [3]Osaka University,Osaka, Japan

Atomic manipulation of the delta-doped B:Si(111)-($\sqrt{3}\times\sqrt{3}$)R30° surface was performed using a low temperature nc-AFM based on the Kolibri sensor. Through a controlled vertical displacement of the probe, a Si adatom was removed in order to create a vacancy. We succeeded to place precisely a Si atom back into the vacancy site, thus showing that this process is completely reversible. The manipulations also lead to the rearrangement of the atoms at the tip apex by sharpening it, thus allowing for a deeper look into the vacancy site. It is shown that the removal of a Si adatom exposes subsurface Si dangling bond (DB) triplets, surrounding the substitutional B dopant in the first bilayer. DFT simulations reproduced the experimental findings and suggest that the tip is likely terminated by two Si atoms at the apex. Interestingly, the closing of the vacancy was possible only when the manipulation was performed with the tip placed off-center the vacancy site.

O 38.5 Tue 18:15 Poster A

**Characterization of Dy induced reconstructions on Si(111)** — •Frederic Timmer[1], Robert Oelke[1], Stephan Appelfeller[2], Henrik Wilkens[1], and Joachim Wollschläger[1] — [1]Physics Department, Osnabrück University, Germany — [2]Institute of Solid State Physics, TU Berlin, Germany

Epitaxial thin films of rare earth silicides are of particular interest because of their possible application as low-resistivity contacts to n-type Si [1]. Therefore the growth of Dy on Si(111) in the monolayer regime has been investigated in-situ by Spot Profile Analysis Low Energy Electron Diffraction (SPA-LEED), Surface X-Ray Diffraction (SXRD) and Auger Electron Spectroscopy (AES).

Dy coverages of 0.1ML - 3ML were deposited by Physical Vapor Deposition (PVD) at different substrate temperatures. A plethora of reconstructions were observed by SPA-LEED, including the ($2\sqrt{3}\times 2\sqrt{3}$), ($\sqrt{3}\times\sqrt{3}$) and ($1\times 1$) reconstructions known by literature [1]. In addition we observed a spot splitting for the ($2\sqrt{3}\times 2\sqrt{3}$)-spots due to the periodically arrangement of domain boundaries.

The in-situ SXRD studies were carried out at the ID03 beamline of ESRF. Dy was deposited by PVD on the Si(111) substrate at 600°C until the ($2\sqrt{3}\times 2\sqrt{3}$) reconstruction signal yielded maximum intensity. Subsequently 30 surface rods and 8 crystal truncation rods were recorded in order to determine the atomic structure of the reconstruction.

[1] I.Engelhardt et al., Surf. Sci. 600 (2006) 755-761

O 38.6 Tue 18:15 Poster A

**Point defects and diffusion on Bi2Te3 surfaces** — •Mert Taskin[1], Ilker Oztoprak[1], Dilek Yildiz[1], Carl Willem Rischau[2], Cornelis J. van der Beek[2], Alberto Ubaldini[3], and Oguzhan Gurlu[1] — [1]Istanbul Technical University, Istanbul, Turkey — [2]Ecole Polytechnique, Palaiseau, France — [3]Université de Genéve, Geneva, Switzerland

Bi2Te3 was shown to be a topological insulator besides being a thermoelectric material, yet the knowledge on the atomic scale defects and their effect on the local electronic structure is still incomplete. Bi2Te3 has rhombohedral crystal structure and bonds between the atoms of Bi/Te1 are the strongest in the lattice. In contrast, Te1/Te1 interface has just van der Waals bonds in between them. Consequently the crystals can be cleaved on this plane and the Te1 surface can be imaged with scanning tunneling microscopy (STM) with out need for further surface preparation. Despite its inertness, point defects were observed on the Te1 surface. In addition to these defects we have observed vacancy defects and clusters on the Te1 surface. In order to understand the nature of these defects, we performed time lapse STM imaging by means of which we have observed their diffusion. Moreover, bias dependent images have shown that the defects were not of single type.

O 38.7 Tue 18:15 Poster A

**Surface Analysis of MOVPE-prepared GaP(111)B** — •Peter Kleinschmidt[1], Pingo Mutombo[2], Oleksandr Romanyuk[2], Marcel Himmerlich[3], Weihong Zhao[1], Andreas Nägelein[1], Matthias Steidl[1], Agnieszka Paszuk[1], Sebastian Brückner[1], Oliver Supplie[1], Stefan Krischok[3], and Thomas Hannappel[1] — [1]Photovoltaics Group, Institute of Physics, Technische Universität Ilmenau, 98684 Ilmenau, Germany — [2]Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 00 Prague 6, Czech Republic — [3]Technical Physics I, Institute of Physics, Technische Universität Ilmenau, 98684 Ilmenau, Germany

We have investigated the MOVPE-prepared GaP(111)B surface by LEED, XPS, and STM as well as ab intio DFT. We obtained atomically resolved occupied-state STM images, characterized by large, atomically flat terraces. Most areas on these terraces exhibit no discernable order, in agreement with the ($1\times1$) LEED pattern we obtained. However, locally, the STM images also show ($\sqrt{3}\times\sqrt{3}$) and c($2\times4$) ordering. Our measurements indicate P-induced surface states. The different surface reconstructions were analyzed by ab initio DFT and relative surface formation energies of the Ga-rich and P-rich structures were derived. The most energetically favorable structures were used for STM image simulations and compared with the experimental STM images.

O 38.8 Tue 18:15 Poster A

**Ordered growth of hexagonal molecules on hexagonal surfaces: a new type of epitaxy?** — •Falko Sojka, Matthias Meissner, Tobias Huempfner, Roman Forker, and Torsten Fritz — Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany

We analyzed the growth of diverse monolayers of organic molecules with hexagonal symmetry on different hexagonal surfaces using coronene and hexa-peri-hexabenzocoronene (HBC). By compensating geometric distortions and other systematic errors in low-energy electron diffraction (LEED), high-precision determination of the epitaxial matrices using numerical fitting routines is feasible [1, 2]. The LEED studies are complemented by other methods like low temperature scanning tunneling microscopy (LT-STM) and differential reflectance spectroscopy (DRS) [3].

We found well-defined ordered structures which are, however, partially in contrast to the literature. Within error margins the lattice alignment cannot be assigned to any known type of epitaxy [4] and may therefore point towards a new type of epitaxy.

References: [1] F. Sojka et al., Rev. Sci. Instrum. 84, 015111 (2013).
[2] F. Sojka et al., Ultramicroscopy 133, 35-40 (2013).
[3] R. Forker et al., Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 108, 34-68 (2012).
[4] S.C.B. Mannsfeld et al., Phys. Rev. Lett. 94, 056104 (2005).

O 38.9 Tue 18:15 Poster A

**Nanostructuring and Dye-Functionalization of Diamond Electrodes for Photoelectrochemical Applications** — •Nina Felgen[1], Christo Petkov[1], Philipp Reintanz[2], Alberto Pasquarelli[3], Thomas Hantschel[4], Menelaos Tsigkourakos[5], Ulrich Siemeling[2], Johann Peter Reithmaier[1], and Cyril Popov[1] — [1]Institute of Nanostructure Technologies and Analytics, Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel, Germany — [2]Institute of Chemistry, Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel, Germany — [3]Institute of Electron Devices and Circuits, University of Ulm, Germany — [4]IMEC, Leuven, Belgium — [5]Instituut voor Kern- en Stralingsfysica, K.U. Leuven, Belgium

Diamond is a prospective electrode material for a number of applications providing efficient electron transport, high stability of electrolytic performance with time, a possibility for dye-sensitizing with photosensitive molecules, etc. Boron-doped diamond (BDD) films have been prepared by hot filament chemical vapor deposition (HFCVD) and structured by reactive ion etching with oxygen plasma applying a gold mask lithographically defined or composed of random droplets. Further, the nanostructured BDD surfaces were modified by O2 or NH3 plasma and grafted with different phthalocyanines. The modified and functionalized BDD were tested as electrodes for photoelectrochemical measurements.

## O 39: Heterogeneous Catalysis

Time: Tuesday 18:15–21:00 Location: Poster A

O 39.1 Tue 18:15 Poster A

**High-resolution X-ray photoelectron spectroscopy investigations of the reaction of $C_2H_4$ and $C_6H_6$ on carbide-modified Mo(110)** — •Udo Bauer, Christoph Gleichweit, Oliver Höfert, Christian Papp, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Carbide-modified molybdenum surfaces have been proposed as noble metal-free catalysts for a variety of reactions, among them the dehydrogenation of hydrocarbons. The modification of Mo surfaces by carbon changes their reactivity towards the behavior of Pt-group metals. Herein, we study and compare the adsorption and reaction of ethylene and benzene on both a thin and a thick carbide layer on Mo(110) in-situ using synchrotron based high-resolution X-ray photoelectron spectroscopy (HR-XPS). Near edge X-ray absorption fine structure (NEXAFS) measurements are used for the identification of the adsorption geometry of the intact molecules and their reaction intermediates, whereas complementary temperature programmed desorption (TPD) experiments revealed the hydrogen evolution on both surfaces. The reaction pathway of all systems was followed by temperature programmed HR-XPS, which enabled us to determine intermediate species during reaction. When comparing the data of both thin and thick carbide overlayers, we only found minor differences concerning the reactivity towards ethylene and benzene. The work was supported by the Cluster of Excellence 'Engineering of Advanced Materials' of the University Erlangen-Nürnberg.

O 39.2 Tue 18:15 Poster A

**Adsorption and Diffusion of Oxygen in Silver** — •Regina Wyrwich, Hendrik Schlomberg, Christian Maak, Florian Rott, Lars Bulthaupt, Linh Nguyen Thuy, and Joost Wintterlin — Ludwig-Maximilians-Universität, München, Germany

The heterogeneously catalyzed selective oxidation of ethylene over silver is a large scale industrial process. Many studies have investigated the oxygen adsorption on silver surfaces to identify the active species for this reaction. A central issue has been the question about a possible role of oxygen atoms on subsurface positions or dissolved in the bulk. We report about a study in which we have investigated exchange processes between surface and bulk oxygen. A home-built reactor system has been used to load polycrystalline silver foils or an Ag(111) single crystal with oxygen at pressures of up to 800 mbar. The sample was then analyzed by TDS. In addition, an UHV apparatus equipped with XPS and LEED was used to investigate the sample surface after loading with oxygen. Depending on the loading parameters, two oxygen species were detected and selectively prepared, the so-called 'electrophilic oxygen' with a desorption temperature of 720 K and an XPS O 1s binding energy of 530.2 eV and the so-called 'O-gamma' with a desorption temperature of >870 K and an XPS O 1s binding energy of 529.3 eV. The species could be located at the surface (electrophilic oxygen) and in the bulk (O-gamma). It was found that the two species do not grow independently from one another, but that the formation of the 530.2 eV-species depends on the amount of O-gamma present.

O 39.3 Tue 18:15 Poster A

**Zn segregation and AuZn alloy formation on Au/ZnO(000$\bar{1}$) model catalysts in methanol synthesis gases ($H_2/CO_2$)** — •Jan Martin, Joachim Bansmann, and R. Jürgen Behm — Institut of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

For methanol (MeOH) synthesis, $Cu/ZnO/Al_2O_3$ is the main catalyst in industrial applications. Although used since the 1960s, many investigations are performed on a fundamental understanding of the reaction. It was recently found, that metallic Zn species are present in the reaction and of importance in MeOH synthesis [1]. Au/ZnO catalysts, which are currently investigated in this reaction, showed a superior selectivity compared to Cu/ZnO at comparable reactions rates.

Here, we will focus on Au/ZnO(000$\bar{1}$) model catalysts and especially on the possible presence of metallic Zn species during MeOH synthesis. For this purpose, we monitored the development of the $L_3M_{45}M_{45}$ Auger peak, which is sensitive to changes in the Zn oxidation state, upon exposure to $H_2/CO_2$ gas mixtures (MeOH synthesis gas). Different from Cu/ZnO catalysts, where a clear relation was observed between metallic Zn species, the presence of Cu and reaction conditions, already the evaporation of Au onto ZnO(000$\bar{1}$) under UHV conditions leads to a chemical modification of the ZnO surface. Exposure to MeOH synthesis gas (200-500mbar at 240°C) also affects the chemical state of the ZnO(000$\bar{1}$) surface. Experimental results are presented for different preparations and MeOH synthesis conditions.

[1] S. Kuld et al., Angew. Chem. 126 (2014) 6051

O 39.4 Tue 18:15 Poster A

**The formox process: catalytic oxidation of methanol to formaldehyde** — •Marcos Rellán and Núria López — Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain

Methanol is an important source to the production of formaldehyde, one of the most important industrial and research chemicals of the world. Comprehension of this process is the first step to understand the catalytic oxidation of heavy molecular weight alcohols. Selectivity is the next frontier in research of new catalytic processes and Density Functional Theory (DFT) has become an essential tool to understand and control catalytic activity and selectivity. In this work, we have performed a DFT study of oxidation mechanism of methanol in $MoO_2$ and $MoO_3$ (formox process) to explain the experimental selectivity.

Some experimental studies concluded that $MoO_3$ can give a good yield and selectivity to formaldehyde under aerobic conditions. In the contrast, $MoO_2$ give a poor relationship between yield and selectivity in the same conditions. In anaerobic conditions the selectivity of $MoO_3$ to formaldehyde also is poor. We have found that the electronic structure stoichiometry controls activity and selectivity, and Mo-sites can be fine tuned to provide best yields.

O 39.5 Tue 18:15 Poster A

**Methanol Adsorption and Reaction on $SmO_x$/Pt(111) Systems Studied by TPD and IRRAS** — •jin-hao jhang[1], andreas schaefer[1], jason f. weaver[2], and marcus bäumer[1] — [1]Institute of Applied and Physical Chemistry, Center for Environmental Research and Sustainable Technology, University of Bremen, Germany — [2]Department of Chemical Engineering, University of Florida, USA

Samaria ($SmO_x$) as one of rare earth oxides has been considered as a promising oxide catalyst as it shows, for instance, high selectivity in the oxidative coupling of methane (OCM). Whereas other rare earth oxides such as ceria have been studied intensively, detailed investigations of the surface chemistry of $SmO_x$ are still lacking. Here we used methanol (MeOH) as a smart probe molecule by means of temperature programmed desorption (TPD) and infrared reflection-absorption spectroscopy (IRRAS) to study the surface chemistry of $SmO_x$ thin films which were grown on a Pt(111) substrate. TPD results show that CO and $H_2$ are main products of the MeOH reaction on $SmO_x$/Pt(111). Moreover, a cooperative effect by $SmO_x$ and the Pt substrate is only observed on the non-fully covered $SmO_x$/Pt(111). Surprisingly $CO_2$ as an unexpected product is also found, and a measurable amount of hydrogen is missing. IRRAS results confirm the existence of methoxy and formate species during MeOH decomposition on $SmO_x$/Pt(111) which indicates the domination of the dehydrogenation process. Additionally, monitoring the shift of the C-O stretch frequency provides information about the adsorption sites of methoxy on $SmO_x$ surfaces.

O 39.6 Tue 18:15 Poster A

**Heterogeneous Catalysis Driven by Piezoelectric and Pyroelectric Materials** — •Maximilian Sonntag, Mateo Ureña de Vivanco, Bianca Störr, Erik Mehner, Juliane Hanzig, Tilmann Leisegang, and Dirk C. Meyer — TU Bergakademie Freiberg, Institut für Experimentelle Physik, Leipziger Straße 23, 09596 Freiberg

Approximately 90 % of all chemical processes are based on heterogeneous catalysis.[1] Conventional catalysis is often limited to high temperatures like for ammonia synthesis in order to activate the catalyst. Nevertheless, the use of low temperature waste heat or vibrations can also enhance catalytic reactions. Pyroelectric materials can generate charges by converting heat, whereas piezoelectric materials can generate charges from vibrations. These coupling phenomena provide electrical charges for the redox reactions (piezocatalysis[2] and pyrocatalysis[3]).

Utilizing $LiNbO_3$, we present catalytic decolorization of organic and inorganic indicators. Oxidation of indigo carmine and reduction of permanganate take place in aquatic solution under ultrasonic vibration. Results show that several radical species may be formed in water during mechanical stimulation.

[1] J. A. Dumesic, G. W. Huber, M. Boudart, *Handbook of Heterogeneous Catalysis*, Vol. 1, 2nd ed., **2008**, p.1. [2] K.-S. Hong, H. Xu, H. Konishi, X. Li, *J. Phys. Chem. Lett.* **2010**, *1*, 997 and *J. Phys. Chem. C* **2012**, *116*, 13045; M. B. Starr, X. Wang, *Sci. Rep.* **2013**, *3*, Art. 2160. [3] E. Gutmann, A. Benke, K. Gerth, H. Böttcher, E. Mehner, C. Klein, U. Krause-Buchholz, U. Bergmann, W. Pompe, D. C. Meyer, *J. Phys. Chem. C* **2012**, *119*, 5383.

O 39.7 Tue 18:15 Poster A

**Suggestion to simulate energy dissipation via electron hole-pair – vibrational coupling using ab initio fitted TD-tight binding** — Michael Grotemeyer and •Pehlke Eckhard — Institut für Theoretische Physik und Astrophysik, Universität Kiel, Germany

The ab initio molecular dynamics simulation of electronically non-adiabatic effects during the interaction (scattering or sticking) of atoms and molecules with solid surfaces using time-dependent density functional theory is computationally extremely expensive, even if simple Ehrenfest dynamics is assumed for the motion of the nuclei. This makes the required statistical averaging over initial conditions of the incoming particles impractical. For strong electron hole-pair – vibrational coupling between molecules and a metal surface, when most of the initial vibrational energy is dissipated during the incoming part of the trajectory (i.e. before reflection at the surface) an approximative approach appears to be feasible. The energy transfer into electron hole-pair excitations is estimated from the integration of a simple time-dependent 3D tight-binding hamiltonian with parameters adapted to ab initio data. In the TB model also distinctly thicker slabs than usually applied in density functional computations can be used, which alleviates the effects of finite bath size in case the simulation time corresponds to several vibrational periods of the molecular vibration. Aspects of this approach will be discussed.

# O 40: Solid-Liquid Interfaces

Time: Tuesday 18:15–21:00 Location: Poster A

O 40.1 Tue 18:15 Poster A

**Towards the Simulation of the Water-Zinc Oxide Interface Employing Neural Network Potentials** — •Vanessa Quaranta, Tobias Morawietz, and Joerg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

The reliability of molecular dynamics and Monte Carlo simulations crucially depends on the quality of the underlying potential-energy surface (PES). In recent years, artificial neural networks (NNs) have emerged as a new method to provide accurate PESs for a variety of systems. NNs are flexible functions able to learn the topology of a PES from a set of reference electronic structure calculations. Here, we report first results for a NN potential based on density-functional theory constructed to describe the water-ZnO interface. We find that the NN potential is able to provide a wide range of structural and energetic properties of water, ZnO as well as of interface structures with close to first-principles accuracy.

O 40.2 Tue 18:15 Poster A

**Interaction of ionic liquids with alkali metal films** — •Mark Olschewski[1], René Gustus[1], Marcel Marschewski[2], Oliver Höfft[1], and Frank Endres[1] — [1]Institut für Elektrochemie, Technische Universität Clausthal, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany — [2]Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany

As RT-ILs exhibit good ion conductivities, high temperature stability and large electrochemical windows together with a good solubility for lithium salts, they are of potential interest as electrolyte for non flammable Li based batteries, like e.g. lithium/air batteries. To enable good cycle stabilities the interaction of electrolyte and lithium on electrode surfaces has to be investigated carefully. Here thin films of [C1C4Pyrr]$Tf_2N$ (1-butyl-1-methylpyrrolidinium bis[trifluoromethylsulfonyl]amide) and [OMIm]$Tf_2N$ (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) were evaporated on lithium and sodium surfaces, interactions subsequently were analyzed by XPS (x-ray photoelectron spectroscopy) and UPS (ultraviolet photoelectron spectroscopy). Both the cation and the anion react with the alkali metals, giving a series of decomposition products. The results exhibit instability of ionic liquids in presence of alkali metal and give a first insight in the differences of the reaction chemistry of pyrrolidinium cations and imidazolium ones.

O 40.3 Tue 18:15 Poster A

**Electrochemistry of natural polycrystalline vs natural single crystal magnetite** — •Diana Hötger[1], Santiago Herrera[1,2], Doris Grumelli[1], Benjamin Wurster[1], Peter Jacobson[1], Rico Gutzler[1], Ernesto Calvo[2], and Klaus Kern[1,3] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]Departamento de Química inorgánica, analítica y fisicoquímica, INQUIMAE, Univerdidad de Buenos Aires, Argentina — [3]Institute de Physique de la Matière Condensée, EPFL, Lausanne, Switzerland

Metal oxides have attracted a lot of interest in catalytic research as a cheap alternative to noble metal devices used in present applications. The electrochemistry of natural polycrystalline magnetite ($Fe_3O_4$) and their reactivity towards oxygen reduction reaction (ORR) has been widely studied [1,2]. Electrocatalysis is a surface dependent process, as surface composition, structure, and defects govern the electrochemical response. For a better understanding of the mechanisms and to improve the efficiency of electrocatalysts, it is crucial to work with very well defined surfaces. Electrochemistry of $Fe_3O_4(001)$ single crystal surfaces prepared under ultra-high vacuum (UHV) conditions has previously been reported [3]. Here we expand this research and compare the electrochemistry of UHV prepared $Fe_3O_4(001)$ single crystals with polycrystalline $Fe_3O_4$ by using a specially designed transfer system between UHV and electrochemical environment.

[1] P. A. Castro et al., J. Chem. Soc. Faraday Trans. 1996, 92, 3371.

[2] E. J. Calvo, Mater. Corros. 2014, 65, 345–350.

[3] R.Bliem et al., 2014, doi: 10.1126/science.1260556.

O 40.4 Tue 18:15 Poster A

**First-principles study of structures and growth processes at metalelectrodes** — •Xiaohang Lin and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Recently, the operation of an atomic-scale quantum switch has been demonstrated, which is controlled by an external electrochemical voltage applied to an independent gate electric field [1]. Pb, Au and Ag are used as candidate materials for the quantum switches. Still, the atomic processes and principles underlying the operation of the switch are not clear yet. Structural changes of the metal-water interface and deposition/diffusion on the metal electrodes in the presence of an electric field might be the elementary processes that are most likely involved in the switching process.

Hence, the self-diffusion and surface structures at the metal-water interface of Pb (Au and Ag) stepped surfaces have been studied using first-principles electronic structure calculations [2]. These studies show that diffusion across the steps is facilitated by the exchange mechanism. Furthermore, the influence of the presence of water on the properties of the metal electrodes will be discussed.

[1] F.-Q. Xie, L. Nittler, Ch. Obermair, Th. Schimmel, Phys. Rev. Lett. **93**, 128303 (2004).

[2] X. Lin *et al.*, Electrochim. Acta **140**, 505-510 (2014).

O 40.5 Tue 18:15 Poster A

**Model Studies on the Electrochemical Decomposition of [BMP][TFSA] on Au electrodes** — •Dorothea Alwast[1,2], Johannes Schnaidt[1,2], Yeuk Ting Law[1], and R. Jürgen Behm[1,2] — [1]Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — [2]Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany

Metal-air batteries like Li-air or Mg-air batteries offer high specific energies and are therefore studied intensively at present. Due to their special physical and chemical properties, the use of ionic liquids (IL) as electrolyte is of great interest. Therefore, the electrochemical stability of these ILs plays a key role for the use in batteries. To gain a better understanding of the stability of the IL n-buthyl-n-methylpyrrolidinium-bis(trifluoromethylsulfonyl) imide ([BMP][TFSA]), its decomposition on Au electrodes is studied using a novel differential electrochemical mass spectrometry (DEMS) set-up. Using cyclic voltammetry, decomposition products of the TFSA anion (m/z = 69, $CF_3^+$; m/z = 64, $SO_2^+$) are detected at positive (oxidative) potentials. In contrast, the decomposition products of the cation occur when applying negative (reductive) potentials. The implications of these findings on the mechanism of the IL's electrochemical decomposition as well as the influence of adding Li[TFSA], Mg$[TFSA]_2$ and $O_2$ to the system as model system for Li-air and Mg-air batteries, will be discussed.

O 40.6 Tue 18:15 Poster A

**Preparation, Characterization and Electrocatalytic Reactivity of Bimetallic $Pt_xAg_y$ and $Pd_xAg_y$ Nanocrystals** — •Isabella Weber[1], Sylvain Brimaud[1], José Solla Gullón[2], Juan M. Feliu[2], and R. Jürgen Behm[1] — [1]Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — [2]University of Alicante, Institute of Electrochemistry, 03080 Alicante, Spain

Bimetallic $Pt_xAg_y$ and $Pd_xAg_y$ nanoparticles with silver contents between 0-35 at% were prepared using water-in-oil microemulsion and seed-mediated growth synthesis, and characterized electrochemically by $CO_{ad}$ electrooxidation. The decrease of $CO_{ad}$ oxidation reactivity of the as-received samples with increasing nominal Ag content indicates an up-shift of the Pt (Pd) d-band center. In order to disentangle contributions from silver dissolution and $CO_{ad}$ oxidation, a combination of in-situ attenuated total reflectance Fourier-transform infra-red spectroscopy (ATR-FTIRS) and on-line differential electrochemical mass spectrometry (DEMS) was employed. Ensemble effects are held responsible for the change of the preferential adsorption configuration from bridge-bonded to linearly bonded $CO_{ad}$ for $Pd_xAg_y$ nanoparticles with Ag >20 at%. After electrochemical dealloying, the samples exhibit the reactivity of pure Pt (Pd) towards $CO_{ad}$ oxidation. An increase in the $CO_{ad}$ saturation coverage with increasing nominal silver content, however, additionally indicates a subtle electronic effect induced by Ag atoms within the bimetallic core of the dealloyed particles.

O 40.7 Tue 18:15 Poster A

**Interplay of Different Reaction Pathways in the Pulsed Galvanostatic Deposition of ZnO** — •Martina Stumpp, Christian Lupo, and Derck Schlettwein — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35390 Gießen

Zinc oxide ($ZnO$) is a promising electrode material for dye-sensitized solar cells (DSCs) and transparent electronics. Electrochemical deposition serves as a low-temperature and an environmentally-friendly technique to prepare crystalline $ZnO$ films even on temperature-sensitive substrates. Aqueous solutions of $Zn(NO_3)_2$ were used for electrodeposition of $ZnO$ on $Au$ microelectrodes of different shape under pulses of controlled current. Three significant stages were observed in potential-time curves. SEM revealed a correlation between a successively completed coverage of $Au$ by $ZnO$ and an abrupt transition of the deposition and rest potential to less negative values. The deposition time at which such a transition was detected depended not only on the amount of deposited $ZnO$ but also on the current density during electrodeposition and on the electrode geometry, pointing at the influence of different diffusion profiles of the reacting ions. In order to elucidate the role of different redox reactions in the course of electrodepositions of $ZnO$, measurements were also carried out in various reference electrolytes. The three stages in the potential were only seen for pauses which were equal or longer than the current pulse. The significance of each stage and the corresponding reactions is discussed.

O 40.8 Tue 18:15 Poster A

**Polymeric Phthalocyanine Sheets as Electrocatalytic Electrodes for Water-Splitting-Reactions** — •Clemens Geis, Simon Schneider, Frieder Müntze, and Derck Schlettwein — Institute of Applied Physics, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Gießen, Germany

Water splitting is an attractive way to convert alternating renewable energy sources to storable chemical fuels. Efficient electrocatalytic materials from abundant sources are needed for widespread applications. Aside from metals or metal oxides as electrode materials, molecular metal complexes are a promising approach for the oxygen evolution reaction. In this work, phthalocyanine metal complexes ($Mn, Fe, Co, Ni, Cu$) with polymerized ligands were synthesized via a CVD process on conductive substrates and used as electrocatalysts in an alkaline solution. Cyclic voltammetry with optical absorption spectroscopy performed *in operando* was applied to characterize the films. Chronoamperometry at positive potentials was used to study the performance of the films as electrocatalysts in the oxygen evolution reaction. Photoelectron spectroscopy was employed to analyze the elemental composition of the films and details of the atomic environment of the metal atoms.

O 40.9 Tue 18:15 Poster A

**The hydrophobic gap under high hydrostatic pressure conditions** — Florian Wirkert[1], •Michael Paulus[1], Julia Nase[1], Johannes Möller[2], Paul Salmen[1], Irena Kiesel[3], Benedikt Nowak[1], Christian Sternemann[1], and Metin Tolan[1] — [1]Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund, Germany — [2]ESRF - The European Synchrotron, 71 Avenue des Martyrs, F-38043 Grenoble, France — [3]Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France

We present an x-ray reflectivity (XRR) study on the influence of high hydrostatic pressure (HHP) on the structure of the so-called hydrophobic gap, a small electron depleted region at the interface between a hydrophobic surface and water. The structure of this gap has been discussed controversially throughout the last few years. In order to obtain a deeper insight into the gap's structural composition, we investigated the interface between a hydrophobic silicon wafer and ultrapure water at HHP conditions using XRR measurements. This technique is known to reliably resolve the shape (thickness, roughness, electron density) of thin layered structures on a molecular length scale.

The experiments have been performed at the synchrotron radiation facilities DELTA (Dortmund, Germany), Diamond Light Source (Didcot, UK) and ESRF (Grenoble, France). It is shown that only a small fraction of the hydrophobic gap is compressed under HHP. The main compression occurs between 1 bar and 1 kbar.

O 40.10 Tue 18:15 Poster A

**COMPARING THE INFLUECNE OF CONCENTRATION CONTROL BY STIRRING OR SONICATING ON THE SELF-ASSEMBLY AT THE LIQUID-SOLID INTERFACE** — •Nguyen Thi Ngoc Ha[1], Nguyen Doan Chau Yen[1], Kathrin Allmaier[1], Thiruvancheril G. Gopakumar[2], and Michael Hietschold[1] — [1]Institute of Physics, Solid Surfaces Analysis Group,Technische Universität Chemnitz, Germany — [2]Indian Institute of Technology, Kanpur 208016, India

Sonication has been successfully applied to change concentrations in organic solutions and this way to engineer different self-assembled molecular structures. We have demonstrated this using trimesic acid solved in different solvents: phenyloctane,[1] alkanoic acids[2,3] and alcohols[3]. Nevertheless there raised some fears that sonication might also chemically influence on these solutions. Therefore we compare here sonication and stirring as two different methods to increase concentration. We demonstrate here that stirring leads to the same series of adsorption pattern as obtained using sonication. The only difference seems to be that stirring times are much larger than corresponding sonication times to obtain the same structures. The corresponding self-assembled structures of TMA in those solvents (phenyloctane, octanoic acids and undecanol solvents) have been monitored by the ambient STM. The study demonstrates the key role of the external control parameter concentration via very simple methods: sonication or stir in the self-assembly.

O 40.11 Tue 18:15 Poster A

**Dynamics of water adsorption on Pt(111): ab initio molecular dynamics study** — •Maryam Naderian and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Ab initio molecular dynamics (AIMD) simulations based on periodic density functional theory (DFT) calculations using the dispersion-corrected RPBE-D3 functional [1] have been performed to study the dynamics of adsorption and sticking probability of water molecules on Pt(111). As typical for molecular adsorption, the sticking probability has been found to decrease as a function of the initial kinetic energy (IKE) of the impinging water molecules. Special attention has been paid to the role of the internal degrees of freedom of the water molecules upon impinging on the Pt substrate. Most of the IKE of the water molecule is initially transferred into the internal molecular degrees of freedom (vibrations and rotations) and later to the kinetic energy of the substrate atoms [2]. This energy redistribution leads to an efficient dissipation of the initial energy of water molecule which is crucial for understanding molecular adsorption dynamics.

To shed some light on the dynamics of the initial water structure formation on metal electrodes, we have performed AIMD simulations of water molecules impinging on Pt(111) that is already precovered by water. Again analysing the energy redistribution upon adsorption, the physical factors which are responsible for the water structure formation on a Pt surface are identified.

[1] S. Grimme *et al.*, J. Comput. Chem. **32**, 1456 (2011).

[2] Axel Groß *et al.*, J. Electrochem. Soc. **161**, E3015-E3020 (2014).

O 40.12 Tue 18:15 Poster A

**The Cu(110) Surface in Hydrochloric Acid Solution: Potential Dependent Surface Restructuring** — •Claudio Goletti[1], Gianlorenzo Bussetti[1,2], Adriano Violante[1,3], Beatrice Bonanni[1], Marco Di Giovannantonio[1], Giulia Serrano[1], Stephan Breuer[4], Knud Gentz[4], and Klaus Wandelt[4] — [1]Dipartimento di Fisica, Università di Roma Tor Vergata, Via della ricerca scientifica 1, 00133 Roma, Italy — [2]Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy — [3]Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7 D-10117, Berlin, Germany — [4]Institut für Physikalische und Theoretische Chemie, Wegeler Str. 12, 53115 Bonn, Germany

Using Cyclic Voltammetry (CV), Reflectance Anisotropy Spectroscopy (RAS) and in situ Electrochemical Scanning Tunneling Microscopy (EC-STM) we have studied the structure and structural transitions at a Cu(110) electrode surface in 10 mM HCl solution as a function of the applied electrode potential. At potentials >= -550 mV (vs. Ag/AgCl) chloride adsorption first leads to the formation of grooves followed by the growth of added stripes, both being aligned in the [001] direction as shown by EC-STM. This "faceting" is accompanied by a clear optical anisotropy peak in RAS centered at about 500 nm (2.48 eV) when the linearly polarized light is aligned along the [001] direction. Continuous monitoring of the RAS signal through a full CV cycle yields a hysteresis-like curve which supports a (reversible) two-step kinetics of the restructuring process in agreement with the CV- and STM-data.

O 40.13 Tue 18:15 Poster A

**Surface-Confined Polymerization on Au(111) in solution by pH control** — Marco Di Giovannantonio[1], Tomasz Kosmala[1,2], Giulia Serrano[1], Beatrice Bonanni[1], Nicola Zema[3], Daniele Catone[3], Stefano Turchini[3], Dario Pasini[4], Klaus Wandelt[2], Giorgio Contini[3], and •Claudio Goletti[1] — [1]Physics Department, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Roma, Italy — [2]Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstraße 12, D-53115 Bonn, Germany — [3]Istituto di Struttura della Materia, CNR, Via Fosso del Cavaliere 100, 00133 Roma, Italy — [4]Chemistry Department, University of Pavia, Via Taramelli 10 27100 Pavia, Italy

Surface-confined polymerization is a promising strategy to produce organic conjugated networks via a bottom-up approach. We have explored the Schiff-base reaction to produce polymers at a solid-liquid interface by changing the pH of an aqueous solution. Here, 4,4'-diaminostilbene dihydrochloride and terephtalaldehyde have been studied to create 1D conjugated polymers on an iodide-modified Au(111) surface from solution. The formation of the molecular superstructure as a function of pH was analyzed in situ by scanning tunneling microscopy (STM), and ex situ by x-ray photoelectron spectroscopy (XPS) using synchrotron radiation at Elettra (Trieste). We found clear differences between the polymerization being confined to the surface compared to that proceeding in bulk solution. Insights into the catalytic effect of the substrate on the reaction steps will be shown and discussed.

O 40.14 Tue 18:15 Poster A

**Investigating the Water-Titanium Dioxide Interface using SFG Spectroscopy** — •Simon Johannes Schmitt, Saman Hosseinpour, and Ellen H.G. Backus — Max-Planck-Institut für PolymerforschungAckermannweg 10, 55128 Mainz, Germany,

Since the world's fossil fuel supply will run out in a few decades, it is crucial to find cheap and environmentally friendly alternatives. Hydrogen is a good candidate, since it is obtainable by photocatalytic dissociation of water, when in contact with titanium dioxide surfaces, as has been discovered over 40 years ago. However, the fundamentals of the process are still not fully understood. To start, we measured Sum Frequency Generation (SFG) spectra of the water-$TiO_2$ interface. By overlapping a visible and an infrared laser beam in space and time on the sample the vibrational spectrum of the molecules at the interface can be obtained. We present data on $TiO_2$ single crystals with different facets and on sputtered thin films of various thicknesses. Moreover we will outline how we plan to use 2D-SFG to investigate the heterogeneity of the water molecules at the interface and time resolved measurements to follow the photo-induced dissociation of water at the interface in real-time.

O 40.15 Tue 18:15 Poster A

**Ab-initio molecular dynamics simulations on wet alumina/isopropanol solid/liquid interfaces** — •Paul Schwarz and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The solid/liquid interface of wet and hydroxylated $\alpha$-alumina/isopropanol is studied using ab-initio Car-Parrinello molecular dynamics (CPMD) simulations. The proper description of liquid isopropanol by our PBE+D2 setup was benchmarked by comparing molecular interaction energies with basis set extrapolated coupled-cluster CCSD(T) results. Furthermore, pair correlation functions and diffusion coefficients from CPMD simulations at different temperatures were compared to experiment. The liquid isopropanol was pre-equilibrated by MD runs with a classical force field. For the alumina slab three different surface models were taken into account: a termination with a full hydroxyl layer (**hyd**), an aluminum termination with dissociated water molecules to saturate undercoordinated surface sites (**w1**) and a third model with adsorbed water molecules between the OH groups of the **w1** structure (**w2**). In the CPMD simulations of the combined system of solid and liquid phase the recombination of dissociated water molecules is observed, especially in the case of **w2**. The mechanism and rate of these proton transfer processes is analyzed and we will discuss the influence of the surface model on the structure of the isopropanol liquid.

O 40.16 Tue 18:15 Poster A

**Influence of halide ions on the anisotropic growth of gold nanoparticles: Insight from molecular dynamics simulations** — •Santosh Meena[1], Andreas Henkel[2], and Marialore Sulpizi[1] — [1]Institute of Physics, Johannes Gutenberg University Mainz, Germany — [2]Physical Chemistry Department, Johannes Gutenberg University Mainz, Germany

Halides ions play a fundamental role in controlling the anisotropic growth of gold nanorods [1]. In particular while Br- is able to promote anisotropic growth in seed mediated synthesis, Cl- is known to induce a faster isotropic growth. We studied the adsorption mechanism of CTAB/CTAC surfactant mixtures at different concentration ratio, namely 1:0, 1:1 1:2 and 0:1 on different gold surfaces, namely the (110), (100) and (111). We use molecular dynamics simulations in order to provide a detailed description of the gold/surfactant/electrolyte solution in the growing solution [2]. we found that Br- is not only responsible for surface passivation, but also acts as the driving force for the CTAB micelle adsorption and stabilization on the gold surface. When Br- is partially replaced by Cl-, the surfactant layer become less and less dense. Finally when all the CTAB is replaced by CTAC no halides or micellar structure protect the gold surface and further gold reduction is possible uniformly on all the facets resulting a isotropic faster growth.

[1] S. E. Lohse, N. D. Burrows, L. Scarabelli,L. M. Liz-Marzan, C. J. Murphy, Chem. Mater. 2014, 26(1), 34 [2] S. K. Meena, M. Sulpizi, Langmuir 2013, 29(48), 14954

## O 41: Inorganic/Organic Interfaces

Time: Tuesday 18:15–21:00 Location: Poster B

O 41.1 Tue 18:15 Poster B

**LEED-IV-Analysis of large planar molecules on Ag surfaces** — •Ina Krieger[1,3], Johannes Ingenmey[1], Georg Held[2], Christian Kumpf[3], and Moritz Sokolowski[1] — [1]Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany — [2]Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, and Diamond Light Source, Didcot, OC11 0DE, UK — [3]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52428 Jülich, Germany

The atomic coordinates of large aromatic molecules adsorbed on surfaces are of great interest in the context of understanding the details of interaction and chemical bonding between the molecules and the substrate. Normal incidence X-ray standing waves (NIXSW) is considered to be the only technique which can provide this information with sufficient precision. Here we report on an alternative, namely the I(V)-analysis of low energy electron diffraction (LEED-IV) on two model molecules, which have been investigated by NIXSW before. The intention was to gain additional structural information by LEED-IV and to test the potential of LEED-IV for larger molecules.

We present results on PTCDA/Ag(100) showing an encouraging agreement with those from DFT and NIXSW studies. We obtained a good Pendry R-factor of 0.19 and derive additional structure information on the internal geometry of the molecules, in particular regarding vertical distortions of the perylene core, as well as the buckling of the substrate surface. In addition, we will present first results of a LEED-IV study on the adsorption of NTCDA on Ag(111). Supported by the DFG.

O 41.2 Tue 18:15 Poster B

**Confinement of surface state electrons by molecular self-assembled networks** — •Jun Li, Stefano Gottardi, Juan Carlos Moreno Lopez, Leonid Solianyk, and Meike Stöhr — Zernike Institute for Advanced Materials, University of Groningen, Netherlands

The controlled tuning of material properties on the nanometer scale is a central goal in nanoscience. Artificial nanostructures can be built atom by atom with scanning tunneling microscopy (STM). Corral structures built by this technique were shown to confine the surface state electrons and to locally modify the electronic surface properties. However, the manipulation process is impractical to change the electronic properties of the entire surface. On the other hand, molecular self-assembly offers the possibility to build well-ordered and defect-free nanostructures due to its intrinsic error-correction. By using different molecular building blocks, networks of different sizes and symmetries can be formed, which allows for tuning the electronic structure not only locally but surface wide. Here, we report on confining the surface state electrons of Au(111) by a porous molecular network, which was formed by self-assembled 1,3,5-benzenetribenzoic acid. STM and STS were performed to spatially characterize the electronic properties and to analyze the confinement of the surface state electrons in the pores of the molecular network

O 41.3 Tue 18:15 Poster B

**Comparison of Electronic Transport Measurements on Carbon Nanomembranes using Conductive Probe Atomic Force Microscopy and $Ga_2O_3$/EGaIn Top Electrodes** — •Emanuel Marschewski, Xianghui Zhang, Paul Penner, and Armin Gölzhäuser — Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld, Germany

Aromatic self-assembled monolayers (SAMs) can be cross-linked via irradiation with low energy electrons and convert to carbon nanomembranes (CNMs). We compare the electronic transport measurements on pristine and cross-linked self-assembled monolayer of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) on polycrystalline Au(111)/mica and Au/Si by using two techniques. The conductance along with friction force mapping of pattern arrays of non-cross-linked and cross-linked NBPT-SAMs is conducted by using conductive probe atomic force microscopy (CP-AFM), where the cross-linked regions clearly show lower conductance and lower friction force. The application of soft $Ga_2O_3$/EGaIn top electrodes allows for a quantitative analysis of conductance and transition voltages (TVs) of molecular junctions incorporating NBPT-SAMs and NBPT-CNMs, respectively. The conductance reduces more than one order of magnitude, despite the fact that the layer thickness reduces slightly upon electron irradiation. The reduction of the TV by $\sim 0.5\,\mathrm{V}$ is also found in the NBPT-CNM based junctions. In addition, a suppression of conductivity in CP-AFM measurements implies that there could exist a certain amount of highly conducting pinholes, which may explain the discrepancy between the two techniques.

O 41.4 Tue 18:15 Poster B

**On the adsorption behavior of the ionic liquid [BMP][TFSA] on $TiO_2$ (110), Cu(111) and Ag(111) and the interaction with Li** — •Maral Hekmatfar[1,2], Benedikt Uhl[1,2], Florian Buchner[1,2], Dorothea Alwast[1,2], and R. Jürgen Behm[1,2] — [1]Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — [2]Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany

The ionic liquid n-butyl-n-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide [BMP][TFSA] is particularly interesting for the application in electrolytes for Li-ion batteries. In this model study we aim at a detailed understanding of the electrode|electrolyte interface at the molecular scale. In a first step [BMP][TFSA] was vapor deposited on Cu(111), Ag(111) and $TiO_2$(110) under ultra-high vacuum conditions. At 80 K [BMP][TFSA] adsorbs intact on all surfaces which was verified by XPS measurements; different molecular arrangements were observed by STM, which will be discussed. Upon co-deposition of Li to mimic electrolyte, decomposition of mainly the anion into, e.g., LiF and $Li_2S$ was found on Cu(111) even at 80 K, while on Ag(111) and $TiO_2$ the IL is little or nearly not affected. Interestingly, on $TiO_2$(110) a new $Ti^{3+}$ species is observed in the Ti 2p region, which points toward the reaction of Li with the surface. In contrast, on Cu(111) we assume that a surface mediated decomposition of [BMP][TFSA] with Li takes place. As the electrode|electrolyte interface strongly determines the functionality of a battery, we believe that our model study gives very new insights.

O 41.5 Tue 18:15 Poster B

**Templated Protein Adsorption on $Cu_2N$** — •Sebastian Koslowski[1], Daniel P. Rosenblatt[1], Sabine Abb[1], Stephan Rauschenbach[1], Klaus Kern[1,2], and Uta Schlickum[1] — [1]Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart,Germany — [2]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne (EPFL),CH-1015 Lausanne, Switzerland

In recent investigations of the protein Cytochrome-C (CytC) deposited on metallic substrates by electrospray ion beam deposition (ES-IBD) it has been shown that the adsorption conformation of the unfolded protein is strongly influenced by surface mobility and the charge state of the gas phase protein ion [1]. The length and the flexibility of the peptide chain allows for a large conformational freedom in the gas phase as well as on homogenous surfaces. Here we present scanning tunneling microscopy (STM) investigations of the conformation of single CytC molecules deposited by ES-IBD on a $Cu_2N$ monolayer. $Cu_2N$ forms an adlayer with a square grid-like superstructure on the underlying Cu(100) substrate and acts as a template for the deposited proteins. This reduces their conformational freedom. We analyzed the surface conformations of CytC using models, which describe polymer adhesion on a grid with and without the assumption of memory of the gas phase conformation. The acquired data are best described by a model, in which elongated molecules try to reach the pure Cu rows with minimal movement.

[1] Z. Deng et al., Nano Lett. 12 (2012) 2452-2458

O 41.6 Tue 18:15 Poster B

**From hydrogen bonding to metal-coordination and back: porphyrin derivatives on Ag(111)** — •Kathrin Müller[1], Florian Studener[1], Nicolas Marets[2], Véronique Bulach[2], Mir Wais Hosseini[2], and Meike Stöhr[1] — [1]Zernike Institute for Advanced Materials, University of Groningen, The Netherlands — [2]Laboratoire de Tectonique Moléculaire, Institut Le Bel, Université de Strasbourg, France

The formation of well-ordered molecular networks on surfaces has gained increasing attention over the last decades from a fundamental point of view as well as for their potential application in organic devices like organic photovoltaics or organic field effect transistors. In our studies we used a porphyrin derivative, which is functionalized at the meso positions with two pyridyl groups and two pentyl chains in trans configuration. We used scanning tunneling microscopy (STM) in order to investigate the self-assembly of this molecule on Ag(111). For submonolayer to monolayer coverage, a close-packed rhombic network is observed, which is stabilized via hydrogen bonding. Upon deposition of Co atoms, a porous hexagonal network forms by coordination of the pyridyl groups to the cobalt atoms. Upon thermal annealing at 450 K the hexagonal network is transformed into a second close-packed structure. We assign these structural changes to the Co-metalation of the porphyrin core. For an excess of Co atoms the porous hexagonal network is stable up to 600 K. These results are compared to a similar porphyrin derivative with a Ni core.

O 41.7 Tue 18:15 Poster B

**Interaction of Ethylene Carbonate and Propylene Carbonate with Lithium on a Cu(111) Model Electrode** — •Maral Bozorgchenani[1,2], Florian Buchner[1,2], Johannes Schnaidt[1,2], Hanieh Farkhondeh[1,2], Benedikt Uhl[1,2], and R. Jürgen Behm[1,2] — [1]Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany — [2]Helmholtz Institute Ulm, 89081 Ulm, Germany

Li-ion battery electrolyte is composed of lithium (Li) salts and a mixture of solvents. Ethylene carbonate (EC) is the key solvent in Li-ion battery; however, EC is solid at room temperature (RT) and has to be solved in other solvents such as propylene carbonate (PC). In order to understand the role of these solvents in the formation of solid-electrolyte interphase (SEI), which determines the function of a battery, it is important to understand how the molecules interact with the electrode and with Li. In the present work, the adsorption behavior and reaction of EC and PC on a Cu(111) model electrode was investigated by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Fourier transformation infrared spectroscopy (FTIR) under ultrahigh vacuum (UHV) condition between 80 - 300 K. EC as well as PC desorb and decompose well below RT. The possible decomposition products as potential species of the SEI will be discussed. Additionally, co-adsorption of Li and EC / PC was investigated at 80 K. Li induced changes compared to EC and PC on bare Cu(111) are discussed.

O 41.8 Tue 18:15 Poster B

**Femtosecond time-resolved two-photon photoemission spectroscopy of C6H5X/D2O/Cu(111)** — •Ishita Agarwal, Isabella Avigo, Samad Abdul Sayed, Manual Ligges, Vesna Mikšić Trontl, Ping Zhou, and Uwe Bovensiepen — University of Duisburg-Essen, Duisburg, Germany

The electron dynamics at a metal-molecule interface is studied with time-resolved two-photon photoemission. We report here energies, workfunction changes and lifetimes of excited electronic states in amorphous $D_2O$/Cu(111) and coadsorbed $C_6H_5F$ systems after optical excitation with 3.8 eV + 1.9 eV femtosecond laser pulses. We observe a decrease in lifetime of the solvated electron state from $90\pm5$ fs for bare $D_2O$ to $60\pm5$ fs for coadsorbed $C_6H_5F$. Further, after a total estimated exposure to $0.5 \times 10^6$ photons per $C_6H_5F$ molecule, a workfunction change of $200 \pm 50$ meV was observed. Due to the absence of photoinduced workfunction changes in the single stack $D_2O$/Cu(111) and $C_6H_5F$/Cu(111), this change is concluded to be mediated by solvated electrons. Additional experiments on $C_6H_5Cl/D_2O$/Cu(111) were performed and an even larger photoinduced workfunction change was observed. The increase in workfunction is explained by the formation of $F^-/Cl^-$ as a photo-chemical dissociation product [1,2]. We conclude to have identified the charge transfer to $C_6H_5F$(/Cl) and a fingerprint of its photoinduced dissociation. Future experiments aim to systematically change the UV photon energy and the molecule acceptor level.

[1] S. Ryu, et al., *J. Am. Chem. Soc.*, **128**, 3500 (2006)
[2] M. Bertin, et al., *Faraday Discuss.*, **141**, 293, (2009)

O 41.9 Tue 18:15 Poster B

**Inelastic Excitations in Rare-Earth-Based Metal-Organic Complexes** — •Daniela Rolf[1], Paul Stoll[1], Tobias R. Umbach[1], Janina N. Ladenthin[1], Matthias Bernien[1], Constantin Czekelius[1,2], Wolfgang Kuch[1], and Katharina J. Franke[1] — [1]Freie Universität Berlin — [2]Heinrich-Heine-Universität Düsseldorf

Rare-earth atoms with a partially filled f shell exhibit interesting magnetic properties due to their large magnetic anisotropy. Embedded in a molecular environment, they are prime examples of single-molecule magnets. The Dy-(aquo)-tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanedionate) (Dy-t-TTB) molecule is a 3-dimensional complex, in which the Dy center is coordinated by three organic ligands. Within this complex, Dy has the oxidation state +3, leading to a total angular momentum of J = 15/2. Due to magnetic anisotropy, the degeneracy of the different $M_J$ levels of the ground state is partially lifted, allowing for transitions between the sublevels. Employing low-temperature STM we show that Dy-t-TTB on a Au(111) surface forms densely packed self-assembled islands. Tunneling spectra show an inelastic step at ±7.7 meV. To identify the origin of this feature, we compare to spectra taken on Gd-t-TTB, showing inelastic steps at the same energy. $Gd^{3+}$ has a half-filled f shell and is not expected to show any magnetic anisotropy. Hence, we conclude that the inelastic step is not due to transitions between the anisotropy-split spin states, but can be explained by the excitation of vibrations. Furthermore, we observe the tip-induced rotation of the upper ligand of Dy-t-TTB and Gd-t-TTB.

O 41.10 Tue 18:15 Poster B

**First steps on the way to a superconductive organic layer** — •Falko Sojka, Tobias Huempfner, Christian Zwick, Roman Forker, and Torsten Fritz — Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany

Since solid coronene was recently discovered to exhibit superconductive properties by intercalation with potassium, we investigated the potassium doping of ultrathin coronene layers in the (sub-) monolayer regime on Ag(111). The doping process was controlled using in situ differential reflectance spectroscopy (DRS) during the preparation. We show that before the formation of monoanions starts, a primary phase seems to appear which shows a stronger hybridization than the undoped molecules. Higher potassium concentration leads to the occurrence of dianions. Trianions or higher doped species were never observed. After stopping the potassium deposition the dianions decay into monoanions and into molecules in the primary phase. All species up to monoanions are stable and could be further investigated electronically via scanning tunneling microscopy / spectroscopy (STM, STS). While the potassium atoms are not resolved in the STM images, the doping process is evidenced by characteristic features in the related STS data we want to show. We also observed a new well-ordered structure of undoped coronene on Ag(111) for a coverage below 1ML determined by low energy electron diffraction (LEED) and STM.

O 41.11 Tue 18:15 Poster B

**Investigation of the growth of terephthalic and benzoic acids on Au(111) and oxidized Aluminum** — •Marcel Marschewski[1], Harun Tas[2], Oliver Höfft[3], Wolfgang Maus-Friedrichs[1], and Andreas Schmidt[2] — [1]Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany — [2]Institut für Organische Chemie, Technische Universität Clausthal, Leibnizstr. 6, 38678 Clausthal-Zellerfeld, Germany — [3]Institut für Elektrochemie, Technische Universität Clausthal, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany

The adsorption behavior of benzoic acids on metal interfaces is of high interest for metal-substrat interactions for catalysis and the construction of metal-organic frameworks. Here we present our results on the growth of thin films of 4-R-benzoic acid (R stands for hydroxyl-, methoxy-, propoxy-, pentoxy- and decyloxy-chains) and terephthalic acid (TPA) on Au(111) and oxidized aluminum. The adsorption was studied with metastable induced electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS(HeI)). For the monolayer on Au(111) we find hints for a flat orientation of the molecules. For the growth on an oxidized aluminum foil we suppose a more upstanding arrangement. The TPA molecules show a similar growth behavior for both surfaces.

O 41.12 Tue 18:15 Poster B

**A light-microscope for samples under ultra-high vacuum con-**

**ditions** — •Christian Marquardt, Nils Rohbohm, Alexander Paulheim, and Moritz Sokolowski — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstraße 12, 53115 Bonn, Deutschland

Talking about microscopy in the field of surface science, most people would think about scanning probe microscopy (SPM) or low energy electron microscopy (LEEM). However, there is less than a handful of publications dealing with conventional light microscopy and samples under UHV-conditions. Such a microscope can be a direct tool to image surfaces prepared inside the UHV. Besides, it may be adapted to observe fluorescence from molecules adsorbed on these.

We modified a Nikon incident light microscope and combined it with our UHV-chamber. Due to the requirements of UHV, which are vacuum and bake-out stability, we place all optical components outside the vacuum and observe our sample through a window at the end of a glass tube. Using this technique, we are able to image our sample at a pressure of $1{\cdot}10^{-10}$ mbar and temperatures down to 6 K directly after preparation.

First images of our Ag(100) crystal show a macroscopic corrugation of the surface with a typical structure size of 10-50 $\mu$m that is not expected from STM or LEED data. Supported by DFG.

O 41.13 Tue 18:15 Poster B

**Structural and electronic properties of metal-organic networks on Pb(111)** — •Gelavizh Ahmadi and Katharina J. Franke — Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

Metal-organic networks provide an interesting playground with flexible building blocks to explore different bonding structures, confinement of electronic states and magnetic properties. The latter are particularly interesting on superconducting substrates, where the competition of superconducting pairing and magnetic interactions can be detected with high energy resolution. Here we employ low-temperature scanning tunneling microscopy and spectroscopy to characterize the structure and electronic properties of metal-organic networks of the organic acceptor tetracyanonaptho-quinodimethane (TNAP) and metal atoms (Na, Pb). Adsorption of TNAP at 170 K leads to the formation of highly ordered hydrogen bonded islands. Annealing to room temperature results in a distinctly different arrangement, where four cyano-groups point towards each other. This bonding motif can only be explained by incorporation of Pb atoms into this windmill-like structure. Co-deposition of Na from NaCl leads to a rectangular structure, where the Na atoms are surrounded by four cyano-groups. This suggests the formation of an ionic bond by charge transfer of the 3s electron from Na to TNAP. However, we detect no sign of magnetic interaction with the underlying superconductor.

O 41.14 Tue 18:15 Poster B

**Reactive Coupling and Self-Assembly of Tetraphenylporphyrins on Cu(111)** — •Malte Zugermeier, Min Chen, Martin Schmid, and J. Michael Gottfried — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

Monolayer films of metalloporphyrins on metal substrates combine the chemical versatility of the tetrapyrrole macrocycle with a well ordered, quasi-crystalline arrangement of the molecules. The structural features and robustness of porphyrin layers may be further modified by the formation of strong chemical bonds between the individual molecules, for example by means of Ullmann coupling reactions. To understand the processes which are involved in the molecular arrangement before the formation of covalent porphyrin networks, we prepared (sub-)monolayers of nickel(II)-tetraphenylporphyrin (NiTPP) and its brominated counterpart nickel(II)-tetrakis-(4-bromophenyl)porphyrin (NiTBrPP) on Cu(111); the resulting layers were examined with XPS and STM. While the structure of NiTPP molecules on the Cu(111) surface is exclusively determined by van der Waals forces, the situation is more complex for NiTBrPP. There, the interaction with the Cu(111) surface results in the selective cleavage of all C-Br bonds already at room temperature, and accordingly, the coexistence of chemisorbed Br atoms and surface-stabilized radicalic moieties. The influence of the co-adsorbed Br atoms on the morphology and chemical state of the layers before and after Ullmann coupling will be discussed in comparison to the reference system NiTPP/Cu(111).

O 41.15 Tue 18:15 Poster B

**Dynamic control of STM-induced luminescence by a single molecule** — Christoph Grosse[1], Alexander Kabakchiev[1], Theresa Lutz[1], Romain Froidevaux[1,4], Frank Schramm[2], Mario Ruben[2,3], Markus Etzkorn[1], Uta Schlickum[1], •Klaus Kuhnke[1], and Klaus Kern[1,4] — [1]Max Planck Institut für Festkörperforschung, Stuttgart, Germany — [2]Karlsruhe Institut für Technologie, Eggenstein-Leopoldshafen, Germany — [3]Université de Strasbourg, Strasbourg, France — [4]Ecole Polytechnique Fédérale de Lausanne, Switzerland

The electronic states of a molecule in a double tunnel junction can control the plasmonic light emission. We locate a single Ir(ppy)$_3$ molecule adsorbed on a fullerene bilayer within the tunnel junction between metallic substrate and metallic tip of a low temperature (4K) ultra high vacuum scanning tunneling microscope. Using the ability to precisely control charging and discharging of the molecule, we demonstrate the gating of plasmonic luminescence. Two mechanisms contribute to the gating: A local one is due to the bias-controlled onset of tunnel current passing through the molecular electronic state. A second, non-local one, is due to the extended band bending in the fullerene layer in proximity to the charged molecule. We measure the delay between bias voltage pulses and light pulses and find a charge transfer time below one nanosecond. The double tunnel junction can be operated as a fast plasmon-emitting field-effect transistor with the molecule fulfilling the transistor function. The luminescence on/off ratio is of several orders of magnitude for a bias amplitude of only a few mV.

O 41.16 Tue 18:15 Poster B

**The adsorption geometry and electronic structure of TCNQ and TCNQ + Mn on Ag(001) and Cu(001) surfaces** — •Martin Graus[1], Vitaliy Feyer[2], Pascal Nigge[1], Giovanni Zamborlini[2], Robert G. Acres[3], Achim Schöll[1], Friedrich Reinert[1], and Claus M. Schneider[2,4] — [1]Universität Würzburg, Experimentelle Physik VII — [2]Research Center Jülich, 52425 Jülich, Germany — [3]Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy — [4]Universität Duisburg-Essen, 47048 Duisburg, Germany

Molecular beam deposited epitaxial monolayers of TCNQ on Cu(001) and Ag(001) were examined by LEED and photoelectron momentum mapping with respect to adsorption geometry and electronic structure. For Ag(001), two commensurate superstructures depending on the organic coverage were found, whereas the superstructure formed on Cu(001) is incommensurate. Subsequent deposition of Mn on top of TCNQ/Ag(001) creates a commensurate metal-organic array with long-range order. Comparing angle resolved photoemission data of the TCNQ LUMO with DFT calculations allows identifying the azimuthal orientation of the TCNQ molecules in the particular unit cells. We furthermore observe a charge transfer from the substrate resulting in filling of the TCNQ LUMO for all investigated interfaces. In case of Mn coadsorption the TCNQ HOMO and LUMO shift by 230 meV towards higher binding energy compared with TCNQ/Ag(001). A detailed analysis of the angle-resolved photoemission data showed no significant lateral band dispersion.

O 41.17 Tue 18:15 Poster B

**Ab initio thermodynamical study of thiolate adsorption on Au(111) using the vdW-DF-CX functional** — •Joakim Löfgren, Henrik Grönbeck, Kasper Moth-Poulsen, and Paul Erhart — Chalmers University Of Technology, Gothenburg, Sweden

Adsorption of alkylthiolates on Au(111) and the formation of self-assembled monolayers (SAMs) has been extensively studied for several decades and is important for many applications in e.g., sensing and nanofabrication. In the years, understanding of the interface and adsorption geometry has been elucidated by the combined efforts of experiment and density functional theory (DFT) calculations. One of the key challenges for DFT calculations of SAMs is the description of van-der-Waals type interactions, which are not captured in conventional exchange-correlation (XC) functionals. As a result, DFT studies have struggled to describe alkylthiolate SAMs with longer hydrocarbon chains. Here, we present DFT calculations based on the recently developed vdW-DF-CX functional, which properly accounts for dispersive interactions while providing an excellent description of both the late transition metals and covalently-bonded systems. We investigate several adsorption geometries suggested in the literature and show that the CX functional gives results that are consistent with experimental findings for short alkyl chains while, in contrast to e.g., generalized-gradient XC functionals, also yields excellent results for chain-chain and chain-substrate interactions for longer alkyl chains. We further examine the relative stability of striped and standing-up phases at different coverages as a function of the chemical environment.

O 41.18 Tue 18:15 Poster B

### ARPES study of the electronic structure and light-induced spin-state switching in Fe(II) spin-crossover films on Au(111)

— •Sebastian Rohlf[1], Eric Ludwig[1], Holger Naggert[2], Matthias Kalläne[1], Erik Kröger[1], Alexander Bannwarth[2], Arndt Quer[1], Kai Rossnagel[1], Lutz Kipp[1], and Felix Tuczek[2] — [1]Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel — [2]Institut für Anorganische Chemie, Universität Kiel, D-24098 Kiel

Coordinative Fe(II) complexes are model systems for organic molecules whose optical, electronic, and magnetic properties can be manipulated by external stimuli. Moreover, the temperature- and irradiation-dependent spin transitions observed in a number of these materials may provide a suitable testbed toward the development of future spintronic devices. Here, we present an angle-resolved photoelectron spectroscopy (ARPES) study of thin films of the spin-crossover complex $Fe(H_2bpz)_2(phen)$ adsorbed on Au(111) [1]. The photoemission results provide detailed insight into the connection between spin transitions and the valence electronic structure at different temperatures and varying irradiation conditions. In particular, evidence is found for a VUV-induced spin-state trapping effect at low temperatures. Furthermore, the results show that a high optical photon flux can stabilize the metastable high-spin state far above the LIESST transition temperature, allowing us to determine the relaxation rates after photoexcitation as a function of temperature.

[1] E. Ludwig *et al.*, Angew. Chem. Int. Ed. **53**, 3019 (2014).

O 41.19 Tue 18:15 Poster B

### Development of a Soft-Landing for Electrospray Deposition

— •Micha Elsebach[1], Maciej Bazarnik[1], Bernhard Bugenhagen[2], Annika Frank[2], Marc H. Prosenc[2], and Roland Wiesendanger[1] — [1]Institute of Applied Physics, University of Hamburg, D-20355 Hamburg, Germany — [2]Institute of Inorganic Chemistry, University of Hamburg, D-20146 University of Hamburg, Germany

”Electrospray Deposition (ESD)” is a technique to prepare clean samples of large molecules on metal substrates. Some of the molecules are fragmented when they land on the substrate. The ”Soft-Landing-ratio” gives the proportion of the intact landed molecules in comparison to the total number of deposited molecules.

In order to improve this ratio we used an electric field to slow down the molecules right before they hit the substrate. When the ionized molecules arrive at the sample they lose their charge. This induces a current flow from the sample to a readout. An electric circuit was implemented to provide a simultaneous measurement of this current and to apply a bias voltage onto the sample producing the electric deceleration field. The effect of this field is tested by depositing triplesalophene molecules on a Au(111)-surface. By the use of STM the SL-ratio was determined in dependence of the electric field strength.

It has been found that the SL-ratio can be improved by the deceleration field. Up to a threshold value of 7.5 eV per charge, for the energy of the molecules, it increases. Additionally, a simulation gives an insight into the electric field’s shape.

O 41.20 Tue 18:15 Poster B

### STM Imaging of Sequence Controlled Polymers

— •Ivan Pentegov[1], Bogdana Borca[1], Verena Schendel[1], Sabine Abb[1], Peter Wahl[1,4], Uta Schlickum[1], Stephan Rauschenbach[1], Tam Trinh[3], Jean-Francois Lutz[3], and Klaus Kern[1,2] — [1]Max-Planck-Institute for Solid State Research, D-70569 Stuttgart — [2]Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne — [3]Institut Charles Sadron, F-67034 Strasbourg — [4]School of Physics & Astronomy, University of St. Andrews, Fife KY16 9SS, St. Andrews

Sequence controlled polymers (SCP) have recently attracted great interest because of their possible application as information storage platform. The SCP can encode a secondary molecular structure which could be used to define the properties of the molecule. A long oligomer sequence consisting of just two single monomers, which could be associated with a «0»and «1»bit is one possible way to realize SCP. The read-out of such a memory device presents a challenge on the atomic scale. Scanning Tunneling Microscopy (STM) is a promising nondestructive approach providing the necessary spacial resolution. We deposited several oligotriamines (OTA), each containing 3 monomers on a Cu(100) surface with electrospray Ion Beam Deposition (ES-IBD) technique under ultra-high vacuum conditions and transfered it in a vacuum suitcase to a low temperature STM, to probe the sequence of monomers in OTA and study its impact on properties of the whole oligomer chain as conductivity and structure. We were able to distinguish between the «1»and «0»monomer and observed that each OTA adsorbs in 2 different conformations on the surface.

O 41.21 Tue 18:15 Poster B

### Modelling X-ray Photoemission Spectra using Density Functional Theory

— •Thomas Christoph Taucher[1], David Alexander Egger[1,2], Michael Zharnikov[3], and Egbert Zojer[1] — [1]Institute of Solid State Physics, Graz University of Technology, NAWI Graz, Austria. — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Israel. — [3]Applied Physical Chemistry, Heidelberg University, Germany.

In this contribution, we investigate the applicability of slab-type density functional theory-based band structure calculations to quantitatively model X-ray photoemission (XPS) core-level shifts at metal-organic interfaces. Applying the GADGET [1] tool in conjunction with the Vienna Ab Initio Simulation Package (VASP) [2], we compare the performance of the initial state approach (neglecting screening effects) and the final state approach (with screening). Furthermore, the contribution of chemically induced shifts versus electrostatic effects to the overall position of a photoemission line is investigated. The simulations are done mainly for partially fluorinated alkylthiolates on a Au(111) surface for which high-resolution XPS experiments [3] reveal five distinct features in the energy range of the C 1s core levels. Overall, very good agreement with the available experimental data is obtained supporting the original assignment of the observed peaks.

[1] T. Bučko, J. Hafner, and J. Ángyán, J. Chem. Phys., 2005, 122, 124508/1-10. [2] G. Kresse and J. Hafner. Phys. Rev. B, 1993, 47:558. [3] Hao Lu et al., J. Phys. Chem. C, 2013, 117, 18967-18979.

O 41.22 Tue 18:15 Poster B

### Crystallization of Tris-HCl on gold and mica surfaces

— •Seyma Nayir, Merve Altay, Toprak Ayaz, Ilker Oztoprak, and Oguzhan Gurlu — Istanbul Technical University, Istanbul, Turkey

Tris molecule crystallizes in the orthorhombic system with a layered structure. Previously we have shown that precipitates from Tris-EDTA-HCl buffer solution crystallize on Au surfaces by forming hexagonal structures. We had shown that Tris-HCl, a component of Tris-EDTA-HCl buffer solution, was the main reason of such crystallites. In this study we investigated the crystallization behavior of Tris-HCl on mica, Au/mica and Au/Cr/mica surfaces from different solutions with various molarities. The samples were prepared by drop-casting of the solution on to surfaces and they were investigated by optical and probe microscopy techniques. Our data indicated that surface roughness directly affects the crystallization behavior of Tris-HCl from the drying droplet, and formation of hexagonal structures depends on the roughness and hydrophobicity of the surfaces. We have observed that the crystallization starts mostly on the rough edges/surfaces and the completed crystallites cover the underlying surface roughness totally. On the other hand we rarely observed hexagonal crystals on initially flat and smooth gold surfaces while they formed on freshly cleaved mica surfaces. We speculate that formations of such structures are strongly related to the electrostatic landscape of substrates used which we investigated by means of Kelvin Probe Microscopy.

O 41.23 Tue 18:15 Poster B

### Optical, electronic, and structural properties of lead phthalocyanine on graphene

— •Matthias Meissner[1], Noriaki Kawakita[2], Christian Zwick[1], Andreas Masek[1], Takashi Yamada[2], Hiroyuki S. Kato[2], Roman Forker[1], Toshiaki Munakata[2], and Torsten Fritz[1] — [1]Friedrich Schiller University, Institute of Solid State Physics, Jena 07743, Germany — [2]Department of Chemistry, Graduate School of Science, Osaka University, Osaka 560-0043, Japan

Lead phthalocyanine (PbPc) thin films on graphite have shown remarkable electronic behavior in ultraviolet photoelectron spectroscopy (UPS) and two photon photoemission (2PPE) measurements [Phys. Rev. B 77, 115404 (2008), Phys. Rev. B 75, 121305 (2007)]. Interestingly, PbPc exhibits a strong electronic intermolecular interaction resulting in a split of the highest occupied molecular orbital (HOMO) in layers of more than one monolayer. We present a detailed analysis of the thickness-dependent optical absorption of PbPc on graphene using differential reflectance spectroscopy (DRS). Additionally, the evolution of the film structures for various film thicknesses was determined by low energy electron diffraction (LEED) and low temperature scanning tunneling microscopy (LT-STM), refining the structural models for a range of substrate temperatures and coverages. Our findings are discussed in relation to the well-established electronic structure of this system. By means of scanning tunneling spectroscopy (STS) we found indications for a splitting of the lowest unoccupied molecular orbital for PbPc monolayer domains similar to 2PPE results.

O 41.24 Tue 18:15 Poster B

**Unveiling the Structure Evolution of CO Adsorption on Ru(0001) and O/Ru(0001) by High-Resolution STM** — •Qiwei Chen and Kai Wu — BNLMS, College of Chemistry and Molecular Engineering, Peking University, Beijing, China

CO adsorption on metal/metal oxide is one of the most basic and extensively focused questions in the study of gas-solid interaction. It serves as fundamental background for many related heterogeneously catalytic and electrochemical processes. Here, we present a scanning tunneling microscope (STM) study of CO adsorption on both bare and oxygen pre-adsorbed Ru(0001) surface. With the aid of CO modified tip, the structure evolution of CO adsorption on bare surface is unambiguously resolved from individual molecule to (<root>3*<root>3)-R30o structure and finally to the (2<root>3*2<root>3)-R30o superstructure. On oxygen pre-adsorbed surface, CO adsorption is induced to form (2*2) structure by the preformed structure of oxygen. It is also suppressed by oxygen adsorption that leads to a much lower saturation coverage at room temperature. Our real time investigation unveils scheme of CO adsorption on Ru(0001) and O/Ru(0001) at various coverage in ultrahigh vacuum condition.

O 41.25 Tue 18:15 Poster B

**Investigation of molecular hydrogen in a tunneling junction using STS** — •Simon Röger, Matthias Stocker, and Berndt Koslowski — Universität Ulm, Ulm, Germany

Functionalization of probes is widely used in Scanning Probe Microscopy to enhance the spatial resolution of the instrument. This is especially important when determining the intramolecular structure of adsorbed molecules. In Scanning Tunneling Microscopy, molecular hydrogen physisorbed at the sample surface can be exploited to enhance the lateral contrast greatly. However, the physical origin of that phenomenon is not really understood, yet. We use Scanning Tunneling Spectroscopy to elucidate the specific influence of hydrogen on tunneling electrons. We speculate that the hydrogen modifies the electromagnetic environment of tunneling electrons by its dynamic properties.

O 41.26 Tue 18:15 Poster B

**Sythesis and characterization of bulk heterojunction solar cells based on nanoporous templates** — •Sven Hilke[1], Stefan Ostendorp[1], Christian Strassert[2], and Gerhard Wilde[1] — [1]Institut für Materialphysik, WWU Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany — [2]Physikalisches Institut, WWU Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

The well-known system ZnPc:C60 (Zn-Phthalocyanine:Fullerene) as a model system of bulk-heterojunction solar cells has been chosen to analyze the effect of a nanoporous pre-structuring on the applicability of the resulting hetero molecular mixture. In this context, the basis of the pre-structuring are Anodic Aluminum Oxide (AAO) membranes made of aluminum oxide constructed by electrochemical processes. The thermal deposition of the ZnPc and C60 is done in an HV-environment so that clean layers are generated and precipitate in the membrane. Obviously, the pre-structuring directly influences the morphology on the nanometer scale. The presented work consists of the controlled growth of the nanoporous templates to obtain regular pore structures with equal and uniformly distributed surface area in the hetero intersection. In addition, every single nanopore is individually functional so that the failure of a single nanopore does not cause the destruction of the whole solar cell because each pore is able to operate by itself. Optical and electrical characterizations are used to analyze the obtained structures.

O 41.27 Tue 18:15 Poster B

**Diindenoperylene film formation on Cu(111)** — •Hazem Aldahhak, Wolf Gero Schmidt, and Eva Rauls — Universität Paderborn, Warburger Str. 100, 33098 Paderborn

The formation of diindenoperylene (DIP) thin films on metal substrates has been intensively investigated in the context of the miniaturization of organic optoelectronic devices, due to the high charge carrier mobilities, good film forming properties and thermal stability of the molecules [1, 2]. Thereby an interesting, terrace *width dependent adsorption characteristics has been observed on Cu(111): On narrow terraces (<15nm), the DIP molecules assemble in a co-directionally oriented adsorption pattern, the symmetry of which is not dictated by the hexagonal substrate symmetry [3]. On wider terraces, in contrast, completely different adsorption patterns with a short-range order determined by the underlying substrate are observed. We performed first principles calculations and investigated the balance between intermolecular and molecule-substrate interactions of DIP molecules on planar surfaces and near step-edges. A detailed analysis of the potential-energy surface is presented. Our calculations show a strong influence of the substrate on the geometric and the electronic properties of single molecules and indicate an important role of the step-edges for molecular self-assembly and film growth.

[1] Zhang et al., Surface Science, 603(2009) 3179. [2] De Oteyza et al., Journal of Physical Chemistry C 112, 18 (2008) 7168. [3] De Oteyza et al., Phys. Chem. Chem. Phys. 11, 8741 (2009).

O 41.28 Tue 18:15 Poster B

**STM Study of the structural formation of cobalt naphthalocyanine on Au(111)** — •Lothar Brosda and Carsten Westphal — Fakultät Physik - Technische Universität Dortmund, Otto-Hahn-Str. 4, D 44221 Dortmund

The class of phthalocyanine (Pc) and its derivates such as naphthalocyanine (Nc) has received considerable attention within the recent years. Especially the tunability of their electrical and optical properties via a central metal atom provides promising results for their integration in organic devices like light-emitting diodes, thin film transistors, solar cells, or single molecule electronic devices. The performance of such a device is particularly dependent on the quality of the self-assembled monolayer (SAM) and the metal-organic interface. Therefore, a detailed knowledge about the adsorption and the structural formation of the molecules on different substrates is required. Here, the CoNc SAMs were prepared via evaporation under ultra high vacuum (UHV) conditions and investigated by means of room temperature scanning tunneling microscopy (RT-STM). On this poster our results of the structural formation of CoNc will be discussed.

O 41.29 Tue 18:15 Poster B

**Self-assembled monolayers of shape-persistent macrocycles on graphite: interior design and conformational polymorphism** — Joscha Vollmeyer, Friederike Eberhagen, Sigurd Höger, and •Stefan-Sven Jester — Rheinische Friedrich-Wilhelms-Universität Bonn, Kekué-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Three shape-persistent naphthylene-phenylene-acetylene macrocycles of identical backbone structures and extraannular substitution patterns but different (empty, apolar, polar) nanopore fillings are self-assembled at the solid/liquid interface of graphite (HOPG) and 1,2,4-trichlorobenzene. Submolecularly resolved images of the resulting two-dimensional crystalline monolayer patterns are obtained by scanning tunneling microscopy. A concentration-dependent conformational polymorphism is found, and open and more dense packing motifs are observed. For all three compounds alike lattice parameters are found, therefore the intermolecular macrocycle distances are mainly determined by their size and symmetry. This is an excellent example that the graphite acts as a template for the macrocycle organization independent from their specific interior. [1] J. Vollmeyer, F. Eberhagen, S. Höger, S.-S. Jester *Beilstein J. Org. Chem.* **2014**, *10*, 2774.

O 41.30 Tue 18:15 Poster B

**Quantum interference in tunneling through a molecular Kondo system** — Isabel Fernandez-Torrente[1], •Michael Ruby[1], Tobias R. Umbach[1], Benjamin W. Heinrich[1], Jose I. Pascual[2], and Katharina J. Franke[1] — [1]Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]CIC nanoGUNE and Ikerbasque, Basque Foundation for Science, Tolosa Hiribidea 78, Donostia-San Sebastian 20018, Spain

The Kondo effect results from a virtual spin scattering process between an unpaired spin of a magnetic impurity and the surrounding spins of the conduction electrons. This leads to a sharp resonance around zero bias in Scanning Tunneling Spectroscopy (STS) spectra at the location of the unpaired spin. Its line-shape depends on the interference between different tunneling pathways in the tip-impurity-surface junction. It is described by a Lorentzian curve for the case of a preferential tunneling into the Kondo state, and shows an increasing asymmetry for higher contributions of direct tunneling paths into the surface.

A prerequisite to study the variation of the line-shape in a molecular network is to have a single electron in a delocalized orbital. An ideal model system for this is a charge transfer monolayer formed by Na atoms and TNAP (tetracyanonaphtoquinodimethane) molecules on an Au(111) surface. The electron donated by the Na atoms is localized in the singly occupied molecular orbital (SOMO) of the acceptor TNAP. We observed intramolecular changes in the shape and intensity of the resonance along the TNAP backbone, with a symmetry change at the nodal planes of the SOMO.

O 41.31 Tue 18:15 Poster B

**Photoswitching Kinetics of Azobenzene SAMs on Gold**(111) — •Thomas Moldt, Daniel Przyrembel, Wibke Bronsch, Larissa Boie, Daniel Brete, Cornelius Gahl, and Martin Weinelt — Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Mixed self-assembled monolayers (SAMs) formed of azobenzene-functionalized alkanethiols and alkanethiol spacers show reversible photoisomerization [1]. Here we examined the photoisomerization kinetics of that system using near edge X-ray absorption fine structure and optical differential reflectance spectroscopy. We determined the photoisomerization cross sections as well as the thermal *cis-trans* isomerization rate and estimated the ratios of *trans* vs. *cis* components in the photostationary states. While in the dark the *cis* isomer is stable for hours under ambient atmosphere, in vacuo it switches back within minutes.
[1] Moldt et al., submitted.

O 41.32 Tue 18:15 Poster B

**Including depolarization effects in molecular dynamics simulations of self-assembled monolayers** — •Iris Hehn[1], Manuel Vieider[1], Otello M. Roscioni[2], Swen Schuster[3], Michael Zharnikov[3], Claudio Zannoni[2], and Egbert Zojer[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria — [2]Dipartimento di Chimica Industriale ”Toso Montanari”, Università di Bologna, Italy — [3]Applied Physical Chemistry, Heidelberg University, Germany

In a regular, ordered arrangement of molecules with aligned electric dipole moments depolarization effects take place and the individual molecular dipoles get reduced. This effect can be quite significant often reducing dipole moments to a small fraction of their original values. Depolarization should also be considered, when determining the non-bonding Coulomb interactions in molecular dynamics (MD) simulations, which are, however, typically based on calculating atomic charges of isolated molecules. Instead, to account for the depolarization we calculate the atomic charges for a molecule surrounded by a cluster of point charges that reproduces the electric field in the self-assembled monolayer (SAM), where the embedding charge distribution has to be determined self-consistently. In a second self-consistency cycle also the geometry of the molecules in the SAM is optimized considering the depolarized charge distribution in the MD runs. We test our approach on SAMs consisting of cyano-substituted biphenylthiol and a mid-chain ester functionalized alkanethiol, which differ both in the rigidity of the backbones and the orientation and location of the dipoles.

O 41.33 Tue 18:15 Poster B

**Structural and Electronic Properties of Thiophene-based Supramolecular Architectures on the Metal Surface** — •Zechao Yang[1,2], Katharina J. Franke[1], and Jose I. Pascual[1,3] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Department für Physik, Universität Erlangen-Nürnberg, Erwin-Rommel-Straße 1, 91058 Erlangen, Germany — [3]CIC nanoGune, 20018 Donostia-San Sebastián, Spain

We investigated the structural and electronic properties of dicyanovinyl-hexathiophenes (DCV6T), a prototype molecule for organic electronics, on Au(111) by using low temperature STM and AFM. DCV6T self-assembles in organic islands and chains simultaneously, stabilized by hydrogen bonding. Interestingly, the molecule is deformed to an energetically unfavorable configuration by the intermolecular interaction upon self-assembly of chains, which can be interpreted by the *Induced Fit Theory*. Moreover, the intermolecular hydrogen-bonds induce an energetic downshift of the lowest unoccupied molecular orbital of molecules within assemblies compared to isolated molecules on the surface. In addition to the organic motifs, metal-organic chains with incorporation of Au atoms are also formed. Here, the coordination modifies the molecular orbital energy alignment and spatial distribution within individual molecules depending on the bonding structure. Our results demonstrate that one can manipulate the molecular structural configuration and electronic geometry by tuning its chemical environments with site-specific.

O 41.34 Tue 18:15 Poster B

**Ultrafast Exciton Dynamics in Thin Sexithiophene Films** — Wibke Bronsch, Malte Wansleben, Kristof Zielke, •Cornelius Gahl, and Martin Weinelt — Freie Universität, Berlin, Deutschland

Sexithiophene (6T) is one of the model systems for organic semiconductors. Therefore we are interested in the details of exciton formation and decay in thin 6T films [1]. As it is known the S1 absorption band of sexithiophene strongly depends on the mutual orientation of the molecules [2]. This allowed us to study the coverage-dependent orientation of 6T on the Au(111) surface by means of UV-vis spectroscopy. Following up these results we investigated the influence of the excitation energy on the exciton dynamics in this system by means of two-photon-photoemission spectroscopy.

[1] Varene et al., Phys. Rev. Lett. 109 (2012), 207106
[2] Egelhaaf et al., Synthetic Metals, 61 (1993), 143

O 41.35 Tue 18:15 Poster B

**Tuning Molecular Electronic ”Set Screws” to Realize Deep-Blue Triplet Emitters - an STM/STS study** — •Pascal Raphael Ewen[1,3], Jan Sanning[1], Nikos Doltsinis[2], Cristian Alejandro Strassert[2], and Daniel Wegner[3] — [1]Physikalisches Institut & CeNTech, Münster, Germany — [2]Institut für Theoretische Physik, Münster, Germany — [3]Institute for Molecules and Materials, Nijmegen, The Netherlands

State-of-the-art organic light emitting diodes (OLEDs) are still under intense investigation both in fundamental research and development as challenges, e.g. efficient deep-blue emitters, are still unsolved. Moreover, the physical and electronic behavior on the nanoscale after thermal sublimation at the molecule-substrate interface is often unknown but can drastically determine the device performance. Using low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) we study the adsorption and electronic structure of new types of Pt(II) complexes on Au(111). These molecules exhibit photoluminescent quantum yields up to 65% and are used in prototype devices. By mapping frontier orbitals of systematically varied organometallic complexes we are able to evaluate and control the impact of the ligands on the HOMO-LUMO gap which basically determines the emitted wavelength. Our findings provide a strategy to characterize and tailor organometallic molecules with targeted properties. Furthermore, we show that potential dissociation during the deposition is an important issue.

O 41.36 Tue 18:15 Poster B

**Self-assembly of thienothiophene based molecules and $C_{60}$ on Au(111)** — •Julia Läger[1], Christian Lotze[1], Nils Krane[1], Lei Zhang[2], Alejandro L. Briseno[2], and Katharina J. Franke[1] — [1]Freie Universität Berlin, Department of Physics, Berlin, Germany — [2]University of Massachusetts, Department of Polymer Science and Engineering, Amherst, USA

Thiophene-containing molecules and fullerenes can form a donor-acceptor heterojunction for use in organic solar cells. The charge transfer between the two compounds and thus the efficiency depends on the interface of the junction and the morphology of the molecules on the surface.

Submonolayer of BTTT were adsorbed on Au(111). We used a combined LT-STM and AFM to examine the resulting structure. We observed two ordered, planar phases and molecular configurations: a windmill-like arrangement with interdigitation of the dodecyl chains on areas with high coverage, and a parallel alignment with lower molecular density and closer proximity of the thiophene rings. The major contribution to the self-assembly is likely to be van der Waals interaction between the alkyl chains. Two isomers with different configurations of the sulfur atoms could be identified in STM and AFM images. Subsequently, we deposited $C_{60}$ on the submonolayer preparation and find islands on clean Au(111) as well as on the BTTT islands.

O 41.37 Tue 18:15 Poster B

**Spectroscopic study of self-assembled monolayers on a Co(0001) surface** — •Runyuan Han, David A. Duncan, Johannes Bauer, Peter Feulner, and Francesco Allegretti — Physics Department e20, TU München, Germany

Self-assembled monolayers (SAMs) are systems of high technological relevance and thiolate-bonded SAMs on gold and other coinage metal surfaces have been regarded as prototypical systems for fundamental understanding [J.C. Love et al., Chem. Rev. 105, 1103]. Currently, there is an increasing demand for application of SAMs on more reactive transition metals, such as Pt, Ni and Fe [Z. Mekhalif et al., Langmuir 19, 637; P. G. Hoertz et al., J. Am. Chem. Soc. 130, 9763], however the increased strength of the sulfur-metal interaction poses strong limitations to the stability of these systems. Here, we test benzoate-bonded SAMs as possible candidates for room temperature stable monolayers and compare the adsorption behavior of a 4-fluorobenzoic acid molecule onto the Co(0001) surface to that of 4-fluorothiophenol by employing a combination of X-ray photoelectron spectroscopy and X-ray absorption spectroscopy with synchrotron radiation. We show that the benzoate SAMs exhibit a much higher thermal stability and lead to well-defined layers. Moreover, by resonant photoemission we investigate the charge transfer dynamics from the end group and head group to the substrate. Supported by the DFG (MAP B.1.3 & B.1.4), Helmholtz-Zentrum Berlin and China Scholarship Council.

O 41.38 Tue 18:15 Poster B

**Ab-initio Calculation of Scanning Tunnelling Spectra of Tin-Phthalocyanine Multilayer Structures** — •Felix Schwarz[1], Yongfeng Wang[2], Richard Berndt[3], Erich Runge[1], and Jörg Kröger[1] — [1]Technische Universität Ilmenau, D-98693 Ilmenau — [2]Department of Electronics, Peking University, Beijing 100871, China — [3]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel

Tin-Phthalocyanine molecules on Ag(111) represent archetypical molecular switches [1]. Two conformations, which are characterized by the central Sn ion pointing towards vacuum and towards the surface have reversibly been interchanged by electron injection from a scanning tunnelling microscope (STM) tip. Using density functional theory the electronic structure of the different conformations has been determined. STM images and spectra of the differential conductance have been simulated and compared to experimental data. Contributions of inelastic electron tunnelling to the spectra due to excitation of molecular vibrations are discussed.

[1] Y. F. Wang, J. Kröger, R. Berndt, W. A. Hofer, J. Am. Chem. Soc. 131, 3639 (2009)

O 41.39 Tue 18:15 Poster B

**On-surface reactions of porphin molecules on Au(111)** — •Nino Hatter, Sonja Schubert, Benjamin W. Heinrich, and Katharina J. Franke — Institut für Experimentalphysik, Freie Universität Berlin, Berlin, Germany

Chemical reactions on surfaces are a key ingredient on the route towards molecular electronics. Yet, reactions on surfaces differ from gas- or liquid-phase reactions, as the surface may act catalytically or selectively, thereby changing the reaction barrier, the yield or the product. Porphin is the parent compound of the porphyrines and has a simple structure, consisting of a conjugated tetrapyrrole macrocycle.

Here, we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of free-base porphin adsorbed on Au(111). Annealing the system to 620 K leads to the formation of covalently linked dimers, as was previously observed for porphin on Ag(111) [1]. We identify three different types of porphin dimers. Furthermore, we use on-surface metalation [2,3] to produce Fe-porphin and metalized dimers on Au(111). Using STS, we probe the electronic and magnetic properties of the free-base porphin, as well as the metalized porphin monomers and dimers.

[1] A. Wiengarten, et al., J. Am. Chem. Soc. 136, 9346 (2014)
[2] J.M. Gottfried, et al., J. Am. Chem. Soc. 128, 5644 (2006)
[3] W. Auwärter, et al., ChemPhysChem 8, 250 (2007)

O 41.40 Tue 18:15 Poster B

**Properties of self-assembled monolayers formed by triarylamine derivatives on metal and insulator substrates** — •Martin Gurrath[1], Christian Steiner[2], Sabine Maier[2], and Bernd Meyer[1] — [1]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — [2]Department of Physics, FAU Erlangen-Nürnberg

The atomic and electronic structure of homo- and bi-molecular networks of triarylamine derivatives with either diaminotriazine (ADTPA) or carboxylic (CDTPA) end-groups, which were observed by low-temperature STM and AFM to form on Au(111) and KBr(001) substrates, were studied by density-functional theory (DFT) calculations. Both molecules exhibit three-fold rotational symmetry. While the carboxylic end-groups of CDTPA can form only one type of contact with other molecules in a flat geometry, the amine groups of ADTPA allow for three different hydrogen bonding motifs, which can be either flat or tilted. First, for all possible combinations the molecule–molecule interaction strength for the different hydrogen bonding motifs was determined by calculation of the dimerization energies. Then, monolayer arrangements were derived from the dimer structures. Preliminary calculations of molecules on a KBr(001) surface give insights into why different monolayers form on metal and insulator substrates. Finally, charge transfers and the mutual influence on the electronic structure were analyzed.

O 41.41 Tue 18:15 Poster B

**Growth and vibrational properties of ultra-thin TiOPc films on Ag(111)** — Laura Fernández, Sebastian Thussing, Sebastian Flade, and •Peter Jakob — Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

The coverage dependent growth of titanyl-phthalocyanine (TiOPc) ultra-thin films on a Ag(111) surface has been studied using IR Spectroscopy, SPA-LEED, and TDS. In the monolayer regime three different phases were found: a 2D-gas phase in the low coverage regime ($\theta < 0.7$ML), a commensurate $(4\sqrt{3}\times7)$rect phase for 0.8-0.9 ML, and finally, a point-on-line phase when the coverage approaches saturation. While the IR spectra of the monolayer phases vary only slightly, the vibrational modes corresponding to the mono- and bilayers of TiOPc/Ag(111) are distinctly different, so that the transition from the ML to the BL regime is clearly defined. Thermal desorption spectroscopy measurements reveal a high thermal stability of the TiOPc bilayer, which requires temperatures above 500K to desorb from the Ag(111) surface. Similarly, the stacked (TiOPc bilayer on PTCDA)/Ag(111) structure displays exceptional stability of the organic heterolayer interface. Only for temperatures above 470K indications of intermixing or degradation of the underlying PTCDA/Ag(111) layer are observed.

O 41.42 Tue 18:15 Poster B

**Probing non-planar porphyrin molecules with nc-AFM** — Florian Albrecht[1], •Felix Bischoff[2], Yuanqin He[2], Willi Auwärter[2], Johannes Barth[2], and Jascha Repp[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — [2]Technische Universität München, Department of Physics, E20, 85748 Garching, Germany

Small amplitude, nc-AFM has been established as advanced imaging tool in scanning probe microscopy. Its capability to determine molecular bond characteristics allows a direct identification of molecular structures, conformation and changes therein caused by chemical reactions. However nc-AFM investigations of surface-confined molecules have so far mainly been applied to planar species. Herein we investigate non-planar porphyrins on metal substrates and compare free-base to metalated species. The substrate-induced saddle-shape conformation and the orientation of molecular moieties can be clearly visualized. However, in a direct comparison of 2H-TPP to CuTPP on Cu(111), a flattening of the macrocycle of Cu-TPP, as reported in literature, could not be unambiguously confirmed. On the other hand, a conformational change of the macrocycle caused by the formation of an SAT-complex can clearly be observed for 2H-TPCN on Ag(111). nc-AFM therefore provides the potential to identify (and quantify) the orientation of sub-molecular units within non-planar molecules in real space and might present a possible alternative to space averaging methods such as NEXAFS.

O 41.43 Tue 18:15 Poster B

**Forced assembly of functional molecules** — •Knud Seufert[1,2], Felix Bischoff[1], Yuanqin He[1], Auwärter Willi[1], Johannes V. Barth[1], and Leonhard Grill[2] — [1]Physik-Department, Technische Universität München, Deutschland — [2]Institut für Chemie, Karl-Franzens-Universität Graz, Österreich

The self-assembly of molecules is essential en route to ordered and utile organic structures - a groundwork of molecular electronics. An archetype of such a functional building block is the porphyrin as it plays a key role in several fundamental processes in nature.

Here we present a study on porphin molecules, the parent compound of all porphyrins, adsorbed on smooth noble metal single crystals. A partial filling of the lowest unoccupied molecular orbital (LUMO) results in a charge redistribution at the porphin/Ag(111) interface and a dominating repulsive intermolecular interaction [1]. This repulsion can be overcome by coadsorption or a modification of the substrate. In the first case well-ordered mixed layers can be produced where small gas molecules between the porphines stabilize a self-assembly process via dipole-dipole interaction [2]. A reduced interaction to the metal surface can be achieved by adding a thin insulating interlayer or a complete exchange of the support resulting in the lack of charge transfer. This leads to a suppression of the main repulsive intermolecular force and the formation of islands.

[1] Bischoff et al., ACS Nano (2013) 3139-3149
[2] Buchner et al., ACS Nano (2009) 1789-1794

O 41.44 Tue 18:15 Poster B

**Structural analysis of ordered monolayers of the lander-type molecule DBP on Ag(100) via STM and LEED** — •Timo Heepenstrick, Yifei Zhang, Ina Krieger, and Moritz Sokolowski — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstraße 12, 53115 Bonn

We investigated the perylene derivate lander-type molecule DBP (dibenzotetraphenylperiflanthene). It consists of a stiff body and four rotatable phenyl groups on the edges. DBP has recently been used as an electron donor in organic solar cells [1]. We investigated the adsorption on the Ag(100) surface via STM and LEED at room temperature. From LEED images we found one incommensurate structure with a quadratic unit cell of 2.98 nm side length containing two molecules each. It exhibits a p4g symmetry with two symmetry equivalent rotation domains. The molecule forms large islands on the substrate, which can be observed by STM.

[1]D. Fujishima et al. Solar Energy Mat. and Solar Cells 93, 1029, (2009).

O 41.45 Tue 18:15 Poster B

**Ordering and Electronic Properties of Porphine on Graphene/Ag(111)** — •Jacob Ducke, Yuanqin He, Felix Bischoff, Manuela Garnica, Johannes Barth, and Willi Auwärter — Physik Department E20, Technische Universität München, James Franck Straße 1, 85748 Garching, Germany

Bonding and organization of functional molecules at interfaces is strongly affected by the interaction with the support. By switching from metal surfaces to sp2-bonded monolayer templates an electrical decoupling of the molecules from their support is possible that recently attracted significant interest [1,2]. This decoupling provides new possibilities to order and structure components at the nanometer scale. Here we focus on the interactions and the electronic modification of free-base porphine (2H-P), a prototype tetrapyrrole compound, on graphene/Ag(111). In STS measurements pronounced peaks corresponding to LUMO and HOMO orbitals appear. Furthermore, the repulsions between 2H-P previously identified on Ag(111) are diminished [3]. Our findings are put into perspective with results for electronically decoupled 2H-P on BN/Cu(111) and 2H-P on bare Ag(111). All measurements were conducted with a low temperature STM. [1] Joshi, Sushobhan, et al. Nano letters 12.11 (2012): 5821-5828. [2] Jaervinen, Paeivi, et al. Nano letters 13.7 (2013): 3199-3204. [3] Joshi, Sushobhan, et al. ACS Nano 8 (2014) 430

O 41.46 Tue 18:15 Poster B

**Controlling Coordination Reaction and Assembly on an Insulating Boron Nitride Monolayer** — José I. Urgel[1], •Martin Schwarz[1], Manuela Garnica[1], Daphné Stassen[2], Davide Bonifazi[2], David Ecija[3], Johannes V. Barth[1], and Willi Auwärter[1] — [1]Physik Department E20, Technische Universität München, Germany — [2]Department of Chemistry and Namur Research Center, Belgium — [3]IMDEA Nanoscience, Madrid, Spain

Two-dimensional metal-organic coordination networks presenting organized arrays of metal centers and functional molecular linkers [1] have not been achieved to date on a highly relevant class of materials, namely atomically thin sp2-bound sheets as boron nitride (BN) or graphene. Here, we report the formation of a metal-organic network on a BN/Cu(111) template [2, 3] by co-deposition of carbonitrile-functionalized porphyrin derivatives (2H-TPCN) with Co atoms in an ultra-high vacuum environment. The resulting metallosupramolecular structure explored by scanning tunneling microscopy and spectroscopy features a distinct four-fold coordination motif. Furthermore, we demonstrate an in-situ metalation of the tetrapyrrole macrocycles with co-adsorbed Co yielding Co-TPCN directly on the BN sheet. Our results provide perspectives for the formation of coordination networks on BN and related systems featuring structural, electronic and magnetic properties unachievable on conventional metallic supports.

[1] Barth, J. V. Annu. Rev. Phys. Chem. 2007, 58, 375-407
[2] Joshi, S. et. al. Nano Lett. 2012, 12, 5821-5828
[3] Joshi, S. et. al. ACS Nano, 2014, 8, 430-442

O 41.47 Tue 18:15 Poster B

**Light-induced ring-closure isomerization of a diarylethene derivate in direct contact with surfaces** — •Fabian Nickel[1], Matthias Bernien[1], Sandro Wrzalek[1], Martin Herder[2], Pantelis Chittas[1], Kai Kraffert[1], Lucas M. Arruda[1], Lalminthang Kipgen[1], Stefan Hecht[2], and Wolfgang Kuch[1] — [1]Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — [2]Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

The photochromic isomerization of molecules in direct contact with solid surfaces can be important for the further miniaturization of molecular electronic devices. A potential candidate for this purpose is T-DAE, a diarylethene derivate with attached phenyl groups. This molecule can be switched reversibly between two metastable states in solution. In the closed-ring configuration, a conjugated conduction path through the molecule exists, making it interesting for photochromic switching of the electronic interaction between two attached end groups. In-situ X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) experiments performed on T-DAE adsorbed on Bi(111), Au(111), and highly oriented pyrolytic graphite (HOPG) revealed a UV-light-induced ring-closure reaction on Bi(111) and HOPG. Spectroscopy of the sulfur 2p core electrons shows the existence of three different species of molecules after light exposure, pointing towards the presence of a byproduct that is known to exhibit no reversible switching.

This work is supported by the DFG through Sfb 658.

O 41.48 Tue 18:15 Poster B

**STM investigations of functional platform adlayers on Au(111) surfaces** — •Talina Rusch[1], Sonja Lemke[1], Sandra Ulrich[2], Hanne Jakob[3], Felix Tuczek[3], Rainer Herges[2], and Olaf Magnussen[1] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität Kiel — [2]Institut für Organische Chemie, Christian-Albrechts-Universität Kiel — [3]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel

The controlled assembly of functional molecules on metal surfaces is an important research topic. We have introduced the so called platform approach, where the Triazatriangulenium (TATA) [1,2,3] or Trioxatriangulenium (TOTA) [4] ions are used as molecular platforms which can be functionalized at the central carbon atom as well as by alkyl side chains to control their steric demand. Using this versatile concept, it is possible to control the orientation and distance of the functional group with respect to the surface and the intermolecular distance. Here, detailed STM investigations of TATA adlayer structures as a function of alkyl side chain length are presented as well as structural investigations of new azobenzene functionalized TATA adsorbate layers, namely methoxy-azobenzene-octyl-TATA adlayers. Additionally, we present the reversible switching of these adlayers by infrared reflection absorption spectroscopy [5] as well as UV/Vis spectroscopy.

[1] Baisch et al., J. Am. Chem. Soc. (2009), 131, 442. [2] Kuhn et al., PCCP (2010), 12, 4481. [3] Kubitschke et al., Eur. J. Org. Chem. (2010), 5041. [4] Kuhn et al., Chem. Commun., 2011, 47, 8880-8882 [5] Jacob et al., Phys. Chem. Chem. Phys., 2014, 13, 22643

O 41.49 Tue 18:15 Poster B

**Hierarchical and charge transfer effects in a bimolecular network of structurally related scaffolds** — •Christian Steiner[1], Maximilian Ammon[1], Bettina Gliemann[2], Ute Meinhardt[2], Martin Gurrath[3], Bernd Meyer[3], Milan Kivala[2], and Sabine Maier[1] — [1]Department of Physics, Universität Erlangen-Nürnberg, Germany — [2]Department of Chemistry and Pharmacy, Universität Erlangen-Nürnberg, Germany — [3]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, Universität Erlangen-Nürnberg, Germany

Functional electron donor-acceptor networks on metal surfaces are integral parts of organic optoelectronic devices such as solar-cells. Understanding and controlling the formation of multi-component molecular self-assemblies is important for the design of efficient donor-acceptor networks. Here, we present a scanning tunneling microscopy and spectroscopy study of a bimolecular network assembled from triarylamines with carboxylic and diaminotriazine functional groups on Au(111). The molecules form a perfectly intermixed honeycomb network via N· · ·H-O hydrogen bonds. Density functional theory (DFT) calculations reveal that mainly geometrical aspects lead to the intermixing as opposed of an increase in binding strength. The HOMO-LUMO gap in the mixed network is defined by the two types of molecules, typical for a charge donor-acceptor scheme. The charge transfer process in the intermixed network will be discussed based on DFT calculations.

## O 42: Overview Talk (Leeor Kronik)

Time: Wednesday 9:30–10:15 Location: HE 101

**Invited Talk** O 42.1 Wed 9:30 HE 101

**Understanding organic/inorganic interfaces from first principles** — •Leeor Kronik — Weizmann Institute of Science, Rehovoth, Israel

In this tutorial lecture, I will review some of the fundamental physical mechanisms affecting the electronic structure at organic/inorganic interfaces, with an emphasis on collective phenomena. I will demonstrate how first principles calculations, based primarily on density functional theory, can be successful in elucidating such phenomena. I will also discuss caveats and limitations in their application, as well as avenues for further research.

## O 43: Inorganic/Organic Interfaces: Electronic Properties I

Time: Wednesday 10:30–13:15 Location: MA 005

**Invited Talk** O 43.1 Wed 10:30 MA 005

**Electronic Interactions and Ultrafast Carrier Dynamics at Hybrid Organic / Inorganic Interfaces** — •Oliver L.A. Monti — Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ 85721, USA

Hybrid organic / inorganic interfaces play a central role in efficient carrier collection and extraction in next-generation organic optoelectronics. Here, I will discuss the consequences of electronic coupling at hybrid interfaces on electronic structure and ultrafast carrier dynamics for the prototypical case of highly conductive ZnO films. The presence of shallow donor states near the conduction band minimum leads to strong coupling across interfaces with organic acceptors such as $C_{60}$ and PTCDA, unambiguously manifested by both charge-transfer and hybridization at the interface. Such interactions have dramatic effects on ultrafast carrier dynamics at the interface, lengthening times for escape from the interface by at least two orders of magnitude. I will show how interfacial coupling can be controlled readily with the chemical potential and further discuss the nature of relevant gap states, as revealed by two-photon photoemission spectroscopy. The results have broad implications for efficient charge harvesting and injection at hybrid interfaces.

O 43.2 Wed 11:00 MA 005

**Can three-dimensional orbitals of adsorbed molecules be measured?** — •Simon Weiss[1,2], Daniel Lüftner[3], Eva-Maria Reinisch[3], Thomas Ules[3], Georg Koller[3], Sergey Soubatch[1,2], Peter Puschnig[3], Michael Ramsey[3], and F. Stefan Tautz[1,2] — [1]Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany — [2]JARA - Fundamentals of Future Information Technology, Germany — [3]Institute of Physics, Karl-Franzens University Graz, 8010 Graz, Austria

Chemical and physical properties of atoms and molecules are determined by their electron wave functions i.e. orbitals. Therefore there is much interest to measure these orbitals, although they are not quantum-mechanical observables. Experimentally only the electron density and energy levels are accessible, the phase information is lost. Using angle resolved photoemission spectroscopy (ARPES) electron density can be measured. Additionally it has been shown that a plane wave final state interpretation of experimental ARPES data allows the retrieval of real space images of molecular orbitals in two dimensions including also phase information. For a complete reconstruction of the molecule it is necessary to introduce the energy dependence to gain the third dimension in momentum space. Here the position of the intensity maximum is of particular importance. As a model system we used the brick-wall monolayer of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) on Ag(110) and measured HOMO and LUMO in an wide energy range. This data we used to reconstruct the orbitals and compare the result with theoretical predictions.

O 43.3 Wed 11:15 MA 005

**Orbital tomography: beyond the plane wave final state approximation** — •Peter Puschnig — University of Graz, Institute of Physics, Austria

In recent years it has been shown that the angle-resolved photoelectron cross section from organic molecular films can be accounted for by approximating the final state of the photoemission process by a plane wave. This simple approach, sometimes termed "orbital tomography", has led to a number of interesting applications for organic molecules adsorbed on metal surfaces, such as the unambiguous identification of molecular orbitals [1], the determination of molecular orientations [2], or even the reconstruction of real space molecular orbitals [3]. However, this technique has also been criticized since it relies on a crude approximation for the final state whose accuracy and range of validity has been questioned by many.

In this contribution, I will present theoretical results ranging from small molecules, such as benzene, up to extended two-dimensional structures, such as graphene. By comparing to available experimental data, I will identify the limitations of the plane wave approximation and discuss approaches to improve upon it. In particular, a simple modification to take into account the free mean path of photoelectrons and a modification of the final state which allows to account for shape resonances and scattering effects will be demonstrated.

[1] Puschnig et al., Phys. Rev. B 84, 235427 (2011)

[2] Puschnig et al., Science 326, 702-706 (2009)

[3] Lüftner et al., Proc. Nat. Acad. Sci. U. S. A. 111, 605-610 (2014).

O 43.4 Wed 11:30 MA 005

**Many-body transitions in a single molecule visualized by scanning tunneling microscopy** — •Fabian Schulz[1], Mari Ijäs[1], Robert Drost[1], Sampsa K. Hämäläinen[1], Ari P. Seitsonen[2], Ari Harju[1], and Peter Liljeroth[1] — [1]Aalto University School of Science, Department of Applied Physics, Espoo, Finland — [2]École Normale Supérieure, Départment de Chimie, Paris, France

Scanning tunneling spectroscopy (STS) of molecular systems is usually interpreted in terms of single-particle electronic transitions. A prominent exception is the Kondo effect [1], a many-body state resulting from the interaction of an unpaired molecular spin with the conduction electrons of a metallic substrate. Probing excited states in single molecules by STS, we demonstrate many-body effects arising purely from electronic states confined in the molecule.

Cobalt phthalocyanine adsorbed on the moiré pattern of monolayer hexagonal boron nitride on Ir(111) [2] allows to carry out STS on molecules that are initially in different charge states [3]. The observed resonances are inconsistent with the single-particle interpretation of tunneling spectroscopy. Instead, these resonances can be understood as a series of many-body excitations of the different ground states of the molecule [4].

[1] I. Fernandez-Torrente *et al.*, Phys. Rev. Lett. **101**, 217203 (2008).

[2] F. Schulz *et al.*, Phys. Rev. B **89**, 235429 (2014).

[3] F. Schulz *et al.*, ACS Nano **7**, 11121 (2013).

[4] F. Schulz *et al.*, Nature Phys., accepted.

O 43.5 Wed 11:45 MA 005

**Electronic structure of organic monolayer films on a Pb/Ag(111) surface alloy** — •Johannes Seidel[1], Norman Haag[1], Benjamin Stadtmüller[1], Christian Tusche[2], Mirko

Cinchetti[1], Jürgen Kirschner[2], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schroedinger-Strasse 46, 67663 Kaiserslautern, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

The ability to control the electronic properties of organic semiconductors at metal-organic hybrid interfaces is crucial for their applicability in future electronic and spintronic devices. Hence, many studies so far focused on tailoring such interfaces by tuning either the properties of the molecular film or of the organic adsorbates. In this study we will extend this concept by altering properties of the metal substrate, i.e., by tuning the metal-organic interface "from the bottom".

We have studied the electronic valence structure of the interface formed by prototypical organic molecules adsorbed on a Pb/Ag(111) surface alloy by ARPES using a k-space microscope. The Pb/Ag(111) surface alloy shows a distinct spin-texture due to the Rashba-Bychkov effect. Our ARPES data reveals almost identical molecular features in the valence band for molecular monolayer films on Ag(111) and the Pb/Ag(111) surface alloy. However, the band structure of the clean Pb/Ag(111) surface alloy is significantly modified by the molecular adsorption which we attribute to a change in the vertical relaxation of the atomic positions of the surface alloy.

O 43.6 Wed 12:00 MA 005

### Strong Interaction between Subphthalocyanines and Copper (111): A computational study

— •Shashank S. Harivyasi[1], Elisabeth Wruss[1], Oliver T. Hofmann[1], Oliver L. A. Monti[2], and Egbert Zojer[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, Austria — [2]Department of Chemistry & Biochemistry, University of Arizona, Tucson, Tucson, AZ, United States

The detailed energetics of a metal-organic interface is influenced by multiple factors. These include: the nature of the interaction between the metal and the molecules, the geometric conformation of each of those adsorbed molecules on the surface, and the packing arrangement and coverage density of the monolayer.

In this work, we use DFT calculations to analyze adsorption of Chloroboron-Subphthalocyanine (SubPc) on a Cu (111) surface. SubPc is an interesting candidate for elucidating the interplay of the above-mentioned aspects given the molecule's cone-shaped geometry in gas-phase, the extended conjugated electron system and the significant dipole moment. We studied the adsorption energetics and electronic structure for various confirmations and simulated STM results. In our findings, we highlight the role of van der Waals forces in adsorption and how they result in an unusually strong interaction between the metal and the molecule that, in turn, leads to planarization of the molecules on the surface and a pronounced hybridization of molecular and metal states. The latter is analyzed on the basis of charge rearrangements and the densities of states projected onto the molecular orbitals.

O 43.7 Wed 12:15 MA 005

### Modeling geometry and electronic structure of flat-lying phthalocyanines on metal surfaces

— •Elisabeth Wruss[1], David Egger[1,2], Yu Li Huang[3], Tomáš Bučko[4], Wissam Saidi[5], Satoshi Kera[3], and Egbert Zojer[1] — [1]Institute of Solid State Physics, Graz University of Technology, Graz, Austria — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel — [3]Graduate School of Advanced Integration Science, Chiba University, Chiba, Japan — [4]Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovakia — [5]Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, United States

The adsorption behavior of metal-phthalocyanine (MPc) molecules on coinage metal surfaces is investigated using density functional theory. To take van der Waals (vdW) interactions into account, the geometry optimization is done using the PBE+vdW-surf [1] approach. The resulting adsorption heights are in excellent agreement with experimental XSW measurements, while in calculations without a vdW correction only a repulsive interaction potential between the metal and the adsorbate is observed. The electronic structure is investigated using generalized gradient (GGA) and hybrid functionals. We find that both approaches provide a highly reliable description of the adsorption-induced work-function modifications, but predict different alignments of the electronic states. This is due to spurious orbital self-interaction error present in GGA calculations, which is strongly mitigated by the use of hybrid functionals. [1] Ruiz et al., PRL. 108, (2012).

O 43.8 Wed 12:30 MA 005

### First-Principles Simulation of Near-Edge X-Ray Absorption Fine-Structure (NEXAFS): Comparison of Core-Level Constraining Approaches

— •Georg S. Michelitsch, Katharina Diller, Reinhard J. Maurer, Tom Bärwinkel, and Karsten Reuter — Technische Universität München, Germany

NEXAFS allows to directly probe the electronic structure of a surface-adsorbate system by excitation of core electrons to unoccupied states. The interpretation of the experimental signatures is greatly facilitated by independent first-principles calculations. For this, ground-state density-functional theory (DFT) based approaches explicitly constraining the occupation of core-levels constitute a numerically particularly efficient approach suited to tackle large adsorbate systems. Notwithstanding, their approximate treatment of core-hole relaxation and hole-excited electron interaction needs to be carefully assessed. Using experimental K-edge spectra for common building blocks of organic adsorbates like benzene and porphine as a reference, we perform such an assessment specifically within the context of the numeric atomic orbital basis sets of the all-electron DFT-package FHI-aims. We find relative peak positions to be quickly converged with basis set size and already at the level of semi-local DFT functionals. While this favors the use of these approaches for the simulation of large adsorbate systems, we critically discuss differences in the core hole occupation strategy and their consequences for the simulation of higher-lying core hole excitations and spin-anisotropic systems.

O 43.9 Wed 12:45 MA 005

### Heteromolecular CuPc-C60 monolayer films on the Co(1000) surface

— •Norman Haag, Johannes Seidel, Johannes Stöckl, Benjamin Stadtmüller, Mirko Cinchetti, and Martin Aeschlimann — Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schroedinger-Strasse 46, 67663 Kaiserslautern, Germany

Heteromolecular monolayer films consisting of two different types of molecules are promising candidates for tailoring the geometric and electronic properties at metal-organic hybrid interfaces. So far, this approach has only been demonstrated on noble metal surfaces where the molecules show a weak chemical molecule-substrate interaction [B. Stadtmüller, Nat. Commun. 5, 3685 (2014)]. In this study, we extend this concept to ferromagnetic surfaces by investigating the formation of heteromolecular CuPc-C60 structures on the Co(1000) surface. On such transition metal surfaces, the strong molecule-substrate interaction usually prevents the formation of long-range ordered molecular structures. We have studied the electronic and structural properties of the heteromolecular CuPc-C60/Co(1000) system using a k-space photoemission microscope. Analyzing the angular dependent photoemission pattern allows us to assign spectroscopic features to molecular orbitals and to determine the orientation of corresponding molecules on the surface. A comparison of these results to the CuPc and C60 homomolecular films on Co(1000) reveals that the formation of ordered heteromolecular films is mainly caused by a site-specific interaction of C60 with Co.

O 43.10 Wed 13:00 MA 005

### Excitation processes in Copper-porphyrin aggregates studied by multi-photon Photoemission Electron Microscopy (PEEM)

— •Hannes Hartmann[1], Ingo Barke[1], Mohammadreza Bahrami[1], Lukas Rathje[1], Tamam Bohammud[1], Per-Arno Plötz[1], J.A.A.W Elemans[2], Oliver Kühn[1], Karl-Heinz Meiwes-Broer[1], and Sylvia Speller[1] — [1]Institute of Physics, University of Rostock, Germany — [2]Institute of Molecules and Materials, Radboud University Nijmegen, Netherlands

Hybrid systems composed of nanoparticles and molecular aggregates are subject to intense research due to potential applications in organic electronics and for photovoltaics. We are interested in the role of the local environment on the various types of excitations in such systems and in their transport. Copper-porphyrin aggregates are prepared on Si(111) covered by native oxide and on highly ordered pyrolytic graphite (HOPG) by self-organized growth. Multi-photon excitation with a tunable fs-laser system leads to emission of photoelectrons that are analyzed in a Photoemission Electron Microscopy (PEEM). Beside the electronic structure, correlative mapping including scanning probe microscopy (AFM) at the same location can help to identify contributing processes and to elaborate the role of structural features and transport properties on the emission intensity and energy.

## O 44: Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces III

Time: Wednesday 10:30–11:30 Location: HE 101

O 44.1 Wed 10:30 HE 101

**AFM investigation of charge distribution and ion adsorption at solid-liquid interfaces** — •Frieder Mugele[1], Igor Siretanu[1], Cunlu Zhan[1], Dirk van den Ende[1], and Daniel Ebeling[1,2] — [1]University of Twente, MESA institute for Nanotechnology; Physics of Complex Fluids, Enschede, The Netherlands — [2]Universität Giessen, Giessen, Germany

Solid surfaces immersed in water almost invariably assume a finite surface charge typically due to either (de)protonation of functional groups on the surface or adsorption of ions from the solution. While the resulting electrostatic interaction forces are crucial for many phenomena in science and technology, such as colloid science, biophysics, foodtechnology, and enhanced oil recovery, important aspects of charge distribution and spatial arrangement of adsorbed ions in the Stern layer are poorly understood. Here, high resolution dynamic atomic force spectroscopy and microscopy experiments in ambient liquid will be described that provide detailed insight into the organization of ions in the Stern layer at various mineral-electrolyte interfaces. The experiments highlight the preferential adsorption of divalent cations (Mg2+, Ca2+) as compared to monovalent ones (Na+, K+), including the incorporation of Cl- co-ions at higher concentrations. Complementary Density Functional Theory calculations demonstrate the role of hydration water upon adsorption.

**Topical Talk** O 44.2 Wed 10:45 HE 101

**Electronic spectroscopy at the solid-liquid interface: a window to electrochemistry and solvation phenomena** — •Miquel Salmeron — Lawrence Berkeley National Laboratory. Berkeley, CA 94720. USA

Basic phenomena in electrochemistry, and environmental science occur at solid-liquid interfaces. To obtain information on the atomic structure, composition, electronic levels of surface and adsorbed molecules optical (IR, SFG), structural (STM, AFM, GIXS), and x-ray spectroscopy techniques (XAS-XES) can be used.

In fluorescence yield mode, XAS provides information on the electronic structure of sample materials within the escape/penetration depth of x-rays, which for soft x-rays is about 100-1000 nm. In my laboratory we use a well-known variant known as electron yield mode (EY-XAS), by measuring the electrode current which is the balance between emission and capture of secondary electrons.

We applied EY-XAS to study electrode interfaces in aqueous electrolytes. In the case of graphene we studied reactions leading to the oxidation. In the case of gold we determined the orientation of water molecules near the interface, due to interaction with gold and as a function of applied bias. In the case of Platinum we studied oxidation-reduction reactions in acid electrolytes.

Because XAS spectra are dependent on x-ray absorption rules and transition probabilities in the presence of core holes, interpretation of the spectra is not trivial and requires theoretical calculations for interpretation.

O 44.3 Wed 11:15 HE 101

**Formation energy of ions in water: an ab-initio molecular dynamics study** — •Anoop Kishore Vatti, Mira Todorova, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Water is the most complex and ubiquitous liquid. Understanding the structure and properties of ions in liquid water is a key feature needed to describe and understand the properties and processes occurring in biological and electro-chemical systems. Using ab-initio molecular dynamics we study charged ions in water using various exchange-correlation functionals. We will discuss the geometric and electronic structure of the studied ions, as well as their formation energies and compare our findings to experimental observations. Evaluating the formation energy of the investigated ions, we find, e.g. that the Zn2+-Ion is the dominant defect over the extent of the theoretical band-gap. Aligning the calculated and measured water band-edges on an absolute scale [1] allows us to compare our calculated formation energy for the Zn2+-Ion with experimental ones, revealing an excellent agreement.

[1] M. Todorova and J. Neugebauer, Phys. Rev. Applied 1, 014001 (2014).

## O 45: Nonaqueous Liquid/Solid Interfaces

Time: Wednesday 11:30–13:00 Location: HE 101

O 45.1 Wed 11:30 HE 101

**Formation of double layers in ionic cells and their relevance for cell voltage and charge transfer** — •René Hausbrand — Darmstadt University of Technology, Materials Science Department, Darmstadt, Germany

Double layers at electrode-electrolyte interfaces in ionic devices determine charge transfer kinetics and cell voltage. Lately, interest to understand the double layer formation of Li-ion electrode - electrolyte interfaces has increased due to the future use of Li-ion cells for energy storage. Under equilibrium conditions, the electric potential gradient at an ion electrode - electrolyte interface is determined by the difference of ion chemical potential between electrode and electrolyte, contributing to the electrode potential. For ion transfer, the formation of diffuse double layers (space charge layers) is relevant. This contribution focuses on the impact of the interfacial electrical potential gradients on cell voltage using the example of an all-solid Li-ion cell. First, the fundamentals regarding the origin of cell voltage are briefly introduced. Then, results of surface science investigations on thin film LiCoO2 electrodes and LiPON solid state electrolytes are presented, and evaluated to yield the energy level diagram of the LiCoO2|LiPON|Li cell. The results demonstrate the formation of space charge layers and indicate that the ionic contribution to the cell voltage remains low.

O 45.2 Wed 11:45 HE 101

**Complementary Theoretical and Experimental Study of Ionic Liquid–Solid Interfaces** — •Zlatko Brkljača[1], Michael Klimczak[2], Andreas Magerl[2], David M. Smith[3,4], and Ana-Sunčana Smith[1,3] — [1]Institut für Theoretische Physik, FAU Erlangen–Nürnberg, Erlangen, Germany — [2]Crystallography and Structural Physics, FAU Erlangen–Nürnberg, Erlangen, Germany — [3]Ruđer Bošković Institute, Zagreb, Croatia — [4]Computer Chemie Centrum, FAU Erlangen–Nürnberg, Erlangen, Germany

Understanding the molecular-level behavior of ionic liquids (ILs) at IL-solid interfaces is of fundamental importance with respect to their application in electrochemical systems and electronic devices. Using a model system consisting of an imidazolium-based IL ([$C_2$Mim][$NTf_2$]) in contact with sapphire substrate, we have approached this problem using complementary experimental and theoretical methodologies. We employed high-resolution X-ray reflectivity measurements, capable of probing buried IL-solid interfaces, and atomistic molecular dynamics (MD) simulations, which can be used to interpret experimental data in atomistic detail. Our strategy enabled us to compare experimental and theoretically calculated reflectivities in a direct manner, thereby critically assessing the applicability of force-field variants we implemented. In turn, using the best-matching MD description, we were able to describe the nature of the model IL-solid interface in appreciable detail, finding that the hydrogen bonding between the imidazolium rings and the surface hydroxyl groups has a dominant role in inducing a bilayering cation/anion profile close to the surface.

O 45.3 Wed 12:00 HE 101

**Alternating Ion Monolayering in Alkylimidazolium Ionic Liquids at the Solid-Liquid Interface** — •Michael Klimczak[1], Nicola Taccardi[2], Johannes Will[1], Matthias Weisser[1], Peter Wasserscheid[2] und Andreas Magerl[1] — [1]Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [2]Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Room temperature ionic liquids (RTILs) in general – and molten alkylimidazolium–bis(trifluoromethylsulfonyl)imide ($[\mathrm{C_nMim}][\mathrm{NTf_2}]$) salts in particular – are promising chemicals in electrochemical application. With the current trend of downsizing technology, interfacial effects take over a dominant role in these systems.

Using specular X-ray reflectivity (XRR) we have therefore systematically studied the solid–ionic liquid interface of $[\mathrm{C_nMim}][\mathrm{NTf_2}]$ RTILs and sapphire (0001) in dependance of the alkyl chainlength and temperature. We observe alternating cation/anion monolayers with an enrichment of $[\mathrm{C_nMim}]^+$ cations close to the interface in all cases. However, the definition and extent of the observed structures varies with chainlength which can be attributed to a size match/mismatch between the anion and cation, leading to more/less compact packing of the molecules.

O 45.4 Wed 12:15 HE 101

**Lithium Ion Transport in LiMn2O4 Nanowire Cathode of Lithium Ion Battery** — •Soyeon Lee[1,3], Yoshifumi Oshima[2,3], and Kunio Takayanagi[1,3] — [1]Tokyo Tech., Tokyo, Japan — [2]JAIST, Ishikawa, Japan — [3]JST-CREST, Tokyo, Japan

Structural phase transition of electrode materials in lithium ion batteries causes capacity decrease. In order to avoid capacity decrease, it is essential to understand mechanism of transport of lithium ions and phase transition in the electrode. In the present work, a lithium ion battery with the LiMn2O4 nanowire, as a positive electrode, was developed specially for in-situ observation by a sub-50pm resolution electron microscope. The LiMn2O4 (LMO) electrode consists of a single nanowire or of a bundle of nanowires, which contacts with ionic liquid electrolyte (ILE) on a Li4Ti5O12 negative electrode. The nanowire electrode is free standing, being suspended between Pt and ILE; little manganese (Mn) ions can dissolves from LMO into the electrolyte to cause capacity decrease. The nanowire battery was proved after in-situ observation to work without capacity degradation at high charge/discharge rate (fully charged within 24 minutes), and structure of LMO transformed reversibly while the cyclic voltammetry between 3.5-5.5 V (vs Li/Li+). The structure of the nanowire at the area of ILE/LMO contact showed cubic to tetragonal phase transformation, while the other area, non-equilibrium structure change has occurred by high charge/discharge rate. Our developed nanowire battery and in-situ study have revealed the nanowire battery can work reversibly without capacity decrease for high-rate charge/discharge operation

O 45.5 Wed 12:30 HE 101

**Temperature-induced different patterns in the self-assembled network of Benzene-1,3,5-triphosphonic acid observed by scanning tunneling microscopy at the liquid-solid interface.** — •Doan Chau Yen Nguyen[1], Thi Ngoc Ha Nguyen[1], Michael Mehring[2], and Michael Hietschold[1] — [1]Solid Surfaces Analysis Group, Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany — [2]Coordinations Chemistry Group, Institute of Chemistry, Chemnitz University of Technology, Chemnitz, Germany

Benzene-1,3,5-triphosphonic acid (BTP), which is the phosphonic acid analogue of trimesic acid (TMA), forms a columnar packing in the crystalline solid state that is characterized by strong hydrogen bonds and ii-stacking involving the aromatic rings. Therefore, BTP is an interesting intermediate to design both three-dimension (3D) supramolecular hydrogen-bonded architectures and organic-inorganic hybrid frameworks. Supramolecular self- assembly at liquid solid interfaces is a thermodynamically complex process producing a variety of structures. The formation of multiple network morphologies from the same molecular building blocks is a common occurrence. We use Scanning Tunneling Microscopy (STM) to investigate the self-assembly of BTP in different kind of solvents (undecanol, octanoic acid) adsorbed on highly oriented pyrolytic graphite (HOPG (0001). The influence of substrate temperature is studied and the STM results reveal that with every kind of solvents, the influence of substrate temperature is strong enough to induce different self-assembled structures of BTP on the substrate.

O 45.6 Wed 12:45 HE 101

**Influence of halide ions on the anisotropic growth of gold nanoparticles: Insight from molecular dynamics simulations** — •Santosh Meena[1], Andreas Henkel[2], and Marialore Sulpizi[1] — [1]Institute of Physics, Johannes Gutenberg University Mainz, Germany — [2]Physical Chemistry Department, Johannes Gutenberg University Mainz, Germany

Halides ions play a fundamental role in controlling the anisotropic growth of gold nanorods [1]. In particular while Br- is able to promote anisotropic growth in seed mediated synthesis, Cl- is known to induce a faster isotropic growth. We studied the adsorption mechanism of CTAB/CTAC surfactant mixtures at different concentration ratio, namely 1:0, 1:1 1:2 and 0:1 on different gold surfaces, namely the (110), (100) and (111). We use molecular dynamics simulations in order to provide a detailed description of the gold/surfactant/electrolyte solution in the growing solution [2]. we found that Br- is not only responsible for surface passivation, but also acts as the driving force for the CTAB micelle adsorption and stabilization on the gold surface. When Br- is partially replaced by Cl-, the surfactant layer become less and less dense. Finally when all the CTAB is replaced by CTAC no halides or micellar structure protect the gold surface and further gold reduction is possible uniformly on all the facets resulting a isotropic faster growth.

[1] S. E. Lohse, N. D. Burrows, L. Scarabelli,L. M. Liz-Marzan, C. J. Murphy, Chem. Mater. 2014, 26(1), 34 [2] S. K. Meena, M. Sulpizi, Langmuir 2013, 29(48), 14954

## O 46: Focus Session: THz meets X-ray

Time: Wednesday 10:30–12:30 Location: MA 001

**Topical Talk** O 46.1 Wed 10:30 MA 001

**Opportunities for THz-pump x-ray-probe experiments at free-electron lasers** — •Wilfried Wurth — Physik Department und CFEL, Universität Hamburg — DESY Photon Science, Hamburg

New light sources based on linear accelerators such as the free-electron laser FLASH at DESY in Hamburg in the extreme ultraviolet and soft x-ray regime provide ultrashort, extremely powerful short wavelength pulses with unprecedented coherence properties.

With these new sources it is possible to extend the well-established x-ray spectroscopy or scattering techniques for the investigation of the static electronic and geometric structure of matter to the time domain. The short electron bunches necessary to produce the short wavelength pulses can at the same time be used to generate coherent THz radiation which is fully synchronized to the XUV- or x-ray pulses.

In the talk the possibilities for THz-pump x-ray-probe at the FLASH facility will be reviewed and examples for THz-pump x-ray probe experiments performed at FLASH will be given.

**Topical Talk** O 46.2 Wed 11:00 MA 001

**Understanding the Ultrafast Insulator-Metal Tranisition in Vanadium Dioxide: An Ultrabroadband Terahertz Perspective** — •Alfred Leitenstorfer, Bernhard Mayer, and Alexej Pashkin — Department of Physics and Center for Applied Photonics, University of Konstanz, 78465 Konstanz, Germany

$VO_2$ is a prototypical oxide with strong electronic correlations. A transition from a dielectric phase to a metal of higher lattice symmetry occurs at 340 K. Interband excitation non-thermally triggers this process on a fs time scale. The multi-THz electronic conductivity sets in instantly after pumping with 12-fs near-infrared pulses. Below a temperature-dependent threshold fluence, the insulating character recovers within 200 fs. Above threshold, switching into the metallic phase occurs. A coherent wave packet motion in the excited state is detected via the anharmonic coupling of V-V stretch motion to optical phonons. The sub-ps damping of the lattice coherent signature is consistent with a retarded structural transition. Surprisingly, a transient metallic phase is reached also when exciting with few-cycle multi-THz pulses at similar fluences. A threshold electric field of 14 MV/cm fits excellently to a model of tunneling breakdown of a Mott insulator with a pair correlation length of 2 Å. The fast decay of conductivity below threshold under NIR excitation is absent: interband tunneling creates electrons and holes in different elementary cells. This fact prevents exciton selftrapping and explains the efficiency of non-resonant multi-

THz switching. Resonant pumping of optical phonons is of minor importance as compared to direct tunneling breakdown of the elctronic energy gap.

**Topical Talk** O 46.3 Wed 11:30 MA 001

**Magnetization Dynamics seen via Pump-Probe Holographic X-ray Imaging** — •Stefan Eisebitt — Institut für Optik und Atomare Physik, Technische Universität Berlin — Division of Synchrotron Radiation Research, Lund University

Magnetism exhibits phenomena on intrinsic timescales spanning many orders of magnitude, due to its electronic nature including ultrafast phenomena on short length scales. I will demonstrate how x-ray Fourier transform holography (FTH) with magnetic dichroism contrast [1] can be used in pump-probe schemes to follow magnetization dynamics on the nano-, pico- and femtosecond time scale in real space. Specifically, results on the GHz dynamic behavior of magnetic bubbles (pumped by magnetic field pulses) [2] and on ultrafast optical demagnetization (pumped by localized IR pulses) [3] will be discussed.

[1] S. Eisebitt et al., *Lensless imaging of magnetic nanostructures by X-ray spectro-holography*, Nature **432**, 885 (2004).

[2] F. Büttner et al., *Dynamics and inertia of skyrmionic spin structures*, (Nature Physics, accepted)

[3] C. von Korff Schmising et al., *Imaging Ultrafast Demagnetization Dynamics after a Spatially Localized Optical Excitation*, Phys Rev Lett **112**, 217203 (2014)

**Topical Talk** O 46.4 Wed 12:00 MA 001

**THz induced spin motions probed by x-rays** — •Urs Staub — Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Multiferroics - materials with more than one type of ferric ordering - have attracted strong interest for potential applications where electric fields control magnetic order. The ultimate speed of control via magnetoelectric coupling, however, remains largely unexplored. I will discuss results on multiferroics that show distinct excitations in the THz absorption spectra that are called electromagnons. Intense few-cycle terahertz (THz) pulses can therefore excite both, the lattice (electric polarization) and the magnetic (spin) subsystems [1], and its motions observed using time-resolved x-ray diffraction. Such a selective excitation has very different impact on the system then the usual 800 nm light excitation. It opens up possible ways of manipulating magnetic and atomic structures using the electric field of light on a sub-picosecond timescale.

[1] T. Kubacka et al. Science 343, 1333 (2014).

## O 47: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale III

Time: Wednesday 10:30–13:30 Location: MA 004

**Invited Talk** O 47.1 Wed 10:30 MA 004

**Transport and excitations in biased nano-junctions: DFT-based simulations** — •Mads Brandbyge — Dept. of Micro and Nanotechnology, DTU-Nanotech, and Center for Nanostructured Graphene (CNG) Technical University of Denmark, Build. 345 east, 2800 Kongens Lyngby, DENMARK

In nano-junctions the electronic current is forced through a bottleneck down to the single molecular or atomic level. The highly non-equilibrium electronic system in such junctions results in various excitations such as phonons or plasmons. The phonon interaction directly yield signals in the current which can be probed in current-voltage spectroscopy, while the plasmon interaction can result in light emission which seems to be related to the current fluctuations/noise at finite frequency. The low frequency shot noise can provide information about the elastic transport channels and underlying spin-dependent electronic structure of the junctions. We will discuss how theory based on non-equilibrium Greens functions in combination with density functional theory or beyond, can be compared to experimental results, and provide important insights into excitations, the underlying transport channels, and electronic structure of the junctions. The electronic current will not only excite phonons. Energy non-conserving current-induced forces may control the resulting heat flow and heat distribution in the junctions, and in some cases lead to a break-down of the harmonic approximation.

O 47.2 Wed 11:00 MA 004

**Role of atomic multiplets in intermediate valence $SmB_6$ and $PuB_6$ systems** — •Alexander B. Shick[1], Alexander I. Lichtenstein[2], and Mikhail I. Katsnelson[3] — [1]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic — [2]Institute of Theoretical Physics, University of Hamburg, Hamburg, Germany — [3]Radboud University Nijmegen, The Netherlands

The materials with strong electron correlations are important because of the fundamental properties, and the technological applications. Recently, $SmB_6$ (as well as $PuB_6$) was proposed as 3D topological insulator [1]. The electronic structure calculations are performed combining the LDA with an exact diagonalization of the Anderson impurity model [2] for [Sm,Pu]$B_6$. For the Sm atom in $SmB_6$, intermediate valence ground state (GS) is found with the $f$-shell occupation $\langle n_{4f} \rangle = 5.6$. The GS is a singlet, and the first excited triplet state $\sim 3$ meV higher in the energy. The $f$-orbital density of states is in agreement with experimental PE spectra. $SmB_6$ is a narrow band insulator already in LDA, with the direct band gap of $\sim 10$ meV. The electron correlations increase the band gap which now becomes indirect. For the Pu atom in $PuB_6$, we also find intermediate valence ($\langle n_{5f} \rangle = 5.5$) singlet GS. The calculations illustrate that many-body effects are relevant to form the indirect band gap, and support the idea of "topological Kondo insulator" in $SmB_6$. [1] M. Dzero *et al.*, Phys. Rev. Lett. **104**, 106408 (2010); [2] A. B. Shick *et al.*, Phys. Rev. B **87**, 020505(R) (2013).

O 47.3 Wed 11:15 MA 004

**Transition paths and cohesive energies in alpha-sexithiophene polymorphs** — •Bernhard Klett, Caterina Cocchi, and Claudia Draxl — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Like many organic crystals, oligothiophenes display polymorphism. Different molecular orientations and stacking arrangements are known to influence electronic and transport properties. An in-depth theoretical understanding of the energetics in these systems is crucial to control their growth and fully exploit their potential. In fact, their outstanding opto-electronic features make oligothiophenes excellent candidates for a number of technological applications, ranging from thin-film transistors to photovoltaic cells. We investigate alpha-sexithiophene in view of the transition between the high-temperature (HT) and low-temperature (LT) phase. With the full-potential all-electron density-functional theory code exciting [1], we analyse the cohesive properties of the two polymorphs. Our results indicate HT as the most stable phase, in agreement with previous molecular-dynamics simulations [2]. We also explore a transition path between the two polymorphs, suggesting different reaction coordinates. Our findings allow for estimating the energy barrier between the two phases, hence gaining insight into the microscopic mechanisms ruling polymorphism in organic crystals. [1] A. Gulans, et al., J. Phys.: Condens. Matter 26, 363202 (2014). [2] R. G. Della Valle, et al., J. Phys. Chem. A, 112, 6715 (2008).

O 47.4 Wed 11:30 MA 004

**Importance of the reorganization energy barrier in computational design of porphyrin-based solar cells with cobalt-based redox mediators** — •Kristian Baruël Ørnsø, Elvar Örn Jónsson, Juan Maria Garcia-Lastra, Karsten Wedel Jacobsen, and Kristian Sommer Thygesen — Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

The shift from iodide based redox mediators in dye sensitized solar cells towards octahedral cobalt complexes has lead to a significant increase in the efficiency. However, due to the nature of this type of complexes the driving force required for the regeneration of the dye is very high and this limits the achievable efficiency. Here we show that the large driving force is a direct consequence of the large reorganization energy of the dye regeneration reaction. The reorganization energies for charge transfer between a simple zinc porphyrin dye and two popular cobalt based redox mediators is calculated using ab-initio molecular dynamics with explicit solvent. These results are then combined with a Marcus based extrapolation scheme to obtain the reorganization energies of more than five thousand porphyrin based dyes.We propose a scheme for scoring the performance of the porphyrin dyes which is able to identify already known high-performance dyes in addition to a number of even better candidates. Our analysis shows that large internal reorganization energy of the Co-based redox mediators is a main bottleneck for achieving higher efficiencies.

O 47.5 Wed 11:45 MA 004

**Ab initio Simulation of Optical Limiting: The Case of Metal-Free Phthalocyanine** — •Caterina Cocchi[1,2], Deborah Prezzi[2], Alice Ruini[2,3], Elisa Molinari[2,3], and Carlo Andrea Rozzi[2] — [1]Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — [2]Centro S3, CNR Istituto-Nanoscienze, Modena, Italy — [3]Dipartimento di Scienze Fisiche, Informatiche, Matematiche, University of Modena and Reggio Emilia, Italy

Optical limiting (OL) is a nonlinear process that is relevant for an entire class of devices related to the protection of light-sensitive elements, including the human eye, from intense light sources. While extensively studied experimentally, an accurate theoretical investigation of this phenomenon is still missing. In the framework of time-dependent density-functional theory, we present a fully ab initio, non-perturbative description of OL properties of a metal-free phthalocyanine, a prototypical macrocyclic organic compound. By applying a broadband electric field of increasing intensity, we confirm that reverse saturable absorption is the leading mechanism for OL phenomena in this class of systems, and reveal that a number of dipole-forbidden excitations are populated by excited-state absorption at more intense external fields. The excellent agreement with the available experimental data supports our approach as an effective and powerful tool to describe and predict OL [1]. [1] C. Cocchi et al., Phys. Rev. Lett. 112, 198303 (2014).

O 47.6 Wed 12:00 MA 004

**High-throughput Screening of Perovskite Oxides and Related Compounds for Light Harvesting Applications** — •Ivano E. Castelli[1], Nicola Marzari[1], Kristian S. Thygesen[2], and Karsten W. Jacobsen[2] — [1]Theory and Simulation of Materials, and EPFL National Center for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, Lausanne, Switzerland — [2]Center for Atomic-scale Materials Design, Technical University of Denmark, Kgs. Lyngby, Denmark

Solar energy harvesting in a photoelectrochemical (PEC) cell, where water is split into hydrogen and oxygen, is an attractive and renewable contribution to our global needs of increasing energy demand and storage. We explore the possibility of identifying novel photocatalysts for PECs with the use of high-throughput quantum mechanical simulations. We devise inexpensive approaches to calculate systematically the structural and electronic properties of 19000 cubic ABX3 perovskites, obtained by combining 52 possible metals as A- or B-cations, together with oxygen, nitrogen, sulfur and fluorine as anions. Using the screening criteria of stability and bandgap, 20 promising materials have been identified for visible-light harvesting [1]. The problem of corrosion has been addressed, determining the Pourbaix diagrams of the candidates through a combination of experimental and computational data [2]. We also suggest a handful of lower symmetry layered and rare-earth perovskites for further theoretical and experimental investigation. References: [1] I. E. Castelli et al., Energy Environ. Sci. 5, 9034 (2012). [2] I. E. Castelli et al., Topics in Catalysis 57, 265 (2014).

O 47.7 Wed 12:15 MA 004

**Understanding and designing novel materials for energy** — •Silvana Botti — Friedrich-Schiller-Universität Jena, Germany

I will present an overview of our most recent theoretical/computational developments and some examples of their application to calculate from first-principles the structural and electronic properties of materials for energy production, storage, and saving.

The systems we are interested in are varied, ranging from thin-films absorbers and transparent conductive oxides for solar cells, to thermoelectrics, light-weight materials for constructions, complex hydrides for on-board hydrogen storage.

Nowadays, ab initio approaches based on density functional theory ally accuracy and efficiency, which make them suitable for understanding the physics not only of simple bulk crystals, but also of nanostructures, crystals with defects, doped crystals, interfaces, alloys, etc. As a consequence, ab initio calculations are finally able to analyze the "real" samples measured in experiments, allowing accurate comparisons of both ground-state and excited-state properties.

Moreover, ab initio methods can be used together with structural prediction algorithms and evolutionary algorithms to solve the inverse problem, i.e. find the best material for a specific application, providing a precious guide for experimental search of novel materials.

O 47.8 Wed 12:30 MA 004

**Accurate density-functional theory calculation of bulk properties of 65 elemental solids** — •Sven Lubeck[1], Andris Gulans[1,2], and Claudia Draxl[1] — [1]Humboldt-Universität zu Berlin, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Density-functional theory (DFT) is a common method for calculating various properties of molecules and solids. While a large part of errors in DFT calculations stems from approximations to the exchange-correlation functional, there are additional not well controlled errors introduced by numerical implementation of electronic structure codes. In this work, we present accurate benchmark calculations of equation of state for 65 non-magnetic elemental solids. The data have been obtained using the full-potential augmented-plane-waves (APW) code `exciting` [1]. High accuracy has been achieved by constructing a converged APW+lo basis set, which yields consistent bulk properties of considered solids for a range of augmentation sphere sizes. Using methodology suggested in Ref. [2], we compare our results to those obtained with WIEN2k [2] and find the average and maximum $\Delta$-values of 0.3 meV/atom and 2.1 meV/atom, respectively.

[1] A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, J. Phys.: Condens. Matter 26, 363202 (2014).

[2] K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier, Critical Reviews in Solid State and Materials Sciences 39, 1-24 (2014).

O 47.9 Wed 12:45 MA 004

**Electronic phase transitions of bismuth under strain from relativistic self-consistent *GW* calculations** — Irene Aguilera, •Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We present quasiparticle self-consistent *GW* (QS*GW*) calculations of semimetallic bulk Bi. We go beyond the conventional QS*GW* method by including the spin-orbit coupling throughout the self-consistency cycle. This approach improves the description of the electron and the hole pockets considerably with respect to standard density functional theory (DFT), leading to excellent agreement with experiment. We employ this relativistic QS*GW* approach to conduct a study of the semimetal-to-semiconductor and the trivial-to-topological transitions that Bi experiences under strain. While DFT predicts that an unphysically large strain is needed for such transitions, we show that the relativistic QS*GW* description of the electronic structure moves the required strain into a regime that is likely to be realizable in experiment. We acknowledge financial support from the Alexander von Humboldt Foundation and from the Helmholtz Association through the Virtual Institute for Topological Insulators (VITI).

O 47.10 Wed 13:00 MA 004

**A GW algorithm of reduced complexity for organic crystals** — •Saber Gueddida[1], Dietrich Foerster[1], Peter Koval[2], and Daniel Sanchez-Portal[2] — [1]Laboratoire Ondes et Matière d'Aquitaine, University of Bordeaux, France — [2]Donostia International Physics Center, San Sebastian, Spain

Density functional theory (DFT) provides a variational estimate of the electronic structure and geometry of many materials in their ground state. By its construction, DFT is unsuited for a description of the excited states, and particularly so for semi conductors. For these, one resorts to Hedin's GW approximation that gives rather good bands and gaps. A practical limitation of this approach is its computational cost that increases with the fourth power (N**4) of the number of atoms N per unit cell. Starting in 2007 [1], we have developed methods of "reduced complexity" that lower the growth of CPU time in calculations of electronic structure from N**4 to N**3, both for optical absorption [2] and in the GW approximation for finite systems [3]. Here we report on the extension of our methods to crystals, where we reduce the growth of CPU time again from N**4 to N**3, with N now the number of atoms in the unit cell of the crystal. Our work is motivated by organic semiconductors that have too many atoms in their unit cell for O(N**4) algorithms to be practical. Our results should help to improve and optimize organic solar cells. [1] D. Foerster, J.

Chem. Phys. 128 (34108) 2008. [2] P. Koval, D. Foerster and O. Coulaud, J. Chem. Theory Comp. 6 (2654) 2010 . [3] D. Foerster, P. Koval, and D. Sánchez-Portal, J. Chem. Phys. 135, 74105 (2011) .

O 47.11 Wed 13:15 MA 004

**Modeling anisotropic organic molecules at patterned semiconductor surfaces** — •Nicola Kleppmann and Sabine H. L. Klapp — Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Hybrid systems consisting of organic molecules at inorganic semiconductor surfaces are gaining increasing importance as thin film devices for optoelectronics. Their large charge carrier densities and tuneable resonance energies make them ideal candidates for semiconductor devices. However, the efficiency of such devices strongly depends on the self-organized structure formed by the adsorbed molecules, which depends, in turn, on the complex interplay of growth conditions and molecular properties. Recent ab initio calculations and experiments inspire us to examine the growth of sexiphenyl (6P) on ZnO(10-10) as a model system to understand self-organization of highly anisotropic molecules [1]. We develop a coarse-grained interaction hamiltonian of 6P molecules using a Gay-Berne potential and a linear quadrupole interaction term with additional substrate influence. We perform both equilibrium and non-equilibrium (growth) Monte Carlo simulations on a 2D lattice, where the rotational degrees of freedom of the molecules are continuous. We use these simulations to investigate orientational ordering in the condensed state, which is characterized by local descriptors such as order parameters and angular distributions.

[1] N. Kleppmann, and S. H. L. Klapp, submitted to JCP

[2] S. Bommel, N. Kleppmann et al., Nat Comm 5, 5388 (2014)

## O 48: Graphene: Dynamics

Time: Wednesday 10:30–13:00 Location: MA 041

O 48.1 Wed 10:30 MA 041

**Electron-phonon interactions and carrier transport in graphene** — •tae yun kim[1], nicola marzari[2], and cheol-hwan park[1] — [1]Department of Physics, Seoul National University, Seoul 151-747, Korea — [2]Theory and Simulations of Materials (THEOS) and National Center for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

The transport properties of graphene have received much attention partly for its possible applications in electronic devices. In particular, as recently reported, electron-phonon interactions are important in determining the intrinsic carrier transport properties [1,2]. Based on previous studies, we investigate further the carrier transport properties of graphene in terms of carrier density and other physical variables and find connection with experimental results on this matter.

This work was supported by Korean NRF funded by MSIP (Grant No. NRF-2013R1A1A1076141). Computational resources have been provided by Aspiring Researcher Program through Seoul National University (SNU) in 2014.

[1] C.-H. Park, N. Bonini, T. Sohier, G. Samsonidze, B. Kozinsky, M. Calandra, F. Mauri, and N. Marzari, Nano Lett. 14, 1113 (2014).

[2] T. Sohier, M. Calandra, C.-H. Park, N. Bonini, N. Marzari, and F. Mauri, Phys. Rev. B 90, 125414 (2014).

O 48.2 Wed 10:45 MA 041

**Non-linear luminescence and four-wave mixing from graphene, probed by femtosecond pulse shaping** — •Richard Ciesielski[1], Alberto Comin[1], Matthias Handloser[1], Torben Winzer[2], Ermin Malic[2], and Achim Hartschuh[1] — [1]Ludwig-Maximilians-Universität, AK Hartschuh, Butenandtstr. 5-11, 81377 München — [2]Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Germany

Ultrafast optical excitation of graphene leads to two main nonlinear emission signals in the visible. The first was described as incoherent non-linear photoluminescence (NLPL). The second results from near-degenerate four-wave mixing which is extraordinarily strong in graphene as compared to other materials. We investigated the two types of emission for different layer thickness using confocal microscopy and a 15 fs pulsed laser at 1.55 eV with a pulse shaper. Spectrally resolved autocorrelation scans revealed a continuously decreasing decay time of the NLPL from 1.2 eV towards 2.8 eV. Comparing the dynamics observed for different layers allows us to identify the influence of substrate induced doping. Finally, we were able to separate a weaker third contribution induced by the microscopic polarization of graphene [1].

Financial support by the DFG through the Nanosystems Initiative Munich (NIM) and the ERC (NEWNANOSPEC) is gratefully acknowledged.

[1] T. Winzer, R. Ciesielski, M. Handloser et al., arXiv:1411.0531v1 (2014).

O 48.3 Wed 11:00 MA 041

**Microscopic description of intraband absorption in graphene** — •Faris Kadi[1], Ermin Malic[1], Torben Winzer[1], Manfred Helm[2], Fabian Göttfert[2], Martin Mittendorff[2], Stephan Winnerl[2], and Andreas Knorr[1] — [1]Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Germany — [2]Helmholtz- Zentrum Dresden-Rossendorf, Dresden, Germany

We present a microscopic explanation for the occurrence of the controversially discussed transient negative differential transmission observed in optical pump-probe measurements in graphene [1]. Within the density matrix formalism we investigate the transient transmission with respect to optical interband as well as phonon-assisted intraband transitions. While interband processes yield a positive contribution due to absorption bleaching, we find intraband transitions to decrease differential transmission. Interestingly, in the low excitation regime, the phonon-assisted absorption prevails over the absorption bleaching resulting in the experimentally observed negative differential transmission [2]. The zero-crossing occurs within the first hundreds of femtoseconds and is followed by a recovery of the transmission spectrum on a picosecond timescale in a good agreement with experimental observations. [1] S.Winnerl, F. Göttfert, M. Mittendorff, et al., Journal of Physics: Condensed Matter 25, 054202 (2013) [2] F. Kadi, T. Winzer, E. Malić, et al., Phys. Rev. Lett. 113, 035502, (2014)

O 48.4 Wed 11:15 MA 041

**Anisotropic Intravalley Scattering in Strongly Doped Graphene** — •Daniela Dombrowski[1], Wouter Jolie[1], Sven Runte[1], Marin Petrović[2], Fabian Craes[1], Jürgen Klinkhammer[1], Marko Kralj[2], Predrag Lazić[3], Eran Sela[4], and Carsten Busse[1] — [1]II. Physikalisches Institut, Universität zu Köln, Germany — [2]Institut za fiziku, Croatia — [3]Institut Ruđer Bošković, Croatia — [4]Raymond and Beverly Sackler School of Physics and Astronomy, Tel-Aviv University, Israel

We perform Fourier-transform scanning tunneling spectroscopy (FT-STS) studies on Cs intercalated graphene on Ir(111). Angle-resolved photoemission spectroscopy (ARPES) measurements show, that the Cs strongly n-dopes graphene and shifts the Fermi level into the region of strong trigonal warping. We observe intervalley scattering and additionally a clear feature of intravalley scattering, which exhibits an anisotropic intensity distribution with dominant scattering in Γ-M direction.

In the linear region of the Dirac cone, conservation of pseudospin leads to the suppression of intravalley scattering since the direction of the pseudospin is either parallel or antiparallel to the momentum, thus the system has well defined chirality. This is no longer valid in the trigonal warping region near the Van-Hove singularity.

The FT-STS results are supplemented by density functional calculations of the electronic band structure and simulations of the scattering pattern based on the T-matrix theory.

O 48.5 Wed 11:30 MA 041

**Theory of coherent light emission in graphene** — •Roland Jago, Torben Winzer, Andreas Knorr, and Ermin Malic — Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Germany

Within the density matrix formalism we present a microscopic and full quantized theoretical description of the coupled carrier, phonon and photon dynamics in graphene implemented in a photonic crystal nanocavity. We demonstrate that under strong optical excitation a spectrally broad and long-lived population inversion can be achieved. In the case of free-standing graphene non-radiative Coulomb-induced carrier-recombination on a femtosecond time scale prevents an efficient emission of coherent photons. To partially suppress this ultrafast recombination, we propose to support graphene on a substrate having high-dielectric screening. In this case, our calculations reveal a temporarily extended population inversion, that remains stable up to some tens of picoseconds under realistic conditions. In particular we observe the emission of coherent laser light suggesting graphene as gain medium for lasers [2].

[1] T. Winzer, E. Malic and A. Knorr, Phys. Rev. B 87, 165413 (2013) [2] R. Jago, T. Winzer, A. Knorr and E. Malic, arXiv:1409.8182 (2014)

O 48.6 Wed 11:45 MA 041

**Phonon dynamics of graphene on copper substrate** — •Naira S. Grigoryan, Eeuwe S. Zijlstra, and Martin E. Garcia — Theoretical Physics, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

In the framework of density functional theoretical calculations, the lattice dynamical properties of graphene with and without a Cu(111) substrate have been investigated and analyzed using our in-house code for highly excited valence electron systems (CHIVES). We find that the lattice dynamics exhibits large sensitivity to the presence of copper. In particular, the appearance of a nearly dispersionless phonon branch at ~1.5THz makes this system a potential mirror for light molecules. We further show that there is a lifting of the degeneracy of the ZO and ZA modes at the M- point.

O 48.7 Wed 12:00 MA 041

**Non-equilibrium Carrier Relaxation in Graphene investigated with tr-ARPES** — •Mariana Chavez Cervantes[1], Raghu Tomar[1], Hubertus Bromberger[1], Haiyun Liu[1], Stefan Link[2], Ulrich Starke[2], Andrea Cavalleri[1,3], and Isabella Gierz[1] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — [2]Max Planck Institute for Solid State Research, Stuttgart, Germany — [3]Department of Physics, Clarendon Laboratory, University of Oxford, Oxford, United Kingdom

We used time- and angle-resolved photoemission spectroscopy (tr-ARPES) based on high order harmonics generation for the extreme ultra-violet (XUV) probe to investigate the relaxation of photo-excited carriers in quasi-freestanding epitaxial graphene samples. From the data we determined the energy dependence of the scattering rate that, according to Ref. [1,2], is predicted to follow the imaginary part of the *equilibrium* self-energy. In order to test this hypothesis we compare the scattering rate measured at different sample temperatures and for different pump fluences with the equilibrium self-energy determined from high-resolution static ARPES experiments as described in Ref. [3,4].

[1] M. Sentef et al., Phys. Rev. X 3, 041033 (2013)
[2] A. F. Kemper et al., Phys. Rev. B 90, 075126 (2014)
[3] A. Bostwick et al., Nat. Phys. 3, 36 (2007)
[4] I. Gierz et al., Faraday Disc. 171 (1), 311 (2014)

**Invited Talk** O 48.8 Wed 12:15 MA 041

**Electronic structure and electron dynamics in two-dimensional materials** — •Philip Hofmann — Department of Physics and Astronomy, Aarhus University

Two-dimensional materials can be grown epitaxially and in high quality on different substrates, and this can be exploited to study their electronic structure and different many-body effects. In this talk I will review the growth and electronic properties of epitaxial graphene, bilayer graphene and single-layer $MoS_2$. Specifically, I will focus on the electronic structure of these materials as studied by angle-resolved photoemission spectroscopy. This technique does not only give access to the materials' band structure but also to many-body effects such as the electron-electron and electron-phonon interaction. This is particularly so for the time-resolved variety of the technique in which the carrier dynamics can be followed in real time.

O 48.9 Wed 12:45 MA 041

**Dirac carrier thermalization on the sub 10fs timescale observed by tr-ARPES** — •Sven Aeschlimann[1,2], Mariana Chavez Cervantes[1], Francesca Calegari[1,3], Cephise Cacho[4], Emma Springate[4], Stefan Link[2], Ulrich Starke[2], Klaus Kern[2,5], Andrea Cavalleri[1,6], Christian R. Ast[2], and Isabella Gierz[1] — [1]MPI for the Structure and Dynamics of Matter, Hamburg, Germany — [2]MPI for Solid State Research, Stuttgart, Germany — [3]IFN, Consiglio Nazionale delle Ricerche, Milano, Italy — [4]Central Laser Facility, STFC Rutherford Appleton Laboratory, Harwell, United Kingdom — [5]EPFL, Lausanne, Switzerland — [6]University of Oxford, United Kingdom

We used time- and angle-resolved photoemission spectroscopy (tr-ARPES) with extreme ultra-violet (XUV) probe pulses from high order harmonics generation (HHG) to observe the ultrafast electron dynamics in photo-excited quasi-freestanding epitaxial graphene monolayers. By the use of the hollow core fiber compression technique, we produced 8 fs pulses, which are utilized both for driving HHG and for photo-excitation. These ultrashort pulses allowed us to observe the initial thermalization of photo-excited carriers via electron-electron scattering with unprecedented temporal resolution. We find that, at early times, the carrier distribution neither follows a Fermi-Dirac distribution nor the non-equilibrium distribution expected for a population-inverted state [1]. We attribute this to the short duration of the pump pulse on the order of the electron-electron scattering time.

[1] I. Gierz et al., Nature Materials 12, 1119 (2013)

## O 49: Metal Substrates: Structure, Epitaxy and Growth

Time: Wednesday 10:30–12:45 Location: MA 042

O 49.1 Wed 10:30 MA 042

**Investigation of nanocluster formation far from equilibrium in heteroepitaxial system: Co/Cu(111)** — •Quang Huy Vu, Sebastian Kunze, and Karina Morgenstern — Physical Chemistry I, Ruhr-Universiät Bochum, Universitätstr. 150,44801 Bochum, Germany

Lattice mismatch plays an important role in heteroepitaxial systems. Here we present such a system, Co adsorbed on Cu(111). Why is so important to study this system? The small lattice mismatch between cobalt and copper of 1.9% makes it attractive to investigate its structural characteristics and study its effect onto submonolayer adsorption. The growth mechanism of cobalt was measured by means of fast-scanning tunneling microscopy within the range of surface temperatures from 100 K to 300 K and for different deposition rates. At very low coverage, cobalt forms nanoclusters on Cu(111). These clusters adsorb favorably at step edges on Cu(111) at 115 K. In contrast at higher coverage, cobalt forms islands of fractal shapes with 1 ML height at 165K. Furthermore, the nucleation of 2 ML island height is studied at 165 K not only on the terraces but also on the step edges. Finally, the etching of Cu is observed at room temperature indicates growth of intermixed nanocluters. In this presentation the atomic processes of the island formation will be discussed

O 49.2 Wed 10:45 MA 042

**Surface induced stabilization of the metallic Sn phases in Sn nanoparticles.** — •Nicolas G. Hörmann[1] and Axel Gross[1,2] — [1]Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, 89069 Ulm — [2]Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm

Sn is a widely used element and besides new applications in optoelectronics [1] it is also a promising electrode material for established and future battery systems ($Li^+$,$Na^+$ and $F^-$ batteries [2,3]). Yet, not many detailed ab-initio studies have been reported so far.

In the presentation we will report results of DFT calculations of bulk and surface structures and energies of elemental Sn. By combining this with vibrational free energy data we derive the Gibbs free energy of Sn nanostructures and show that the phase stability diagram of Sn is significantly altered, which has significant impact on the expected performance of Sn nanostructures in real-world application. Furthermore we discuss briefly the initial steps of battery charging which occurs via atomic adsorption processes.

[1] S. Küfner et al., *Nanotechnology* **24**, 405702 (2013). [2] H. Zhu et al., *Nano Lett.* **13**, 3093–3100 (2013). [3] M. Anji Reddy et al. *J. Mater. Chem.* **21**, 17059–17062 (2011).

O 49.3 Wed 11:00 MA 042

**Intermixing of Pt and Cu atoms in PtCu/Ru(0001) surface alloys** — •Luis Mancera[1], Axel Gross[1], Albert Engstfeld[2], Andreas Bensch[2], and R. Jürgen Behm[2] — [1]Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany — [2]Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

In this contribution, we report on a joint theoretical and experimental study addressing model surface catalysts consisting of bimetallic PtCu surface alloys formed on a Ru(0001) substrate. The PtCu/Ru(0001) surface is obtained by deposition of Pt onto a previously prepared monolayer of Cu on Ru(0001) surface. In spite of the high stability of Ru(0001) that prevents exchange of Cu or Pt atoms with the substrate, Ru(0001) can still induce strain on the deposited Cu layer, due to the different lattice parameter, and thus modulate the formation of the PtCu alloy. Using STM imaging, it has been observed that the surface alloy is formed following a specific nucleation behavior that shows an atypical island density increase with growing Pt coverage. Here we apply periodic density functional theory (DFT) calculations to study various situations for atom diffusion on different surface alloy configurations in order to elucidate the origin of those nucleation patterns. We determine the stability of PtCu surface alloys and address the diffusion of Pt and Cu atoms on PtCu/Ru(0001) as well as Pt-Cu atom-exchange processes that lead to the formation of these alloys. Based on these findings, the effect of Pt substitutional atoms in the nucleation is discussed.

O 49.4 Wed 11:15 MA 042

**Alloying and dealloying of Mg on the Ag(100) surface** — •Marina Schuler, Pascal Ferstl, Lutz Hammer, and M.Alexander Schneider — Lst. für Festkörperphysik, FAU Erlangen-Nürnberg

Ultrathin oxide films on metal substrates play an important role in basic surface research and technological applications. Since these oxide films are often prepared via postoxidation of pre-deposited metal films, their structural properties may strongly influence the quality of the growing oxide. In this study we investigate the structures developing during Mg deposition on Ag(100) prior to oxidation to MgO by means of quantitative LEED and STM.

Submonolayers of Magnesium adsorbed at 90 K on top of the plain Ag(100) surface form an ordered $(\sqrt{5} \times \sqrt{5})$R arctan 0.5 phase. Annealing to 150 K leads to an atomic reorganisation at the surface and a c(2×2) phase appears, which has been reported already [1]. The crystallographic structure of this c(2×2) phase is shown to be a bimetallic surface alloy by means of a quantitative LEED analysis: every second Ag atom of the toplayer is substituted by Mg, which relaxes outward by 0.13 Å. The Mg/Ag-c(2×2) structure persists further Mg deposition at elevated temperatures dissolving surplus Mg atoms into the underlying substrate layers. By offering $1 \cdot 10^{-7}$ mbar oxygen at 400 K the dissolved Mg is driven at the surface of the crystal again, forming MgO films of the corresponding thickness.

[1] C. Tegenkamp Appl. Surf. Sci. 151 40 (1999)

O 49.5 Wed 11:30 MA 042

**Comparative study of the carbide-modified surfaces C/Mo(110) and C/Mo(100) using high resolution x-ray photoelectron spectroscopy** — •Christoph Gleichweit, Udo Bauer, Max Amende, Stefan Schernich, Oliver Höfert, Jörg Libuda, Hans-Peter Steinrück, and Christian Papp — Lehrstuhl f. Physikal. Chemie II

We present a comparative study of the carbide-modified surfaces C/Mo(100) and C/Mo(110) using synchrotron-based high-resolution x-ray photoelectron spectroscopy (HR-XPS), with the objective of elucidating the differences and similarities of the two crystal facets depending on the C/Mo ratio. We are interested in changes at the surface due to exposure to carbon and oxygen right at the temperature sufficient to drive carbon into the interstitial sites of the Mo lattice. Carburization by dosing ethylene, i.e. carbide preparation, and subsequent oxidative carbon removal by dosing $O_2$ at 1200 K is followed in great detail through careful analysis of the C 1s, Mo 3d and O 1s core levels. We show that the thin carbide overlayers show spectroscopic differences compared to the thick carbides obtained at high carbon dose. Furthermore we show that the carbide thickness on Mo(110) influences the adsorption properties towards $H_2$ and CO, pointing towards the importance of the surface structure for reactivity.

O 49.6 Wed 11:45 MA 042

**Surface self-diffusion of the battery anode materials lithium, sodium and magnesium studied using DFT** — •Markus Jäckle[1,2] and Axel Gross[1,2] — [1]Helmholtz Institut Ulm - Elektrochemische Energiespeicherung, 89069 Ulm, Germany — [2]Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Lithium, sodium and magnesium represent rather interesting anode materials for next-generation batteries. These metals vary in their tendency to form dendrites which represent a hazard as their formation can lead to short-circuits during battery operation. As metal growth processes are intimately linked to diffusion, we have studied the self-diffusion properties of the metals in order to understand the differences in their tendency towards dendrite formation.

According to our calculations, self-diffusion of Mg is much faster than the one of Li or Na on the energetically most stable surface terminations [1]. These results can be connected to the fact that Mg is an hcp metal, whereas Li and Na are bcc metals. In addition, we have determined the interaction between adatoms of these metals. We will discuss the relevance of our findings for the understanding of the dendrite growth on battery anodes. Furthermore, we will address first attempts to assess the influence of the electrochemical environment on metal diffusion properties.

[1] M. Jäckle and A. Groß, J. Chem. Phys. **141**, 174710 (2014).

O 49.7 Wed 12:00 MA 042

**Ultra-thin stepped iron oxide films on high index Pt surfaces** — •Elin Grånäs[1,2], Niclas Johansson[1], Mohammad A. Arman[1], Jacek Osiecki[3], Karina Thånell[3], Jesper N. Andersen[1,3], Joachim Schnadt[1], and Jan Knudsen[1,3] — [1]Division of Synchrotron Radiation Research, Lund Universiy, Sweden — [2]Deutsches-Elektron Synchrotron (DESY), Hamburg, Germany — [3]MAX IV Laboratory, Lund University, Sweden

Iron oxide films grown on metal surfaces show high catalytic activity for reactions such as CO oxidation and the water-gas shift, and it has been suggested that the high activity is due to under-coordinated Fe atoms at the edge of FeO islands[1]. Whether the metal substrate is essential for the activity of the edge sites remain an open question and the few and heterogeneous edge sites present on FeO islands make it difficult to characterize them with chemically sensitive techniques like X-ray photoelectron spectroscopy (XPS).

We have grown FeO films on Pt(322), producing films with a very high density of homogenous FeO-FeO edge sites. Scanning tunneling microscopy show that approx. 20 % of the sites are edge sites. In water adsorption studies on the stepped FeO film we observe an enhanced ability to split water compared to planar FeO. As the Pt(322) substrate is fully covered by stepped FeO we assign the high water splitting ability to the pure FeO-FeO step site.

[1] L. Xu, Z. Wu *et al.*, J. Phys. Chem. C 115, 14290 (2011)

O 49.8 Wed 12:15 MA 042

**MD study of gold growth on MnAs** — •Andreas Rühl and Christian Heiliger — I. Physikalisches Institut, Justus Liebig Universtität Giessen, D-35392 Giessen, Germany

We present the results of our Molecular Dynamics (MD) study concerning the atomic deposition of gold atoms on different MnAs surfaces. Those growth simulations show a 'layer-plus-island growth', also known as the Stranski-Krastanov (SK) growth. Our research is motivated by the experimental work on ferromagnetic MnAs nanoclusters, which can be easily tuned in different shapes and sizes. Taking two of those clusters and connect them via a non-magnetic metal, for example gold, leads to a GMR-like structure (Giant magnetoresistance).

In order to analyze the structure of the deposited gold atoms, needed for later calculation of the electric transport, we created an EAM potential for the MnAsAu system in the scope of Force Matching by fitting the potential model to ab initio data. The resulting potential is validated by different tests, including the comparison of bulk and surface energies to the corresponding ab initio data. We then carried out growth simulations for different MnAs surfaces and different substrate temperatures. The observed SK-growth exhibits a critical layer thickness at which the island growth starts and by using Bond-Angle analysis we see the gold atoms mainly relaxing to fcc phases.

O 49.9 Wed 12:30 MA 042

**Development and testing of a plasma coating apparatus** — •Cornelia Kunz[1], Sebastian Dahle[1,2], and Wolfgang Maus-Friedrichs[1,2] — [1]Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstraße 4, D-38678 Clausthal-Zellerfeld, Germany — [2]Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Agricolastraße 2, D-38678 Clausthal-Zellerfeld, Germany

Thin coatings on metal surfaces have known advantages in many applications, e.g. passivation or corrosion protection. In this work, a plasma coating apparatus was constructed and tested to develop uniform, particle-free coatings on titanium surfaces. A primary $Si_3N$-coating was achieved via plasma ignition in nitrogen diluted silane at atmospheric pressure. A procedure was devised to control the growth mechanisms yielding particle-free coatings. In order to minimize particle formation, nucleation and agglomeration of radicals formed in the plasma have to be inhibited. The critical parameter leading to a silicon radical controlled growth mode and thus to minimized nucleation was found to be the excitation frequency. In a secondary step, these $Si_3N$-coatings were treated with air plasma, leading to oxidation and clean silicon dioxide coatings. Surface topography was analysed using atomic force microscopy (AFM) in order to determine a growth mode suppressing particle formation mode. In a following step, surface stoichiometry was determined via X-ray photoelectron spectroscopy (XPS).

## O 50: Coupled Nanostructures and Light Localization

Time: Wednesday 10:30–13:00 Location: MA 043

O 50.1 Wed 10:30 MA 043

**Babinet to the half: Coupling of solid and inverse plamonic structures** — •Mario Hentschel[1,2], Thomas Weiss[1], Shahin Bagheri[1], and Harald Giessen[1] — [1]4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany — [2]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA

We study the coupling between the plasmonic resonances of solid and inverse metallic nanostructures [1]. While the coupling between solid-solid and inverse-inverse plasmonic structures is well-understood, mixed solid-inverse systems have not yet been studied in detail. We find that an efficient coupling between inverse and solid resonances is possible, identify the necessary geometrical prerequisites, and demonstrate a novel solid-inverse plasmonic electromagnetically induced transparency (EIT) structure as well as mixed chiral systems. We furthermore show that for the coupling of asymmetric rod-shaped inverse and solid structures symmetry breaking is crucial. In contrast, highly symmetric structures such as nanodisks and nanoholes are straightforward to couple. Moreover, we demonstrate our concept experimentally in lithographically fabricated multilayered systems and explore a novel fabrication route combining top-down ion-etching techniques with high quality wet-chemically synthesized nanoparticles. Our results constitute a significant extension of the plasmonic coupling toolkit, and we thus envision the emergence of a large number of intriguing novel plasmonic coupling phenomena in mixed solid-inverse structures. [1] M. Hentschel et al., Nano Lett. 13, 4428 (2013)

O 50.2 Wed 10:45 MA 043

**Tunable plasmon polaritons in cubic crystals of interacting metallic nanoparticles** — •Simon Lamowski[1], Felicitas Hellbach[1], Guillaume Weick[2], and Fabian Pauly[1] — [1]Department of Physics, University of Konstanz, D-78457 Konstanz, Germany — [2]Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg, CNRS UMR 7504, F-67034 Strasbourg, France

In this work we extend previous studies of plasmons supported by interacting metallic nanoparticles in honeycomb [1] and simple cubic lattices [2] to body-centered cubic (bcc) and face-centered cubic (fcc) lattices. The near-field interaction between the localized surface plasmons on each nanoparticle results in collective plasmons that extend over the whole lattice. Considering dipolar interactions up to fourth nearest neighbors, we derive analytical expressions for the collective plasmon dispersion. Following Hopfield [3], we couple the collective plasmons to light to form plasmon polaritons. The plasmon polariton dispersion depends on the direction of the wavevector and the polarization of light. We discuss this dependence for the different lattices and the range of the dipolar interactions [4].

[1] G. Weick, C. Woollacott, W. L. Barnes, O. Hess, and E. Mariani, Phys. Rev. Lett. 110, 106801 (2013).

[2] G. Weick and E. Mariani, Eur. Phys. J. B (2014), to appear; arXiv:1403.2205

[3] J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

[4] S. Lamowski, F. Hellbach, G. Weick, and F. Pauly, in preparation.

O 50.3 Wed 11:00 MA 043

**Dirac-like plasmons in honeycomb lattices of metallic nanoparticles** — •Guillaume Weick[1], Claire Woollacott[2], William L. Barnes[2], Ortwin Hess[3], and Eros Mariani[1] — [1]Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg, CNRS UMR 7504, F-67034 Strasbourg, France — [2]Centre for Graphene Science, Department of Physics and Astronomy, University of Exeter, EX4 4QL Exeter, UK — [3]The Blackett Laboratory, Department of Physics, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

We consider a two-dimensional honeycomb lattice of metallic nanoparticles, each supporting a localized surface plasmon, and study the quantum properties of the collective plasmons resulting from the near field dipolar interaction between the nanoparticles. We analytically investigate the dispersion, the effective Hamiltonian and the eigenstates of the collective plasmons for an arbitrary orientation of the individual dipole moments. When the polarization points close to the normal to the plane the spectrum presents Dirac cones, similar to those present in the electronic band structure of graphene. We derive the effective Dirac Hamiltonian for the collective plasmons and show that the corresponding spinor eigenstates represent Dirac-like massless bosonic excitations that present similar effects to electrons in graphene. We further discuss how one can manipulate the Dirac points in the Brillouin zone and open a gap in the collective plasmon dispersion by modifying the polarization of the localized surface plasmons. Ref: G. Weick et al., PRL 110, 106801 (2013)

O 50.4 Wed 11:15 MA 043

**Mode normalization and mode sensitivity in metallic photonic crystal slabs and complex plasmonic nanostructures** — •Thomas Weiss[1], Martin Mesch[1], Harald Giessen[1], Wolfgang Langbein[2], and Egor A. Muljarov[2] — [1]4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany — [2]School of Physics and Astronomy, Cardiff University, United Kingdom

The optical properties of a given structure are strongly determined by its resonances. Of significant importance are plasmonic resonances, which occur in metallo-dielectric systems. Problems arise whenever it becomes necessary to properly normalize the optical resonances, because optically active resonances couple to the far-field, so that a straight-forward integral over the whole space will diverge. In 2010, Muljarov et al. have developed an analytical mode normalization [1], which allows not only to expand the Green's function in terms of resonant states, but also to derive the modification of the optical response due to changes in the occurring material distributions via the so-called resonant state expansion. We will present how to adapt the analytical normalization to periodic structures such as metallic photonic crystal slabs, for which we have developed efficient procedures for finding the optical modes [2]. Moreover, we will show how we can use first order perturbation theory in order to derive the sensitivity of plasmonic resonances with respect to refractive index changes, which provides new routes to develop advanced sensing devices.

[1] E. A. Muljarov et al., Europhys. Lett. 92, 50010 (2010).

[2] T. Weiss et al., J. Opt. Soc. Am. A 28, 238-244 (2011).

O 50.5 Wed 11:30 MA 043

**Simple plasmonic design for homogeneous chiral near-fields** — •Martin Schäferling[1], Nader Engheta[2], Thomas Weiss[1], and Harald Giessen[1] — [1]4th Physics Institute and Research Centers SCoPE and SimTech, University of Stuttgart, Germany — [2]Department of Electrical and Systems Engineering, University of

Pennsylvania, Philadelphia, USA

Chiroptical spectroscopy utilizes chiral electromagnetic fields to probe the handedness of natural chiral molecules. The strength of the chiroptical interaction can be quantified by the so-called optical chirality, which is a property of the electromagnetic field [1].

Plasmonic nanostructures can tailor the optical chirality of their near-fields [2]. We have shown recently that geometrically chiral nanostructures can lead to strong chiral fields over an extended region [3]. However, our proposed design of four intertwined helices is difficult to fabricate and therefore not the optimum for potential applications.

In this contribution, we present a novel design combining a layer of diagonal slits with a mirror for the generation of chiral near-fields. The design is easy to fabricate by electron-beam lithography. Access to the chiral near-fields is straightforward. Although the optical chirality is weaker than for helices, our structure might be preferable for applications due to its simplicity. We examine the strength and shape of the generated chiral near-fields and discuss optimization strategies.

[1] Y. Tang and A. E. Cohen, Science **332**, 333 (2011).
[2] M. Schäferling et al., Phys. Rev. X **2**, 031010 (2012).
[3] M. Schäferling et al., ACS Photonics **1**, 530 (2014).

O 50.6 Wed 11:45 MA 043

**Superluminescence from an Optically Pumped Molecular Tunneling Junction by Injection of Plasmon Induced Hot Electrons** — •Kai Braun, Xiao Wang, Dai Zhang, Heiko Peisert, Thomas Chassé, and Alfred J. Meixner — Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Here, we introduce and experimentally demonstrate amplification of the tip enhanced optical signal from a very low number of molecules enclosed in the optically pumped gap of a STM. The gap between a sharp gold tip and a flat gold substrate covered with a self-assembled monolayer of 5-chloro-2-mercaptobenzothiazole (Cl-MBT) can be used as an extremely small optical gain medium. When a bias-voltage is applied between tip and sample such that electrons tunnel from the Cl-MBT's highest occupied molecular orbital (HOMO) to the tip, holes are left behind in the molecules. These can be repopulated by hot electrons that are created by the laser-driven plasmon oscillation on the metal surfaces. Emission of photons occurs from the recombination of plasmon excited hot electrons with holes in the HOMO of surface bound molecules facing the tip apex. Varying the laser pump power or alternatively the applied bias voltage shows in both cases a distinct threshold above which amplification of the optical signal occurs. Solving the laser-rate equations for this system shows that the repopulation process can be efficiently stimulated by the gap modes near field. TERS scattering from neighboring molecules acts as an optical seed and feed-back is provided by the cavity plasmon-polariton.

O 50.7 Wed 12:00 MA 043

**Experimental verification of super- and hyperlensing with two dimensional materials: Graphene and Bornon nitride** — •Peining Li[1], Martin Lewin[1,2], Fabian Gaussmann[2], Joshua Caldwell[3], and Thomas Taubner[1,2] — [1]1st Institute of Physics (IA), RWTH Aachen University, Aachen 52056, Germany — [2]Fraunhofer Institute for Laser Technology ILT, 52074 Aachen, Germany — [3]U.S. Naval Research Laboratory, 4555 Overlook Ave, S.W., Washington, D.C. USA

Two-dimensional atomic crystals (TDACs), such as graphene [1] and hBN [3], support highly confined plasmon- or phonon-polaritons for concentrating electromagnetic energies into manometer scale, which open ups the possibility for many different subdiffractional nanophotonic applications.

Here, we present the experimental studies that use these two typical TDACs,graphene and hexagonal boron nitride (hBN), to overcome the diffraction limit for achieving high-resolution infrared near-field imaging[4-6].

[1] J. Chen et al.,Nature 487, 77 (2012). Z. Fei et al.,Nature 487, 82 (2012).
[3] S. Dai et al.,Science 343, 1125 (2014).
[4] P. Li and T. Taubner., ACS nano 6, 10107 (2012).
[5] P. Li, et al., Nano Lett. 4, 4400 (2014)
[6] P. Li, et al., Submitted

O 50.8 Wed 12:15 MA 043

**Real space imaging of nano-tip plasmons using electron energy-loss spectroscopy** — •Thorsten Weber[1,2], Benjamin Schröder[3], Sergey Yalunin[3], Christian Matyssek[4], Thomas Kiel[4], Felix von Cube[1,2], Stephan Irsen[2], Kurt Busch[4,5], Stefan Linden[1], and Claus Ropers[3] — [1]Physikalisches Institut, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany — [2]Research center caesar, center of advanced european studies and research, Bonn, Germany — [3]IV. Physikalisches Institut, Georg-August-Universität Göttingen, Germany — [4]Institut für Physik, Humboldt-Universität zu Berlin, Germany — [5]Max-Born-Institut, Berlin, Germany

Focusing light beyond the diffraction limit is of great interest in photonics. Metallic nano-tips offer the ability to concentrate light in nanometric volumes on femtosecond timescales using adiabatic compression of surface plasmon polaritons, facilitating applications in tip-enhanced Raman scattering, optical near field microscopy or ultra fast photoemission. Here, we show real-space imaging of surface plasmon polaritons on a gold nano-tip using electron energy-loss spectroscopy (EELS) in combination with scanning transmission electron microscopy. We demonstrate the predicted nanofocussing towards the apex and measure the local dispersion relation of the plasmon. The observations are in good agreement with ab-initio electrodynamic computations via the discontinous-Galerkin time-domain method and a semi-analytical model including reflection at the apex and higher order azimuthal modes.

O 50.9 Wed 12:30 MA 043

**Localization of Light in ZnO Nano-Forests** — •David Leipold[1], Manfred Maschek[2], Martin Silies[2], Christoph Lienau[2], and Erich Runge[1] — [1]Technische Universität Ilmenau, Germany — [2]Carl von Ossietzky Universität Oldenburg, Germany

The localization of waves due to multiple scattering is a particularly interesting phenomenon. In this contribution we present several aspects of ongoing research in light localization. Earlier, we reported hot spots in the second harmonic generation in random ZnO nano-needle arrays[1]. These were interpreted as due to the localization of light by multiple scattering. We compare theoretical results of electromagnetic calculations to the experiments in order to give further insight to the formation of localized optical near-fields. While the 3D calculations reproduce various aspects of the experimental results very well, the open-boundary 2D calculations proof the coexistence of propagating and lossy localized modes[2].

[1] M. Maschek et al., Nature Photonics **6**, 293 (2012)
[2] D. Leipold et al., Annalen der Physik **525**, 199 (2013)

O 50.10 Wed 12:45 MA 043

**Observation of Anderson localization in disordered plasmonic waveguide arrays** — •Tim Vogler, Felix Bleckmann, and Stefan Linden — Physikalisches Institut, Nussallee 12, 53115 Bonn

Evanescently coupled waveguide arrays have become important model systems to investigate the evolution of coherent waves in complex structures. Here, we use arrays of dielectric loaded surface plasmon polariton waveguides (DLSPPWs) to study the propagation of surface plasmon polaritons (SPPs) in disordered media. The DLSPPWs consist of dielectric ridges that are deposited by negative-tone gray-scale electron beam lithography on top of a gold film. Disorder is intentionally introduced by either varying the heights of the individual DLSPPWs (on-diagonal disorder) or by varying their separations (off-diagonal disorder). The evolution of the SPP intensity inside of the arrays is monitored by leakage radiation microscopy. We observe a cross-over from discrete diffraction to Anderson localization as we increase the degree of disorder. Our experimental results are in excellent agreement with theoretical predictions from condensed matter physics and numerical calculations based on the coupled mode theory.

## O 51: Topological Insulators: Theory (HL with DS/MA/O/TT)

Time: Wednesday 9:30–11:30 Location: ER 270

O 51.1 Wed 9:30 ER 270

**Weyl and Dirac semimetals: A platform for new interface phenomena** — •Adolfo G. Grushin[1], Jorn W. F. Venderbos[2], and Jens H. Bardarson[3] — [1]Max Planck Institute for the physics of Complex Systems, Dresden, Germany — [2]Massachusetts Institute of Technology, Cambridge, MA, USA — [3]Max Planck Institute for the physics of Complex Systems, Dresden, Germany

The Weyl semimetal (WSM) state is sometimes loosely referred to as the three-dimensional cousin of graphene since its low energy theory is described by an even number of copies of the Weyl Hamiltonian. Closely related to WSM, the Dirac semimetals hosts the Weyl nodes at the same point in the Brillouin Zone and it is realised in $Cd_3As_2$ and $Na_3Bi$ compounds. In this talk I will explore the rich surface state physics that these states can host and how can it be probed, including coexistence of Dirac and Fermi arc states at the topological insulator-weyl semimetal interfaces as well as signatures of the chiral anomaly.

O 51.2 Wed 9:45 ER 270

**Spin chirality tuning and Weyl semimetal in strained $HgS_{1-x}Te_x$** — •Tomáš Rauch[1], Steven Achilles[1], Jürgen Henk[1], and Ingrid Mertig[1,2] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle (Saale), Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle (Saale), Germany

We have theoretically investigated the phase diagram of $HgS_{1-x}Te_x$. The parameters which have been varied are the concentration $x$ and the in-plane strain, which could be applied by an appropriate substrate in an experiment. In the topological phase diagram we found a normal metallic phase, two topological insulator phases with different spin chiralities of the surface states and a Weyl semi-metal phase. The phases have been probed by calculating topological invariants and the dispersion of the surface states for both crystal terminations of the (001) surface by an *ab-initio* based tight-binding model.

O 51.3 Wed 10:00 ER 270

**Topological phases in (interfacial) phase-change materials** — •Peter Schmitz, Wei Zhang, and Riccardo Mazzarello — Institute for Theoretical Solid State Physics, RWTH Aachen University

We investigate the topological, spectral and structural properties of $[Sb_2Te_3]_x[GeTe]_y$ (GST) compounds, some of which are interfacial phase change materials (IPCMs), as a function of strain and stacking sequence by performing a DFT study of bulk and slab models and discuss the relevance of a 3D (topological) Dirac semimetal phase ((T)DSM), eg. to GST225.

IPCMs can perform fast reversible transitions, induced by electric fields or heat, between crystalline states of different stacking. Since they also possess strong spin-orbit coupling and a strong topological insulator (STI) + normal insulator(NI) layering, they are a promising platform to investigate nontrivial interface states and direct applications to data storage in terms of switching topological phases. Until now they were shown to exhibit STIs and *unstable* DSM-like critical states corresponding to STI/NI transitions [1]. Then recently [2] a *robust* TDSM phase was predicted for crystals having certain rotational symmetries: The STI/NI transition point can be extended to a line and 2 Dirac points appear in the bulk spectrum.

Analyzing whether such phases can be obtained in GST compounds is also interesting since the problem of a TDSM in a multilayer structure has not yet been discussed.

[1] J. Tominaga et al, Adv. Mat. Inter. 1 (2014);
[2] B. Yang and N. Nagaosa, Nature Commun. 5, 4898 (2014)

O 51.4 Wed 10:15 ER 270

**Effect of Bi bilayers on the topological states of $Bi_2Se_3$: A first-principles study** — Kirsten Govaerts[1], Kyungwha Park[2], Christophe De Beule[1], Dirk Lamoen[1], and •Bart Partoens[1] — [1]CMT-group and EMAT, University of Antwerp, Belgium — [2]Virginia Tech, Department of Physics, USA

$Bi_2Se_3$ and vice versa, has not been explored much. Bi bilayers are often present between the quintuple layers of $Bi_2Se_3$, since $(Bi_2)_n(Bi_2Se_3)_m$ form stable ground-state structures. Moreover, $Bi_2Se_3$ is a good substrate for growing ultrathin Bi bilayers. By first-principles techniques, we first show that there is no preferable surface termination by either Bi or Se. Next, we investigate the electronic structure of Bi bilayers on top of, or inside a $Bi_2Se_3$ slab. If the Bi bilayers are on top, we observe a charge transfer to the quintuple layers that increases the binding energy of the surface Dirac cones. The extra states, originating from the Bi bilayers, were declared to form a topological Dirac cone, but here we show that these are ordinary Rashba-split states. This result, together with the appearance of a new Dirac cone that is localized slightly deeper, might necessitate the reinterpretation of several experimental results. When the Bi bilayers are located inside the $Bi_2Se_3$ slab, they tend to split the slab into two topological insulators with clear surface states. Interface states can also be observed, but an energy gap persists because of strong coupling between the neighboring quintuple layers and the Bi bilayers.

O 51.5 Wed 10:30 ER 270

**Topological states in $\alpha$-Sn and HgTe quantum wells: a comparison of ab-initio results** — •Sebastian Küfner and Friedhelm Bechstedt — Friedrich Schiller Universität Jena

Quantum well (QW) structures based on HgTe are theroretically predicted and experimentally verified to exhibit the quantum-spin Hall phase. Despite the similarities of the bulk band structures, studies of $\alpha$-Sn QW structures are missing. We compare the properties of QW structures made by the different zero-gap semiconductors $\alpha$-Sn and HgTe, but both sandwiched in nearly lattice-matched CdTe barriers by means of first-principles calculations including quasiparticle corrections and spin-orbit interaction. The two well materials possess different space groups $O_h^7$ (diamond structure) and $T_d^2$ (zinc-blende structure). The spin-orbit interaction, in particular that in the $p$-derived valence states, is different due to the contribution of both atoms in the unit cell ($\alpha$-Sn) and mainly the anion (HgTe) to the states at the top of the valence bands, and the different local electrostatic properties due to the different bonding character in the QW layers and their interfaces with the CdTe barrier material. We investigate the similarities and differences of the two embedded zero-gap semiconductors on the formation of quantum-well, edge and interface states in detail.

O 51.6 Wed 10:45 ER 270

**Quasiparticle band structure of the topological insulator $Bi_2Se_3$** — •Tobias Förster, Peter Krüger, and Michael Rohlfing — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany

$Bi_2Se_3$ is a prototype topological insulator. Its simple surface band structure with only one Dirac point makes it an ideal system for exploring the properties of topological surface states. Up to now, the vast majority of theoretical investigations of the electronic structure of $Bi_2Se_3$ has utilized DFT calculations. In $Bi_2Se_3$ and related compounds, however, many body perturbation theory in the $GW$ approximation yields both quantitative and qualitative quasiparticle corrections of the DFT bulk band structures [1].

Here we discuss results for bulk $Bi_2Se_3$ from $GW$ calculations employing a localized basis as well as from a perturbative LDA+$GdW$ approach [2]. The latter provides a numerically very efficient method for the calculation of quasiparticle corrections with only slightly reduced precision compared to $GW$. The applicability of the LDA+$GdW$ formalism to the $Bi_2Se_3$ surface with the Dirac state will also be addressed.

[1] I. Aguilera *et al.*, Phys. Rev. B **88**, 045206 (2013)
[2] M. Rohlfing, Phys. Rev. B **82**, 205127 (2010)

O 51.7 Wed 11:00 ER 270

**Calculation of topological invariants from a maximally localized Wannier functions derived model Hamiltonian** — •Patrick M. Buhl, Chengwang Niu, Yuriy Mokrousov, Daniel Wortmann, Gustav Bihlmayer, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Using density-functional methods it is possible to provide an accurate description of topological phases in complex materials. We demonstrate how topological characterization can be performed in a unified manner based on Wannier functions generated from the full-potential linearized augmented plane-wave method as implemented in the `FLEUR` code [1]. Taking as examples bcc Fe, $Na_3Bi$ and PbTe we compute various topological invariants and identify topologically non-trivial points in the electronic structure of these materials in bulk and their close relation to the surface electronic structure. In particular, we focus on the Weyl semimetallic phase as a transitional phase between various topological phases in the same material and on the role of the Weyl points in the electronic structure for topological properties. Financial support by the HGF-YIG Programme VH-NG-513 and SPP 1666 of the DFG is gratefully acknowledged.

[1] F. Freimuth *et al.*, Phys. Rev. B **78**, 035120 (2008)

O 51.8 Wed 11:15 ER 270

**Functionalized Bismuth Films: Giant Gap Quantum Spin Hall and Valley-Polarized Quantum Anomalous Hall States** — •Chengwang Niu, Gustav Bihlmayer, Hongbin Zhang, Daniel Wortmann, Stefan Blügel, and Yuriy Mokrousov — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The search for new large band gap quantum spin Hall (QSH) and quantum anomalous Hall (QAH) insulators is critical for their realistic applications at room temperature [1,2]. Here we predict, based on first principles calculations, that the band gap of QSH and QAH states can be as large as 1.01 eV and 0.35 eV in an H-decorated Bi(111) film [3]. The origin of this giant band gap lies both in the large spin-orbit interaction of Bi and the H-mediated exceptional electronic and structural properties. Moreover, we find that the QAH state also possesses the properties of quantum valley Hall state, thus intrinsically realising the so-called valley-polarized QAH effect. We further investigate the realization of large gap QSH and QAH states in an H-decorated Bi($\bar{1}10$) film and X-decorated (X=F, Cl, Br, and I) Bi(111) films.

This work was supported by the Priority Program 1666 of the DFG and project VH-NG-513 of the HGF.

[1]M. Hasan and C. Kane, Rev. Mod. Phys. **82**, 3045 (2010).

[2]X.-L. Qi and S.-C. Zhang, Rev. Mod. Phys. **83**, 1057 (2011).

[3]Chengwang Niu, Gustav Bihlmayer, Hongbin Zhang, Daniel Wortmann, Stefan Blügel, and Yuriy Mokrousov, submitted.

## O 52: Focus Session: Nanophotonic Concepts and Materials for Energy Harvesting - Plasmonics, Transformation Optics, Upconversion, and beyond

Nanostructured and novel photonic materials can control the spectral composition of light, its propagation characteristics, and its interaction with matter. The use of these abilities is particularly rewarding in the context of energy harvesting in semi-conductor materials. This focused session appreciates and presents the most recent advancement in this field of research, where progress has been made from a conceptual but also from a materials perspective.

Organization: Carsten Rockstuhl (KIT, Karlsruhe), Jan Christoph Goldschmidt (FhG ISE, Freiburg), Ralf Wehrspohn (MLU Halle), Uli Lemmer (KIT, Karlsruhe)

Time: Wednesday 11:00–13:00 Location: EW 201

**Invited Talk** O 52.1 Wed 11:00 EW 201

**Transformation Optics: From Fundamentals to Applications for Energy Harvesting** — •Martin Wegener and Martin Schumann — Institute of Applied Physics and Institute of Nanotechnology, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

Transformation optics can be seen as a versatile tool for designing devices in optics and other areas of physics. In this talk, we start by giving a broad introduction into this concept. A striking paradigm is invisibility cloaking. We briefly review experimental demonstrations in optics, thermodynamics, and mechanics. Next, we discuss a possible application: In order to extract the electrical power from solar cells, metal contacts at the sun-facing surface are required. Unfortunately, these contacts create optically dead areas, reducing the overall current per area by a few percent. We present a solution to this problem by using microstructures that are designed by transformation optics and that cloak the contacts. An experimental proof-of-principle demonstration based on three-dimensional direct-laser-writing optical laser lithography is given.

**Invited Talk** O 52.2 Wed 11:30 EW 201

**Nanostructures and materials for intermediate band solar cells** — •Antonio Martí — Instituto de Energía Solar, ETSI Telecomunicación, Universidad Politécnica de Madrid

Intermediate band solar cells (IBSCs) seek for materials that can harvest photons with energy lower than the semiconductor bandgap without degrading the output voltage of the cell. One of these material systems relies on the use of quantum dots (QDs). Under this approach, photons are harvested thanks to the energy states of the electrons confined in the quantum dots. In this contribution we review the theory that sustains the use of QDs for IBSC applications, the design constrains of these kind of solar cells, its limitations and challenges as well as the most recent experimental results. These experimental results refer to the empirical demonstration of the use of two below bandgap energy photons to generate an electron-hole pair and the preservation of the output voltage of the cell.

O 52.3 Wed 12:00 EW 201

**Emission quenching of magnetic dipole transitions near an absorbing optical nanoantenna** — •Dmitry Chigrin, Deepu Kumar, and Gero von Plessen — RWTH Aachen University, 52074 Aachen, Germany

The optical emission of an ionic emitter near an absorbing optical nanoantenna (such as a metal nanoparticle) can be enhanced or quenched due to near-field effects induced by the nanoantenna. A comparison of emission quenching of electric dipole (ED) and magnetic dipole (MD) transitions in the close vicinity of a metal nanoparticle has been carried out in this work. It is demonstrated that the emission quenching of the MD transitions becomes dominant at substantially shorter distances to the surface of the absorbing nanoantenna as compared to the ED transitions. This difference in quenching behaviour is due to different asymptotic dependencies of the quasi-static radiative and non-radiative decay rates of ED and MD transitions near a metal nanoparticle. It is shown that in the extreme near-field regime the non-locality of the dielectric response of the metal cannot be neglected, which leads to a reduction in the emission quenching for both ED and MD transitions near the absorbing optical nanoantenna.

O 52.4 Wed 12:15 EW 201

**Light trapping with combined photonic elements** — •Aimi Abass[1] and Bjorn Maes[2,3] — [1]Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany — [2]Photonics Research Group (INTEC), Ghent University-imec, Sint-Pietersnieuwstraat 41, B-9000 Ghent, Belgium — [3]Micro- and Nanophotonic Materials Group, Faculty of Science, University of Mons, 20 place du Parc, B-7000 Mons, Belgium

Nanophotonics offers many avenues for enhancing solar cells. For example, one can tailor the incoming light flow to boost absorption via nanostructures. To ensure strong absorption over the whole spectral range of interest, one has to utilize many photonic phenomena. Oftentimes however, the nanoscale geometrical requirements for optimum excitation of one phenomenon can be at the expense of another. To address this challenge, we examine light trapping strategies with combined photonic elements and study conditions under which different elements complement each other. Here, we discuss the usage of dual interface gratings (DIGs) and diffuser-grating structures. The former enhances absorption by relying on guided mode excitation while the latter focuses on antireflection and scattering management. In such structures the responsibility of different optical components is split, enabling more flexibility in optimization. One main point of discussion is multiperiodic DIG systems, which provide a rich Fourier spectrum, while maintaining a straightforward geometry. In studying combined diffuser-grating structures, we developed a memory efficient calculation method, which evades dealing with rough diffuser geometries directly.

O 52.5 Wed 12:30 EW 201

**Tailoring Disorder of Nanophotonic Light-Trapping Concepts for Thin-Film Silicon Solar Cells** — •Ulrich W. Paetzold[1], Karsten Bittkau[1], Y. J. Donie[2], Guillaume Goumard[2], Radwanul H. Siddique[2], Michael Smeets[1], Hendrik Hölscher[2], Reinhard Carius[1], Uwe Rau[1], and Uli Lemmer[2] — [1]IEK5 * Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — [2]Light Technology Institute and Institute for Microstructure Technology, Karlsruhe Institute of Technology, Engesserstr. 13, 76131 Karlsruhe, Germany

Light-trapping is essential for high performance thin-film solar cells applying optically thin photoactive absorber layer such as a-Si:H with thicknesses below 500 nm. Conventional devices apply randomly textured transparent conductive oxide substrates serving as light-scattering front contacts as well as reflective light-scattering metal back contacts. In recent years, a substantial progress in the development of nanophotonic light-trapping schemes has been reported. In order, to further advance the nanophotonic concepts, the role of tailored disorder in these nanophotonic light trapping concepts is investigated. We present a systematic experimental as well as simulation study on the impact of disorder in nanophotonic light-trapping employing periodic grating couplers in thin-film solar cells. Our results demonstrate a spectrally broad enhanced light trapping effect, i.e., a significant improvement of photocurrent generation, after introducing disorder in advanced nanophotonic light trapping concepts which already beat state-of-the-art light trapping concepts.

O 52.6 Wed 12:45 EW 201

**Opaline Photonic Crystals as Back Side Reflector for Thin-Film Silicon Solar Cells** — •Daniela Schneevoigt[1], Frederik Bub[1], Alexander N. Sprafke[1], Ralf B. Wehrspohn[1,2], André Hoffmann[3], Karsten Bittkau[3], Reinhard Carius[3], Samuel Wiesendanger[4], and Carsten Rockstuhl[5] — [1]Martin-Luther-Universität Halle-Wittenberg, Germany — [2]Fraunhofer IWM, Halle, Germany — [3]Forschungszentrum Jülich GmbH, Germany — [4]Friedrich-Schiller-Universität Jena, Germany — [5]Karlsruher Institut für Technologie, Germany

3D photonic crystals, such as opaline structures, have a tremendous potential to increase the efficiency of solar cells by enabling advanced light management concepts. Especially opaline structures applied to the back side of a solar cell provide various functions that can enhance the light path in the cell. Light in a specific spectral interval that is not absorbed during its first passage through the solar cell is strongly back reflected if the opal satisfies a Bragg condition. Light at other wavelengths might be diffracted back into the cell by the opal. By both means the probability of light absorption and thus the efficiency of the solar cell is increased. Here, we present the successful fabrication of large-area opaline structures at the back side of 1$\mu$m thick hydrogenated microcrystalline silicon ($\mu$c-Si:H) single junction solar cells via an automated spray coating process. The optical, structural, and electrical characteristics of these structures on different $\mu$c-Si:H textures were analyzed and the photovoltaic characteristics of the completely integrated system were evaluated and compared to simulations.

## O 53: Topological Insulators: Transport (HL with DS/MA/O/TT)

Time: Wednesday 11:45–13:00 Location: ER 270

O 53.1 Wed 11:45 ER 270

**Surface Transport on a Bulk Topological Insulator** — •Frederik Edler[1], Lisa Kühnemund[1], Marco Bianchi[2], Ellen M.J. Hedegaard[3], Martin Bremholm[3], Bo B. Iversen[3], Philip Hofmann[2], and Christoph Tegenkamp[1] — [1]Inst. f. Festkörperphysik, Uni. Hannover — [2]Dep. of Physics and Astronomy, Uni. Aarhus — [3]CMC, Dep. of Chemistry and iNANO, Uni. Aarhus

Topological insulators are guaranteed to support metallic surface states on an insulating bulk, and one should thus expect that the electronic transport in these materials is dominated by the surfaces states. Alas, due to the high remaining bulk conductivity, surface contributions to transport have mainly only been singled out indirectly via quantum oscillations, or for devices based on gated and doped topological insulator thin films, a situation in which the surface carrier mobility could be limited by defect and interface scattering. This issue was first overcome for $Bi_2Te_2Se$ where compensation of defects leads to low bulk conductivity and surface-dominated transport could directly be observed [1]. Here we present a direct measurement of surface-dominated conduction on atomically clean surfaces of $Bi_2Te_3$. Using a four tip STM for nano-scale four point transport measurements with variable contact distance we show that the transport at 30 K is again two-dimensional rather than three-dimensional. The sheet conductivity is $7.9(3)\times10^{-4}\Omega^{-1}$ corresponding to a mobility of 505 cm$^2$/Vs. Besides, results regarding the temperature dependence of the conductivity and the influence of structural defects, e.g steps, present after cleavage will be discussed. [1] Barreto et al., Nano Lett. **14**, 3755 (2014)

O 53.2 Wed 12:00 ER 270

**Aharonov-Bohm oscillations in quantum wire of topological insulator** — •Louis Veyrat[1], Joseph Dufouleur[1], Romain Giraud[1], Emmanouil Xypakis[2], Jens Bardarson[2], Christian Nowka[1], Silke Hampel[1], and Bernd Büchner[1] — [1]IFW-Dresden — [2]MPIPKS

Studying Aharonov-Bohm (AB) effect in a nanowire of topological insulator is a convenient way to reveal the specific properties of the topological surface states (SS), which are spin-chiral Dirac fermions. In the short perimeter limit, we evidenced in a previous work the ballistic transport of the SS in the perimeter of the nanowire, revealed by the temperature dependance of the phase coherence length [1] and showing the weak scattering effect of disorder on Dirac fermions. The quantum transverse confinement of SS is further revealed by the observation of non-universal conductance fluctuations. In the longer perimeter limit, we surprisingly find that the transport remains ballistic in the perimeter, despite the presence of disorder. The interaction with disorder is revealed by specific phase-jump of the AB oscillations under transverse magnetic field.

[1] Dufouleur et al., Phys. Rev. Lett. 110, 186806 (2013)

O 53.3 Wed 12:15 ER 270

**The effect of strain on the two-dimensional topological insulator HgTe** — •Philipp Leubner, Andreas Budewitz, Christoph Brüne, Hartmut Buhmann, and Laurens Molenkamp — Experimentelle Physik III, Fakultät für Physik, Universität Würzburg, Germany

In the past years, HgTe quantum wells have been used extensively to study the magnetotransport signature of two-dimensional topological insulators, namely the quantum spin Hall effect. It has been shown that the band structure of those systems strongly depends on the thickness of the quantum well, and that, in particular, the topology changes from trivial to nontrivial at a critical thickness of 6.3 nm.

As an additional degree of freedom, the influence of strain on the band structure is investigated in this work. By using different CdTe-ZnTe superlattices grown on GaAs as virtual substrates, we are able to tune the strain of the HgTe quantum well layer from tensile to compressive, and thus modify the shape of the valence band.

Depending on strain, temperature dependent transport measurements on nominally identical wells reveal either features of topological insulators or semimetals, with the obtained fitting parameters nicely agreeing with band structure calculations. Further experiments focus on the correlation between the magnitude of the inverted bandgap and stability of the quantum spin Hall edge states.

O 53.4 Wed 12:30 ER 270

**Transport measurements on Mn-doped HgTe quantum wells** — •Andreas Budewitz, Kalle Bendias, Philipp Leubner, Christoph Brüne, Hartmut Buhmann, and Laurens W. Molenkamp — Universität Würzburg, Lehrstuhl für experimentelle Physik III

In 2007 HgTe quantum wells have been experimental identified as a quantum spin Hall system [1]. One open question is how quantum spin Hall states interplay with magnetic impurities. Especially the formation of the anomalous quantum Hall effect raises a lot of interest [2, 3]. Since Mn-doped HgTe is a paramagnetic topological insulator it is important to investigate the onset of the $\nu = -1$ plateau at low fields. Here we present transport measurements on Mn-doped HgTe quantum wells. Therefore we show results on different temperatures, magnetic fields, Mn concentration and quantum well width. We discuss our results in comparison to undoped HgTe quantum wells.

[1] M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X.-L. Qi and S.-C. Zhang, Science 318, 766 (2007)

[2] Chao-Xing Liu, Xiao-Lang Qi, Xi Dang, Zhong Fang and Shou-Cheng Zhang, PRL 101, 14682 (2008)

[3] Hsiu-Chang Hsu, Xin Liu and Chao-Xing Liu, Phys. Rev. B 88, 085315 (2013)

O 53.5 Wed 12:45 ER 270

**Quantum hall states equilibration in lateral heterojunctions on inverted HgTe quantum wells** — •M. Reyes Calvo[1,2], Christoph Brüne[3], Christopher Ames[3], Philipp Leubner[3], Hartmut Buhmann[3], Laurens W. Molenkamp[3], and David Goldhaber-Gordon[1] — [1]Department of Physics, Stanford Universtiy, Stanford, U.S.A. — [2]C.I.C. Nanogune, San Sebastián, Spain — [3]Physikalisches Institut (EP3), Universität Würzburg, Würzburg, Germany

We study lateral heterojunctions on HgTe quantum wells with inverted band structure. At high densities and fields, we can explore the equilibration between Quantum Hall (QH) states with different filling factor. The resulting resistance plateaus are particularly clear in the n-n'-n quadrant and fit the expected values for a 2D electron gas heterojunction. The low density and moderate magnetic field regime is of more interest, since due to the inverted band structure of HgTe, Quantum Spin Hall (QSH) edge states could be present. In this regime, we observe unexpected features in the Hall resistance, which could be associated with the interplay between chiral QH edge modes and helical QSH edge modes.

## O 54: Gaede Prize Talk

Time: Wednesday 13:15–13:45 Location: HE 101

**Invited Talk** O 54.1 Wed 13:15 HE 101

**Porphyrin molecules at interfaces** — •Willi Auwärter — Physik Department E20, Technische Universität München, Germany

Porphyrins and related tetrapyrrole molecules possess an impressive variety of functional properties - including axial ligation, electron transfer, light harvesting and catalytic transformations - that have been exploited in natural and artificial systems. From a surface science perspective, porphyrins are thus ideally suited as building blocks for surface-anchored functional nanostructures [1-3]. We will review recent scanning tunneling microscopy and spectroscopy results, complemented by space-averaging techniques and computational modeling based on density functional theory, addressing such porphyrin systems with sub-molecular resolution. Key aspects include molecular switching, conformation, axial ligation, metalation and self-assembly protocols. Particular emphasis is put on on-surface dehydrogenation reactions yielding novel porphyrin species on Ag(111), including covalently linked dimers and longer oligomers. Furthermore, the formation of metal-organic coordination networks and porphyrin arrays on atomically thin boron nitride (BN) layers grown on Cu(111) is discussed [4]. The BN template dictates the electronic level alignment of the porphyrin nanostructures and supports distinct coordination motifs.

[1] W. Auwärter et al., Nature Chem., DOI: 10.1038/NCHEM.2159 (2015)

[2] K. Seufert et al., Nature Chem. 3, 114 (2011)

[3] W. Auwärter et al., Nature Nanotech. 7, 41 (2012)

[4] S. Joshi et al., ACS Nano 8, 430 (2014)

## O 55: Inorganic/Organic Interfaces: Electronic Properties II

Time: Wednesday 15:00–18:15 Location: HE 101

**Invited Talk** O 55.1 Wed 15:00 HE 101

**Electronic structure of Organo-Metal Halide Perovskites Films and Interfaces** — •Antoine Kahn — Princeton University, Princeton, NJ, USA

This talk reviews direct and inverse photoemission data on the electronic structure of organo-metal halide perovskites, i.e., methylammonium lead tri-halides (MAPbX, X=Br3, I3, I3-xClx), and of their interfaces with hole- and electron-transport layers (HTL, ETL). Valence and conduction band edges of the MAPbX films, ionization energy and electron affinity (IE, EA) are determined [1]. Good alignment of the MAPbX conduction band minimum with that of the electron-collecting oxide is found, suggesting minimal energy loss during electron extraction at this interface. The hole-extraction interface is investigated for several HTLs. Results clearly puts into evidence the role of interface energetics in terms of carrier loss-less extraction or confinement in the perovskite layer [2]. The electronic structure of the inverted solar cell, with MAPbI3 on sol-gel processed NiOx, is also investigated [3]. The perovskite takes on a p-type character, indicative of a low density of deep gap states in the material. The NiOx/ MAPbI3 interface energetics provide barrier-free hole extraction (0.2 eV energy loss) and a high electron-blocking barrier. On the other side of the cell, C60 and derivatives form adequate ETLs, with neither a barrier for electron extraction nor a loss in accessible open circuit voltage.

[1] P. Schulz et al., Energ. & Envir. Sci. 7, 1377 (2014) [2] E. Edri et al., J. Phys. Chem. Lett., 5, 429 (2014) [3] P. Schulz et al. (under review)

O 55.2 Wed 15:30 HE 101

**Site-specific transport levels in a crystalline organic thin film** — •Tomoki Sueyoshi, Martin Willenbockel, Serguei Soubatch, and Stefan Tautz — Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich, Germany

Recent studies have revealed that the electronic properties of organic semiconductor thin films are not only determined by the nature of individual constituent molecules, but also correlated with geometric structure in which the molecules arrange. If a crystalline organic thin film consisting of single-component molecules contains several different molecular species in its unit cell, molecular orbital energies of such species could be different from species to species depending on their relative geometry and orientation. Since it is the highest occupied/lowest unoccupied molecular orbitals (HOMO/LUMO) which are involved in charge transport, the energy dispersity of these transport levels may dominate the transport properties of organic semiconductors.

A previous scanning tunneling spectroscopy study revealed that a LUMO energy dispersity up to 0.5 eV originates from the intermolecular polarization/interaction on the LUMO of six different tetracene species in the complex bilayer $\beta$-phase on Ag(111). To access the one on the HOMO, we have performed photoelectron spectroscopy of the tetracene $\beta$-phase and observed a similar energy dispersity of the HOMO. In this talk, we will discuss the assignment of the observed HOMO components and provide a comprehensive picture of the transport levels of the tetracene $\beta$-phase.

O 55.3 Wed 15:45 HE 101

**Charge Transport through Molecular Monolayers: Impact of Collective Effects and Docking Groups** — •Veronika Obersteiner[1], David Egger[1,2], Georg Heimel[3], and Egbert Zojer[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, Austria. — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth, Israel. — [3]Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany.

For advancing the exciting field of molecular electronics, a microscopic understanding of charge transport through molecule-based systems is essential. Over the past years, the fundamental physical differences between devices comprising an individual molecule or a homogeneous monolayer have been increasingly acknowledged. Here, we relate those differences to collective electrostatic effects arising from the combined electric fields of all molecules within a monolayer. Employing density functional theory in conjunction with a Green's function approach, we theoretically investigate current-voltage characteristics of metal-molecule-metal systems that comprise either single molecules or an assembly.We show that, depending on the chemical nature of the molecular backbones and the used docking groups, collective effects either significantly increase or decrease the current at a given voltage. As a consequence, the 'ideal' docking group is clearly different for monolayer and single-molecule devices. These insights are also used to design molecules in which collective effects cancel, and thus transport characteristics remain largely unaffected by environmental effects.

O 55.4 Wed 16:00 HE 101

**Inverse electron transfer in nitro-substituted monomolecular films** — Prashant Waske[1,2], •Tobias Wächter[1], Andreas Terfort[2], and Michael Zharnikov[1] — [1]Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — [2]Institut für Anorganische und Analytische Chemie, Universität Frankfurt, 60438 Frankfurt, Germany

Self-assembled monolayers of nitro-substituted aromatic thiols were prepared on Au(111) substrates and characterized by several complementary spectroscopic techniques. The introduction of the nitro tail group had a positive effect on the quality of the monolayers, which were either superior or comparable to their non-substituted analogues. All molecules in the films were found to be bound to the substrate via the thiolate anchor and to have an upright orientation. The [N 1s]$\pi^*$ and [O 1s]$\pi^*$ decay spectra of the monolayers did not exhibit any trace of charge (electron) transfer (CT) through the molecular framework to the substrate, following the resonant excitation of the tail group. This was explained by the energy considerations hindering CT to the substrate but enabling a reverse process (ICT), i.e. the neutralization of the core ionized state by electron transfer from the substrate/molecular backbone. Traces of this process could be tentatively identified as an admixture of resonant contributions to the non-resonant decay spectra at the O K-edge. The experimental data suggest that only the ring adjacent to the nitro group was involved in the ICT process.

O 55.5 Wed 16:15 HE 101

**Probing single donor-acceptor molecules on thin insulating films** — •Tobias Meier[1], Rémy Pawlak[1], Shigeki Kawai[1], Shi-Xia Liu[2], Silvio Decurtins[2], Ernst Meyer[1], and Thilo Glatzel[1] — [1]Department of Physics, University of Basel, Switzerland — [2]Department of Chemistry and Biochemistry, University of Bern, Switzerland

Fused Donor-Acceptor molecules have attracted a broad interest due to their potential applications for example in organic solar cells. The intrinsic electronic properties of such organic compounds determine the device performance, notably the intramolecular charge transfers (CT) between the donor and acceptor parts. However, the CT is still poorly understood at the single molecular scale.

In this work we used the TTF-dppz [1], a planar and and pi-conjugated molecule with size of less than 2 nm, adsorbed on thin layers of NaCl on Cu(111). By combining STM and AFM, we spatially characterized the separation of the HOMO and LUMO with respect to the chemical structure of the TTF-dppz molecule observed by AFM. We further investigated with force and current based spectroscopic techniques [2,3] the electronic properties of the molecule and its charge redistribution. To gain more insights into the charge transfer of a single molecule under illumination, we further performed such spectroscopic measurements under illumination.

[1] C. Jia et al., Chemistry 13, 3804 (2007). [2] R. Pawlak et al., Nano Lett. 13, 5803 (2013). [3] S. Kawai et al., ACS Nano 7, 9098 (2013).

O 55.6 Wed 16:30 HE 101

**Integer versus fractional charge transfer at metal/organic and metal/insulator/organic interfaces: Cu(/NaCl)/TCNE** — •Oliver T. Hofmann[1,2], Patrick Rinke[1,3], Viktor Atalla[1], Georg Heimel[4], and Matthias Scheffler[1] — [1]FHI Berlin, Germany — [2]TU Graz, Austria — [3]Aalto University, Helsinki, Finland — [4]Humboldt University Berlin, Germany

We use semilocal and hybrid density functional theory to study the charge transfer and level alignment at a representative interface between a metal and an organic molecule. To reduce the hybridization strength between the adsorbate and the substrate, we also insert thin insulating NaCl buffer layers. We find that upon direct adsorption on the metal, charge is perfectly delocalized across all molecules, leading to a laterally homogenous layer. However, when the hybridization between metal and organic is prevented by an insulating interlayer, charge localizes on individual moieties, creating laterally inhomogenous charge distributions. This spontaneous breaking of the translation symmetry is reflected in several observables, such as the molecular geometry or the valence and core densities of states. We find that the amount of charge transfer is determined, to a significant extend, by the ratio of the lateral spacing of the molecules and their energetic distance to the electron reservoir, i.e., the metal. Therefore, the amount of charge transfer does not only depend on the electronic structure of the individual components, but also on the interface geometry. Furthermore, we discuss the impact of the lateral charge distribution on the coverage dependence of the work function for different growth models.

O 55.7 Wed 16:45 HE 101

**Controlled photo-induced work function manipulation of the TCNQ/Au(111) interface** — •David Gerbert and Petra Tegeder — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany

One of the most important tasks to improve the performance of organic electronic devices is the development of deeper understanding and purposeful employment of metal electrode*s work function manipulation [1]. In the first layer TCNQ is known to be negatively charged on various metal surfaces [2,3], however only on Au(111) it is neutral [4]. We investigated the electronic structure of the TCNQ/Au(111) interface by means of two-photon-photoemission (2PPE) and observed a photo-induced work function shift of several hundred meV, which points towards photo-induced electron transfer from the gold substrate to the molecule. Interestingly the work function can be continuously tuned across the clean surface value which establishes new application possibilities of TCNQ as device-adapted hole-injection layer.

[1] N. Koch, ChemPhysChem. 8, 1438-1455 (2007).

[2] C. Park et al., Phys. Rev. B 90, 125432 (2014).

[3] T.-C. Tseng et al., Nat. Chem. 2, 374 (2010).

[4] I. Fernandez-Torrente et al., Int. J. Mass Spectrom. 277, 269-273 (2008).

O 55.8 Wed 17:00 HE 101

**The geometric and electronic structure of TCNQ and TCNQ+Mn on Ag(001) surface** — Vitaliy Feyer[1], Martin Graus[2,3], •Giovanni Zamborlini[1], Robert G. Acres[4], Achim Schöll[2,3], Friedrich Reinert[2,3], and Claus M. Schneider[1,5] — [1]Research Center Jülich, 52425 Jülich, Germany — [2]Universität Würzburg, Experimentelle Physik VII & Röntgen Research Center for Complex Material Systems RCCM, 97074 Würzburg, Germany — [3]Karlsruher Institut für Technologie KIT, Gemeinschaftslabor für Nanoanalytik, 76021 Karlsruhe, Germany — [4]Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy — [5]Universität Duisburg-Essen, D-47048 Duisburg, Germany

We have investigated the geometric and electronic structure of ordered monolayers of TCNQ and of TCNQ+Mn on Ag(001) surface by LEED and photoelectron momentum microscopy (at the NanoESCA beamline of the Elettra synchrotron). Two coverage dependent, commensurable superstructures are established on Ag(001) while the coadsorption of Mn results in the formation of a long-range ordered mixed metal-organic superstructure, which is also commensurate. From ARPES pattern of the TCNQ LUMO the azimuthal orientation of the molecules in the respective unit cell can be determinate. The PES data shows, in the case of TCNQ/Ag(100) a filling of the TCNQ LUMO by charge transfer from the substrate while the coadsorption of Mn leads to an energy shift of the TCNQ HOMO and LUMO of 230 meV with respect to TCNQ/Ag(001). No significant lateral band dispersion in the adsorbate layers was observed in ARPES data.

O 55.9 Wed 17:15 HE 101

**Adsorption and electronic properties of tetraazaperopyrene derivatives on Au(111)** — •Friedrich Maass[1], Stephan Stremlau[1], Lena Hahn[2], Lutz H. Gade[2], and Petra Tegeder[1] — [1]Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany — [2]Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany

The adsorption behavior of large N-heterocyclic pi-conjugated molecules is of immense interest for understanding the structural and electronic properties of this new class of organic n-channel semiconductors.

We investigated the adsorption geometry and the electronic properties of 1,3,8,10-tetraazaperopyrene (TAPP) and its 2,9-bisperfluoroalkyl-4,7,11,14-tetra-X derivatives (X is H, Cl, Br or I) on the Au(111) surface with vibrational and electronic high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). We found a different adsorption behavior between substituted and unsubstituted TAPP and also between monolayer and corresponding multilayers. HOMO-LUMO gaps have been investigated by electronic HREEL spectroscopy and are in good agreement with previously made UV/VIS and calculated data.

O 55.10 Wed 17:30 HE 101

**Effects of embedded dipole in alkanethiolate self-assembled monolayers** — Swen Schuster[1], Nichole Sullivan[2], Orlando Cabarcos[2], Iris Hehn[3], Jean-François Morin[4], Egbert Zojer[3], David L. Allara[2], and •Michael Zharnikov[1] — [1]Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — [2]Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA — [3]Institute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria — [4]Département de chimie, Faculté des sciences et de genie, Université Laval, Québec QC G1V 0A6, Canada

Self-assembled monolayers (SAMs) bonded to metal electrodes are capable to improve charge-carrier injection across the metal-organic interface. This is usually achieved by use of the terminal dipolar groups (terminal dipole) comprising the outer interface of SAMs. But such an architecture affects the growth mode of an organic semiconductor (in the standard device configuration) entangling it with the dipole control. In contrast, for the molecules with an embedded dipolar element, the dipole control and the chemistry at the SAM-ambience interface are decoupled. In this context, we studied a series of SAMs prepared on Au{111} from the mid-chain ester functionalized alkanethiols. The presence of the ester moiety leads to interesting electrostatic effects in photoemission and allows to modify the work function of the substrate in a certain range. The results are rationalized with a help of theoretical simulations, involving a combination of DFT and molecular dynamics methods.

O 55.11 Wed 17:45 HE 101

**The Role of Pauli-Pushback fort he Electronic Properties of Self-Assembled Monolayers at Reduced Coverage** — •Elisabeth Verwüster[1], David A. Egger[1,2], Oliver T. Hofmann[1], and Egbert Zojer[1] — [1]Institute of Solid State Physics, Graz University of Technology, NAWI Graz, Petersgasse 16, 8010 Graz, Austria — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

Using density-functional theory, advanced geometry optimization tools and accounting for van der Waals interactions we explain the coverage-dependent electronic structure of self-assembled monolayers (SAMs). As model systems for our calculations we choose acceptor- (-CN, -CF3) and donor- (-CH3, -NH2) substituted biphenylthiols on a Au(111) surface. Our focus lies on changes in the SAM-induced work-function modification, $\Delta\Phi$. Upon reducing the coverage the tilt angle of the molecules strongly increases. The latter significantly affects the molecular dipole perpendicular to the surface. The resulting changes in $\Delta\Phi$ are, however, much more pronounced than one could expect on purely geometric grounds. For example, $\Delta\Phi$ vanishes already at a coverage of 50% for the acceptor-substituted SAMs. This can only partly be explained by the tilt-angle dependence of the charge-rearrangements arising from the S-Au bond formation. Instead, we show that especially at low coverage the interaction-induced charge-rearrangements at the interface are dominated by Pauli-pushback, an effect well known for flat-lying adsorbates.

O 55.12 Wed 18:00 HE 101

**Electrostatic design of monolayer properties** — Bernhard Kretz[1], David A. Egger[1,2], and •Egbert Zojer[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

For raising the full potential of molecular electronics, it is necessary to control the nature of the electronic states within organic layers. In this contribution we present the concept of a modular toolbox that allows realizing a high level of control as far as the energetics and spatial localization of the states is concerned. By quantum-mechanical modelling we show that - based on this toolbox - it is, for example, possible to realize monolayer-based quantum-cascades and electron or hole quantum-well structures. This becomes possible by exploiting collective electrostatic effects naturally emerging in ensembles of polar molecules. As another element of the toolbox we discuss neutral radicals that can be applied for generating locally spin-polarized layers.

## O 56: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale IV

Time: Wednesday 15:00–18:30 Location: MA 004

**Invited Talk** O 56.1 Wed 15:00 MA 004

**Ultrafast coherent dynamics in photovoltaics** — •Carlo Andrea Rozzi[1], Sarah Maria Falke[2], Daniele Brida[3,4], Margherita Maiuri[4], Michele Amato[5], Ephraim Sommer[2], Antonietta De Sio[2], Angel Rubio[6,7], Giulio Cerullo[4], Elisa Molinari[1,8], and Christoph Lienau[2] — [1]CNR-NANO, Modena, Italy — [2]Carl von Ossietzky Universität, Oldenburg, Germany — [3]University of Konstanz, Germany — [4]CNR-IFN, Politecnico di Milano, Italy — [5]Universitè Paris-Sud, Orsay, France — [6]Universidad del País Vasco San Sebastián, Spain — [7]Fritz-Haber-Institut, Berlin, Germany — [8]Università di Modena e Reggio Emilia, Modena, Italy

The photoinduced charge-separation events occurring in photovoltaic systems have traditionally been interpreted in terms of the incoherent kinetics of optical excitations and of charge hopping, but recently signatures of quantum coherence were observed in energy transfer in photosynthetic bacteria and algae. We have studied charge separation in reference systems for artificial photosynthesis and photovoltaics by combining TDDFT simulations of the quantum dynamics and high time resolution femtosecond spectroscopy. We provide evidence that the coherent coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer both in covalently bonded molecules and in bulk heterojunctions[1]. We have exploited the results of our research to design, syntesize and characterize a novel molecular scaffold for photovoltaic applications.[2] [1] Falke S., et al., Science, 344, 1001 (2014) [2] Pittalis S., et al., Adv. Func. Mat. (2014)

O 56.2 Wed 15:30 MA 004

**Real-time propagation of coupled Maxwell-Kohn-Sham systems** — •Rene Jestädt[1], Heiko Appel[1,3], and Angel Rubio[1,2,3] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [2]NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain — [3]Max-Planck-Institut für Struktur und Materie, Hamburg

Based on a recent extension of time-dependent density-functional theory to quantum electrodynamics [1], we show first steps of an implementation of Maxwell's equations coupled to time-dependent Kohn-Sham equations. Our implementation utilizes the Riemann-Silberstein vector of the electromagnetic field which allows to write Maxwell's equations in a symplectic spinor representation similar to the Dirac equation. This spinor representation allows us to use standard unitary propagation techniques [2] developed for the Schrödinger equation also for the coupled solution of Maxwell's equations and Kohn-Sham equations. We illustrate our implementation of such coupled Maxwell-Kohn-Sham systems in the real-space real-time code octopus [3] for small molecules coupled to optical cavities [4].

[1] M. Ruggenthaler et al., Phys. Rev. A **90**, 012508 (2014).
[2] A. Castro et al., J. Chem. Phys. **121** (2004).
[3] X. Andrade et al., J. Phys. Cond. Mat. **24** (2012).
[4] M.S. Tame et al., Nature Physics 9, 329-340 (2013).

O 56.3 Wed 15:45 MA 004

**Correlated Light-Matter Interactions in Cavity QED** — •Johannes Flick[1], Camilla Pellegrini[2], Michael Ruggenthaler[3], Heiko Appel[1,4], Ilya V. Tokatly[1,5], and Angel Rubio[1,2,4] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Nano-bio

Spectroscopy Group/ETSF Scientific Development Centre, Universidad del Pais Vasco UPV/EHU, San Sebastian — [3]Universität Innsbruck — [4]MPI for the Structure and Dynamics of Matter, Hamburg — [5]IKERBASQUE, Basque Foundation for Science, Bilbao

In the last decade, time-dependent density functional theory (TDDFT) has been successfully applied to a large variety of problems, such as calculations of absorption spectra, excitation energies, or dynamics in strong laser fields. Recently, we have generalized TDDFT to also describe electron-photon systems (QED-TDDFT) [1, 2]. Here, matter and light are treated on an equal quantized footing.
In this work, we present the first numerical calculations in the framework of QED-TDDFT. We show exact solutions for fully quantized prototype systems consisting of atoms or molecules placed in optical high-Q cavities and coupled to quantized electromagnetic modes. We focus on the electron-photon xc-contribution by calculating exact Kohn-Sham potentials using fixed-point inversions and present the performance of the first approximated xc-potential based on an optimized effective potential (OEP) approach.

[1] I. Tokatly, Phys. Rev. Lett. **110**, 233001 (2013).
[2] M. Ruggenthaler et.al., Phys. Rev. A **90**, 012508 (2014).

### O 56.4 Wed 16:00 MA 004

**A hybrid QM/EMT approach to charge state corrections** — •Osman Baris Malcioglu[1] and Michel Bockstedte[2] — [1]Lst.f.Theor.Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — [2]FB Materialwissenschaften & Physik Universität Salzburg, 5020 Salzburg, Austria

Localized charge at surfaces, interfaces, or in volume materials naturally occur due to the ionization of adsorbates or defects. A robust quantitative description of charged systems is a prerequisite to explore the physics of adsorbates, surface and bulk defects of materials such as metal oxides. The popular supercell approach requires charge neutrality per supercell. For charged systems this is enforced by compensation charges. The resulting spurious interaction can be corrected a-posteriori [1,2]. Recently, a scheme based on model fitting the localized charge and dielectric screening was proposed [1]. Here, we present a fully automated and efficient hybrid QM/EMT approach for handling long-reach fields. The response of the medium and the localized charge density of the ab-initio calculations are represented by a finite element function space. The relevant physical observables are obtained using an auto-adaptive mesh solver. We demonstrate applications of our approach to charge state corrections of surface and bulk defects slabs in comparison with the earlier approaches [1,2].

[1] H.-P. Komsa and A. Pasquarello, Phys. Rev. Lett. **110**, 095505 (2013).

[2] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 016402 (2009).

### O 56.5 Wed 16:15 MA 004

**Plasmon assisted double photoemission** — •Michael Schüler, Yaroslav Pavlyukh, and Jamal Berakdar — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Coincidence measurements of double photoemission (DPE) represent a direct way of tracing the various facets of electronic correlations in molecular as well as extended systems, such as e. g. dynamical screening and collective excitations. One prominent example in this respect is the $C_{60}$ molecule, for its plasmon resonances dominate the electronic excitation spectrum. Motivated by recent experiments on this molecule we demonstrate how the phenomenon of plasmon-mediated DPE can be described by an effective four-level system coupled to the bosonic plasmon excitations. The model generalizes the classical *s*-model and is treated within the *GW* approximation with the parameter estimates from *ab initio* calculations. We solve the coupled fermionic-bosonic time-dependent Kadanoff-Baym equations governing the dynamics of the model triggered by the interaction with the laser field. The use of the generalized Kadanoff-Baym Ansatz allows to significantly reduce the computation cost of our method.

### O 56.6 Wed 16:30 MA 004

**Calculating photoemission spectra with real-time density-functional theory** — •Matthias Dauth and Stephan Kümmel — University of Bayreuth, Germany

Photoemission spectroscopy is one of the primary tools for characterizing molecules and solids. A traditional approach of predicting photoemission signals relies on the interpretation of single-particle eigenvalues, e.g., from Hartree-Fock or Density Functional Theory (DFT). Here we demonstrate that real-time DFT allows for going beyond this static picture. We calculate photoemission signals dynamically and estimate ionization cross sections. We first investigate gas phase spectra, in which an ensemble of molecules with random orientation is probed. However, our approach in particular also allows for calculating angular resolved signals, i.e., we can track the ejected electron distribution with respect to a fixed light polarization. Furthermore, no a priori assumptions about the final state of the outgoing electrons need to be made, but the final state emerges naturally from the calculation. Thus, real-time DFT emerges as a powerful tool for the dynamical first-principles prediction of photoemission processes.

### O 56.7 Wed 16:45 MA 004

***Ab initio* local field effects for surface second harmonic generation** — •Nicolas Tancogne-Dejean[1,2] and Valérie Véniard[1,2] — [1]Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS-CEA/DSM, F. 91128, Palaiseau, France — [2]European Theoritical Spectroscopy Facility (ETSF), France

A comprehensive understanding of the nonlinear optical properties of solids is crucial to improve the design and the analysis of new optical devices. Among these processes, Second-Harmonic Generation (SHG) is probably one of the most studied and has become, through the years a very powerful-non-invasive technique to characterize materials, because of its particular sensitivity to the symmetry of a system. In materials where inversion symmetry is present, optical Second Harmonic Generation is forbidden within the dipole approximation. But at a surface or an interface between two such materials, the inversion symmetry is broken and SHG is allowed.

Crystal local fields are generated by the induced microscopic response of the system to an external perturbation. As a consequence their effects will be particularly important close to discontinuities as interfaces or surfaces. Local fields are important for a good description of optical properties of materials, but their effects on surface SHG have never been studied.

We present here a new ab initio formalism that allows us to calculate the frequency-dependent surface second-order susceptibility $\chi^{(2)S}$ within TDDFT, where the local field effects are fully included and we have applied this formalism to Silicon surfaces.

### O 56.8 Wed 17:00 MA 004

**Mapping atomic orbitals in the transmission electron microscope: seeing defects in graphene** — •Lorenzo Pardini[1], Stefan Löffler[2,3], Giulio Biddau[1], Ralf Hambach[4], Ute Kaiser[4], Claudia Draxl[1,5], and Peter Schattschneider[2,3] — [1]Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — [2]Institute of Solid State Physics, Vienna University of Technology, Austria — [3]University Service Centre for Transmission Electron Microscopy, Vienna University of Technology, Austria — [4]Central Facility for Electron Microscopy, University of Ulm, Germany — [5]European Theoretical Spectroscopy Facility (ETSF)

The possibility of mapping atomic orbitals by using energy-filtered transmission electron microscopy (EFTEM) has been considered for a long time and was recently demonstrated from a theoretical point of view. With the example of graphene, we predict how this approach can be used to map orbitals of a particular character. To this purpose, we have investigated graphene in its pristine structure and with two different kinds of defects, namely an isolated vacancy and a substitutional nitrogen atom. We show that basically three different kinds of images are to be expected, depending on the orbital character as determined from the corresponding projected density of states. To judge the feasibility of mapping such orbitals in a real microscope, we investigate the effect of the optics' aberrations, by simulating the lens system of two microscopes that are commonly used for electron energy loss spectrometry. We find that it should indeed be feasible to see atomic orbitals in a state-of-the-art EFTEM.

### O 56.9 Wed 17:15 MA 004

**Inelastic X-Ray Scattering: Insights from and Benefits for Many-Body Theory** — •Claudia Rödl, Igor Reshetnyak, Francesco Sottile, and Lucia Reining — Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau cedex, France

Non-resonant inelastic x-ray scattering (IXS) probes the momentum- and frequency-dependent dynamic structure factor $S(\mathbf{q},\omega)$. It captures the neutral excitations of a many-body system, such as excitons, plasmons, and interband transitions. In particular, localized excitations that are forbidden in the optical limit of vanishing momentum transfer are accessible. $S(\mathbf{q},\omega)$ is proportional to the diagonal element of the electric susceptibility $\chi(\mathbf{q},\mathbf{q}',\omega)$. Thus, IXS directly probes the dielectric screening and, hence, the screened Coulomb interaction which governs, for instance, the formation of quasiparticles in photoemission spectroscopy and excitons in optical spectroscopy. Therefore, IXS provides a unique tool to disentangle the many-body physics of renormalized quasiparticles and neutral excitations. It may serve as a solid experimental reference for the development of new approaches in many-body theory. Moreover, the off-diagonal elements of $\chi(\mathbf{q},\mathbf{q}',\omega)$ can be probed by coherent inelastic x-ray scattering (CIXS). This technique, which is still at a pioneering stage, allows one to visualize plasmon-like and localized neutral excitations in real space. We calculate diagonal and off-diagonal elements of $\chi(\mathbf{q},\mathbf{q}',\omega)$ for semiconductors and transition-metal oxides in good agreement with experiment and discuss the rich physics that is contained in $\chi(\mathbf{q},\mathbf{q}',\omega)$.

O 56.10 Wed 17:30 MA 004

**Real-Space Multiple-Scattering X-ray Absorption Spectroscopy Calculations of $d$- and $f$-state Materials using a Hubbard Model** — •Christian Vorwerk[1], Kevin Jorissen[1], John Rehr[1], and Towfiq Ahmed[2] — [1]Department of Physics, University of Washington, Seattle, Washington 98195 USA — [2]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

We present calculations of the electronic structure and x-ray spectra of materials with correlated $d$- and $f$-electron states treated with the Hubbard model in a real-space multiple scattering (RSMS) formalism, and using a rotationally invariant local density approximation (LDA+$U$). Values of the Hubbard parameter $U$ are calculated ab initio using the constrained random-phase approximation (cRPA). The real-space Green's function approach with Hubbard model corrections is an efficient way to describe localized electron states in strongly correlated systems, and their effect on core-level x-ray spectra. The method is shown to give the correct density of states and x-ray absorption spectra for Transition Metal- and Lanthanide-oxides such as Ce2O3 and NiO, where the traditional RSMS calculations fail.

Supported by DOE BES DE-FG02-97ER45623

O 56.11 Wed 17:45 MA 004

**Variants of Second Order Screened Exchange for spin polarized and non-polarized Uniform Electron Gas** — •Felix Hummel and Georg Kresse — University of Vienna, Austria

The commonly used Random Phase Approximation (RPA) only contains exchange processes of first order. The Second Order Screened Exchange (SOSEX) correction includes one exchange process beyond first order, which is considered the leading order correction to the RPA, and it has proven to be very accurate for the Uniform Electron Gas (UEG) as well as for solids.

The memory requirement of SOSEX is however of $O(N^4)$. We present an approach with a memory requirement of $O(N^2)$ and its differences to other approaches with comparable complexity, such as AC-SOSEX, for the spin polarized and non-polarized UEG.

O 56.12 Wed 18:00 MA 004

**Ferromagnetism from strongly correlated electrons at the LaAlO$_3$/SrTiO$_3$ interface** — •Frank Lechermann, Lewin Boehnke, Malte Behrmann, Daniel Grieger, and Christoph Piefke — I. Institut für Theoretische Physik, Universität Hamburg

We shed light on the interplay between structure and many-body effects relevant for itinerant ferromagnetism in LaAlO$_3$/SrTiO$_3$ heterostructures. The realistic correlated electronic structure is studied by means of the (spin-polarized) charge self-consistent combination of density functional theory (DFT) with dynamical mean-field theory (DMFT) beyond the realm of static correlation effects [1]. A ferromagnetic instability occurs only with oxygen vacancies and it is possible to account for the basic mechanism by an derived minimal Ti two-orbital $e_g-t_{2g}$ description for the correlated subspace. Magnetic order affected by quantum fluctuations with a Ti moment of $0.2\mu_\mathrm{B}$ builds up from effective double exchange, which can be traced to the dilute defect regime. [1] F. Lechermann, L. Boehnke, D. Grieger and C. Piefke, Phys. Rev. B 90, 085125 (2014)

O 56.13 Wed 18:15 MA 004

**NanoDMFT: Full ab initio description of strong correlations in nanoscale devices** — •David Jacob — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle

In order to obtain a full first-principles description of the correlated electronic structure and transport properties of nanoscale devices we combine the Coulomb-Hole-Screened-Exchange (COHSEX) approximation with Dynamical Mean-Field Theory (DMFT). While the former yields an effective mean-field description of the weakly correlated conduction electrons, the DMFT part accounts for the dynamic correlations originating e.g. from the strongly interacting $3d$- or $4f$-shells of transition metal atoms or from the molecular orbitals of weakly coupled molecular devices. The combination with COHSEX instead of Density Functional Theory (DFT) improves upon our NanoDMFT approach [1] in two important aspects: First, from the screened interaction $W$ we can calculate the effective Coulomb interaction $U$ for the strongly interacting electrons. Second, unlike in DFT+DMFT calculations the double-counting correction for COHSEX+DMFT is exactly known and straight-forward to calculate. Hence the two quantities which are essentially parameters in the DFT based approach can now be calculated ab initio so that it is now possible to actually predict e.g. the occurance of the Kondo effect in magnetic atoms and molecules on metal surfaces and attached to metallic leads.

[1] D. Jacob *et al.*, PRL **103**, 016803 (2009); D. Jacob *et al.*, PRB **82**, 195115 (2010); M. Karolak *et al.*, PRL **107**, 146604 (2011); D. Jacob *et al.*, PRB **88**, 134417 (2013)

## O 57: 2D Materials beyond Graphene: TMDCs, Slicene and Relatives

Time: Wednesday 15:00–17:45 Location: MA 005

O 57.1 Wed 15:00 MA 005

**Imaging spin-valley-layer locking in a transition-metal dichalcogenide** — J.-M. Riley[1], F. Mazzola[2], M. Dendzik[3], M. Michiardi[3], T. Takayama[4], L. Bawden[1], C. Granerød[2], M. Leandersson[5], T. Balasubramanian[5], M. Hoesch[6], T. Kim[6], H. Takagi[4], W. Meevasana[7], Ph. Hofmann[3], M.-S. Bahramy[8], J.-W. Wells[2], and •Phil D.C. King[1] — [1]SUPA, University of St. Andrews, UK — [2]Norwegian University of Science and Technology, Norway — [3]Aarhus University, Denmark — [4]Max Planck Institute for Solid State Research, Germany — [5]MAX IV Laboratory, Sweden — [6]Diamond Light Source, UK — [7]Suranaree University of Technology, Thailand — [8]University of Tokyo, Japan

A strong locking between the spin and the valley pseudospin in monolayer transition-metal dichalcogenides (TMDCs) such as MoS$_2$ and WSe$_2$ opens unique potential for their use in novel quantum devices exploiting the valley degree of freedom. Here, using spin- and angle-resolved photoemission spectroscopy, we show that such spin-valley coupling persists in bulk 2H-WSe$_2$ where it becomes further entangled with the layer pseudospin [1]. Enormous spin splittings up to $\sim$0.5 eV result, despite the centrosymmetric nature of the bulk structure which would conventionally preclude the presence of spin polarised states. We argue these occur here due to local inversion symmetry breaking within constituent sub-units of the bulk unit cell, leading to a spin texture that is strongly modulated in both real and momentum space, and allowing us to directly image TMDC spin-valley-layer locking for the first time. [1] Riley *et al.*, Nature Phys. **10** (2014) 835.

O 57.2 Wed 15:15 MA 005

**From optics to superconductivity: Many body effects in transition metal dichalcogenides** — Malte Rösner[1,2], Gunnar Schönhoff[1,2], Alexander Steinhoff[1], Frank Jahnke[1], Christopher Gies[1], Stephan Haas[3], and •Tim Wehling[1,2] — [1]Institute for Theoretical Physics, University of Bremen, D-28359 Bremen, Germany — [2]Bremen Center for Computational Material Sciences, University of Bremen, D-28359 Bremen, Germany — [3]Department of Physics and Astronomy, University of Southern California, Los Angeles, CA 90089-0484, USA

We discuss many body effects in MoS$_2$ ranging from optical properties to the emergence superconductivity (SC) and charge density wave phases (CDW). Combining ab-initio theory and semiconductor Bloch equations we show that excited carriers cause a redshift of the excitonic ground-state absorption line, while higher excitonic lines disappear successively due to a huge Coulomb-induced band gap shrinkage of more than 500 meV and concomitant exciton binding-energy reductions. Upon strong charge doping, we observe a succession of semiconducting, metallic, SC, and CDW regimes. Both, the SC and the CDW instabilities trace back to a Kohn anomaly and related softening of Brillouin zone boundary phonons.

**Invited Talk** O 57.3 Wed 15:30 MA 005

**2D silcon materials: From single layer silicene to double-layer structures and multi-layer stacks** — •Patrick Vogt — Institut für Festkörperphysik,Technische Universität Berlin, Deutschland

Silicene, a new silicon allotrope with a graphene-like honeycomb structure, has attracted considerable interest, because its topology confers to it the same remarkable electronic properties as those of graphene [1]. Additionally, silicene might have a potential advantage of being easily integrated in current Si-based nano/micro-electronics offering novel technological applications. However, silicene does not exist in nature and had to be synthesized on a substrate material [2].

We will describe the recent development on the epitaxial formation of single layer silicene on Ag(111), including structural and electronic properties. Based on these results we will look at the growth of silicene double-layer and multi-layer structures and discuss if they can be explained by the stacking of single silicene sheets [3]. If confirmed, such multi-layer structures could open the way towards the technological applicability of silicene.

[1] G.G. Guzmán-Verri, L.C. Lew Yan Voon, Phys. Rev. B 76, 075131 (2007); S. Lebègue and O. Eriksson, Phys. Rev. B, 79 115409 (2009); S. Cahangirov et al., Phys. Rev. Lett. 102, 236804 (2009).

[2] P. Vogt et al., Phys. Rev. Lett. 108, 55501 (2012); C.-L. Lin et al., Appl. Phys. Exp. 5, 045802 (2012); B. Feng et al., Nano Lett. 11, 3507 (2012); A. Fleurence et al., Phys. Rev. Lett. 108, 245501 (2012).

[3] P. Vogt et al., Appl. Phys. Lett. 104, 021602(2014), De Padova et al., Appl. Phys. Lett. 102, 163106 (2013)

O 57.4 Wed 16:00 MA 005

**The electronic band structure of MoS$_2$ investigated by ARPES** — •Mathias Gehlmann[1], Sven Döring[1], Markus Eschbach[1], Ewa Mlynczak[1], Irene Aguilera[2], Gustav Bihlmayer[2], Stefan Blügel[2], Lukasz Plucinski[1], and Claus M. Schneider[1] — [1]PGI-6, FZ-Jülich — [2]PGI-1/IAS-1, FZ-Jülich

MoS$_2$ belongs to transition metal dichalcogenides and has drawn a large amount of attention in recent years. While the main area of interest in this material lies in the possibility of integrating it into two dimensional semiconductors and transistor devices, a growing number of researchers focuses on the valley polarization at the edge of the Brillouin zone.

We combine angle-resolved photoemission spectroscopy (ARPES) with density functional theory calculations to perform a thorough analysis of the valence band electronic structure of MoS$_2$. Our focus lies on the splitting of the valence band around the K point at the edge of the Brilluin zone, and on the comparison of the electronic states of the bulk material and its surface to a free standing monolayer.

O 57.5 Wed 16:15 MA 005

**Photocurrent studies on semiconducting MoS$_2$** — •Anna Vernickel[1,2], Marina Hoheneder[1,2], Eric Parzinger[1,2], Alexander Holleitner[1,2], and Ursula Wurstbauer[1,2] — [1]Walter Schottky Institut and Physik-Department, Technische Universität München, Am Coulombwall 4a, 85748 Garching, Germany — [2]Nanosystems Initiative Munich (NIM), Schellingstr. 4, 80799 München, Germany

Atomically thin molybdenum disulfide (MoS$_2$) has gained increasing interest as very promising material for novel and innovative device applications. Its bandgap in the visible range and the transition to a direct semiconductor in the single-layer case make MoS$_2$ particularly suitable for optoelectronic devices. We report on extensive photocurrent spectroscopy studies of single and few-layer MoS$_2$ in order to investigate their optoelectronic properties. We discuss the impact of Schottky contacts and thermoelectric contributions to the observed photocurrent. To further investigate the underlying photocurrent dynamics, nanoscale electronic circuits facilitating access to the photocurrent evolution on a picosecond time scale are prepared. We gratefully acknowledge financial support by NIM and BaCaTec.

O 57.6 Wed 16:30 MA 005

**Hot electron dynamics at $2H$-MoS$_2$ surfaces: Time- and angle-resolved photoelectron spectroscopy results** — •Petra Hein, Ankatrin Stange, Kerstin Hanff, Gerald Rohde, Michael Bauer, and Kai Rossnagel — Institute of Experimental and Applied Physics, University of Kiel, Germany

Recent research on the layered semiconductor $2H$-MoS$_2$ has been concentrated on MoS$_2$ monolayers: In contrast to the bulk crystal, MoS$_2$ monolayers are direct bandgap semiconductors without an inversion center, making them an appropriate material for valleytronic devices with hot carrier lifetimes in the picosecond regime. However, $2H$-MoS$_2$ surfaces could be equally exciting: Due to the symmetry breaking at the surface or a decoupling of the topmost sandwich, similarities to monolayers seem possible. For an investigation of this system, time- and angle-resolved photoelectron spectroscopy is the method of choice, as it provides high surface sensitivity and momentum resolution, while enabling us to map electronic processes on their fundamental time scales. Here, we present a $\vec{k}$-resolved study of the transient photoelectron intensity in the conduction band after excitation of $2H$-MoS$_2$ surfaces with 3.2 eV pump pulses. Momentum-dependent intensity rise times between 30 fs and 150 fs and decay times of several 100 fs allow us to identify direct electronic excitations and to track the electrons' relaxation pathway into the lowest energy states. The conduction band minima are finally depopulated within $\sim$1 ps. Possible explanations for this observation – such as diffusion processes, optical electron-hole recombination and trapping in defect states – are discussed.

O 57.7 Wed 16:45 MA 005

**Charge carrier trapping and electron-phonon coupling in MoS$_2$ revealed by $\mu$-Raman spectroscopy** — Bastian Miller[1,2], Eric Parzinger[1,2], Alexander Holleitner[1,2], and •Ursula Wurstbauer[1,2] — [1]Walter Schottky Institut and Physik-Department, Technische Universität München, Am Coulombwall 4a, 85748 Garching — [2]Nanosystems Initiative Munich (NIM), Schellingstr. 4, 80799 München, Germany

Two-dimensional layered van-der Waals materials are of increasing interest for fundamental research as well as device applications in the areas of electronics, spin- and valleytronics, optoelectronics, and sensing. We utilize power and gate voltage dependent non-resonant and resonant $\mu$-Raman spectroscopy on dual-gate field-effect transistor devices to study doping effects, e-ph coupling and the impact of trap states in mono-, bi- and few layer MoS$_2$. In non-resonant Raman measurements we observe a strong power- and gate voltage dependence of zone-center Raman modes with contrasting behavior for mono- and bilayer MoS$_2$. Under resonant excitation, a rich scattering spectra with signatures of multistep scattering processes are observable pointing towards contribution from phonon-phonon and electron-phonon interaction. The origin of the different modes, their dependence on the exciting light energy and evolution with number of layers will be discussed. We acknowledge the financial support by the DFG excellence cluster Nanosystems Initiative Munich (NIM).

O 57.8 Wed 17:00 MA 005

**Newly observed first-order resonant Raman modes in few-layer molybdenum disulfide** — •Nils Scheuschner, Roland Gillen, Matthias Staiger, and Janina Maultzsch — Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin

We show measurements of two newly observed first-order Raman modes in few-layer MoS$_2$ with phonon energies of 286 cm$^{-1}$ and 471 cm$^{-1}$. These modes are strongly resonant and appear only when using excitation energies above $\approx$ 2.4 eV. At 2.7 eV, their intensity is comparable to the second-order Raman modes; their absence thus provides an easy and accurate method to identify single-layer MoS$_2$. At UV excitation, the intensity of the new modes is even larger than the typically examined $A_1'/A_{1g}$ and $E'/E_g$ modes. We provide a systematic analysis of the phonon modes, their symmetries, and their frequencies in few-layer materials, including the newly observed modes.

O 57.9 Wed 17:15 MA 005

**Near-field microscopy and nano-FTIR spectroscopy on monolayer MoS2 grown on periodically poled LiNbO3** — •Georg Ulrich[1], Piotr Patoka[1], Peter Hermann[2], Bernd Kästner[2], Ariana Nguyen[3], Tom Scott[4], Arne Hoehl[2], Ludwig Bartels[3], Peter Dowben[4], Gerhard Ulm[2], and Eckart Rühl[1] — [1]Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany — [2]Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, Berlin, 10587 Berlin, Germany — [3]Department of Chemistry, U California Riverside, Riverside, CA 92521, USA —

[4]Department of Physics and Astronomy, U Nebraska, Lincoln, NE 68588-0299 USA

Coupling of synchrotron radiation from the Metrology Light Source to a scanning near-field optical microscope (SNOM) has emerged as a possibility for highly sensitive spectroscopic investigations in the mid-infrared regime [1]. It also allows the simultaneous collection of topographic information and optical response from the samples with a spatial resolution below 30 nm. Here we will present the results of nano-FTIR spectroscopy and near-field imaging of monolayer MoS2 islands on a periodically poled lithium niobate (PPLN) sample using synchrotron radiation in the infrared regime and tunable CO2 laser radiation, respectively. The results show the influence of the ferroelectric polarization of the PPLN structure on the MoS2 semiconductor which enhances the surface polarization of the ferroelectric domains only in one direction. [1] P. Hermann et al., Opt. Express 22, 17948 (2014)

O 57.10 Wed 17:30 MA 005

**Growth and Characterization of Epitaxial Single-Layer $MoS_2$ on Au(111)** — •Jill Miwa, Søren Ulstrup, Signe Sørensen, Maciej Dendzik, Antonija Grubišić Čabo, Marco Bianchi, Jeppe Vang Lauritsen, and Philip Hofmann — Dept. of Physics & Astronomy, Aarhus University, Aarhus, Denmark

We present a method for synthesizing epitaxial single-layer $MoS_2$ on the (111) face of Au. Using scanning tunnelling microscopy (STM) and low energy electron diffraction, the evolution of the growth is followed from nanoscale single-layer $MoS_2$ islands to a robust high quality epitaxial $MoS_2$ layer that is stable in air. We investigate the electronic structure of epitaxial single layer $MoS_2$ by angle resolved photoemission spectroscopy. Pristine and potassium-doped layers are studied in order to gain access to the conduction band. The potassium-doped layer is found to have a (1.39±0.05) eV direct band gap at $\bar{K}$ with the valence band top at $\bar{\Gamma}$ having a significantly higher binding energy than at $\bar{K}$. A pronounced moiré superstructure of the epitaxial system observed in STM does not lead to the presence of observable replica bands or minigaps. The degeneracy of the upper valence band at $\bar{K}$ is found to be lifted by the spin-orbit interaction, leading to a splitting of (145±4) meV. Finally, it is shown that the potassium doping does not only lead to a rigid shift of the band structure but also to a distortion, giving rise to the possibility of band structure engineering in single-layers of transition metal dichalcogenides.

## O 58: Electronic Structure of Surfaces II

Time: Wednesday 15:00–18:00 Location: MA 041

O 58.1 Wed 15:00 MA 041

**Two-band superconductivity of lead probed by scanning tunneling spectroscopy** — •Michael Ruby[1], Benjamin W. Heinrich[1], Jose I. Pascual[2], and Katharina J. Franke[1] — [1]Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]CIC nanoGUNE and Ikerbasque, Basque Foundation for Science, Tolosa Hiribidea 78, Donostia-San Sebastian 20018, Spain

The type I superconductor lead (Pb) has been theoretically predicted to be a two-band superconductor [1]. We use scanning tunneling spectroscopy to resolve two superconducting gaps with an energy difference of 130 $\mu$eV. Tunneling into Pb(111), Pb(110) and Pb(100) crystals reveals a strong dependence of the two coherence peak intensities on the crystal orientation. We show that this is the result of a selective tunneling into the two bands at the energy of the two coherence peaks. This is further sustained by the observation of signatures of the Fermi sheets in differential conductance maps around subsurface defects.

[1] A. Floris *et al.*, *Phys. Rev. B* **75**, 054508, (2007)

O 58.2 Wed 15:15 MA 041

**Core-resonant double photoemission studies of S-overlayers** — •Gianluca Di Filippo[1], Frank Oliver Schumann[1], Mario Italo Trioni[2], Guido Fratesi[3], Zheng Wei[1], Chang-Hui Li[1], Lucie Behnke[1], Swapnil Patil[1], Giovanni Stefani[4], and Jürgen Kirschner[1,5] — [1]Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany — [2]CNR, ISTM, Milano, Italy — [3]Università degli Studi di Milano Bicocca, Mlano, Italy — [4]Università degli Studi Roma Tre, Roma, Italy — [5]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

The power of core-resonant double photoemission (DPE), i.e. Auger decay, in determining the strength of electronic correlations in the valence band of solids is well established [1,2]. We employed this technique to investigate the properties of sulfur overlayers on metal substrates. We exposed a Cu(100), a oxygen passivated Cu(100) and a Ni(100) surface to $H_2S$ gas. This caused the formation of S overlayers with nominal coverages of 0.25, 0.48 and 0.5 ML. We focused on the process in which the de-excitation of the S 2p level results in a doubly-ionized final state with two vacancies in the S/metal surface states. The measured DPE line shapes show small differences which are mainly ascribable to the variation of the density of states at the different surfaces. We determined the strength of the electron-electron interaction energy, which is hardly affected by coverage or substrate variations.

[1] M. Cini, Solid State Comm. **24**, 681 (1977)
[2] G.A. Sawatzky, Phys. Rev. Lett., **39**, 504 (1977)

O 58.3 Wed 15:30 MA 041

**Dynamic screening probed by core-resonant double photoemission from surfaces** — •Frank O. Schumann[1], Zheng Wei[1], Changhui Li[1], Lucie Behnke[1], Gianluca Di Fillippo[1], Giovanni Stefani[2], and Jürgen Kirschner[1] — [1]Max-Planck-Institut für Mikrostrukturphysik,06120 Halle, Germany — [2]CNISM and Dipartimento di Fisica, Università Roma Tre, I-00146 Rome, Italy

The universal response of an electronic system upon a suddenly created core hole is predicted to occur on an attosecond time scale, but lacks an experimental demonstration. A core hole switches on a local potential and triggers a series of dynamic electron screening processes, such as the shake-up of the outer-shell electrons, plasmon excitations and the emission of Auger electrons.

It is a well-known experimental fact that the 4p photoelectron lines for the elements ranging from Ag to Xe are exceptionally broad. This can be explained by a dynamic fluctuation between a continuous and discrete electron configuration.

With coincidence spectroscopy, we demonstrate an extensive energy sharing between the Ag 4p photoelectron and the NVV Auger electron exceeding 10 eV. This energy width provides access to the time scale of the emission process. We convert this to a timescale of 60 as over which the fluctuations takes place. This value is fair agreement with the theoretical calculation of the timescale to fill an exchange-correlation hole. This shows that core-resonant double photoemission is a powerful tool to probe the ultra-fast dynamic screening processes in the very beginning of the photoemission process on an attosecond timescale.

O 58.4 Wed 15:45 MA 041

**Photon-energy dependent double photoemission spectroscopy from transition metal oxides** — •Andreas Trützschler[1,2], Cheng-Tien Chiang[1,2], Michael Huth[1], Frank O. Schumann[1], Jürgen Kirschner[1,2], and Wolf Widdra[2,1] — [1]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120, Halle(Saale), Germany — [2]Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Von-Danckelmann-Platz 3, D-06120, Halle(Saale), Germany

In the double photoemission (DPE) process, the excitation by a single photon leads to the emission of a pair of photoelectrons. The corresponding transition probability is closely related to the strength of electron correlation in the material [1]. In this contribution we report on DPE experiments on weakly correlated Ag(100) and strong correlated NiO(100) and CoO(100) surfaces [2]. By using a high-order harmonic generation light source at MHz repetition rates in combination with two time-of-flight spectrometers, we are able to compare single and double photoemission propabilities for these materials at different photon energies from 15 to 30 eV. At all photon energies, the ratio between single and double photoemission probability is significantly higher for NiO(100) and CoO(100) as compared to Ag(100), reaching about a factor of 4 at 30 eV photon energy.

[1] Berakdar, Phys. Rev. B 58, 9808 (1998)
[2] Huth, Chiang, Trützschler, Schumann, Kirschner, Widdra, Appl.

Phys. Lett. 104, 061602 (2014)

O 58.5 Wed 16:00 MA 041

**Simultaneous ARPES and transport measurements** — •Lukasz Plucinski[1,2], Ewa Mlynczak[1], Markus Eschbach[1], and Claus M. Schneider[1,2] — [1]PGI-6, FZ Jülich, 52425 Jülich, Germany — [2]Universität Duisburg-Essen, 47048 Duisburg, Germany

It is an open secret, that from the perspective of materials science, angle-resolved photoemission (ARPES) measurements are typically interpreted having in mind transport properties. Electrons measured in high resolution ARPES have kinetic energies for which the inelastic mean free path inside the crystal is in order of few atomic layers, therefore in practice ARPES probes at most a nanometer or two of the surface region of the sample. Spectral contribution from electronic states deeper inside the crystal is negligible. Yet, in "volume" samples, with each dimension larger than (to provide some number) 10 nm, it is the volume of the sample that typically has the dominant contribution to its transport properties. I will present first results of simultaneous ARPES and transport measurements on ultrathin, conducting films grown on insulating substrates and electrically contacted *in situ* under UHV. Furthermore, I will provide an overview of new exciting scientific avenues which will be opened up by this new approach.

O 58.6 Wed 16:15 MA 041

**Anomalous d-like Surface Resonance on Mo(110) Analyzed by Time-of-Flight Momentum Microscopy** — •Sergey Chernov[1], Katerina Medjanik[1], Christian Tusche[2], Dmytro Kutnyakhov[1], Sergej Nepijko[1], Andreas Oelsner[3], Jürgen Braun[4], Jan Minár[4,5], Stephan Borek[4], Hubert Ebert[4], Hans Joachim Elmers[1], Jürgen Kirschner[2], and Gerd Schönhense[1] — [1]Johannes Gutenberg-Universität, D-55128 Mainz — [2]Max Planck Institut für Mikrostrukturphysik, D-06120 Halle — [3]Surface Concept GmbH, D-55124 Mainz — [4]Ludwig-Maximilians-Universität, D-81377 München — [5]University of West Bohemia, 306 14 Pilsen, Czech Republic

The d-like surface resonances on Mo(110) have been investigated by the novel technique of Time-of-Flight (ToF) momentum microscopy at BESSY (single-bunch). Regions of 3.4 $\mathring{A}^{-1}$ dia. in $k$-space and 4 eV binding energy range were detected simultaneously. 3D $(k_x, k_y, E_B)$ maps of the electronic bands in the full surface Brillouin zone were acquired with high efficiency. Photoemission calculations were performed by means of the one-step model in its density matrix formulation. Band symmetries were probed by linear dichroism. It will be shown that close to the midpoint between $\bar{\Gamma}$ and $\bar{N}$ an anomalous band crosses the symmetry center of a band gap at $E_B$=0.8 eV. The anomalous band has linear dispersion in a very large energy range and shows much analogy to a similar state previously found on W(110) [Miyamoto et al., PRL 108, 066808 (2012)]. The project is funded by BMBF (05K12UM2, 05K12EF1, 05K13WMA) and COST.

O 58.7 Wed 16:30 MA 041

**Electronic band structure of thin Fe films epitaxially grown on Au(001) and MgO(001)** — •Ewa Mlynczak[1,2], Markus Eschbach[1], Pika Gospodaric[1], Vitaliy Feyer[1], Giovanni Zamborlini[1], Lukasz Plucinski[1,3], and Claus M. Schneider[1,3] — [1]Peter Grünberg Institut PGI-6, Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland — [3]Fakultät für Physik and Center for Nanointegration Duisburg-Essen (CeNIDE), 47048 Duisburg, Germany

Detailed knowledge of the electronic band structure of thin ferromagnetic films is a first step towards the proper understanding of the spin-based phenomena important for future spintronics such as tunneling anisotropic magnetoresistance or spin-orbit torque. In this contribution, we will present results of comprehensive angular resolved photoemission (ARPES) studies of the electronic band structure of thin Fe(001) films grown on Au(001) and MgO(001). In both cases, Fe shows high crystalline quality providing perfect model systems for these fundamental investigations. The studies conducted using a laboratory based high resolution ARPES apparatus operated with an unpolarized discharge source were complemented by the k-space microscopy (NanoESCA) performed at Elettra light source (Trieste, Italy). The experimentally obtained electronic band structures will be confronted with the results of the DFT calculations.

O 58.8 Wed 16:45 MA 041

**Probing the magnetic properties of Cr atoms adsorbed on copper nitride** — •Zsolt Majzik[1], Roberto Robles[2], Carmen Rubio-Verdú[1], Martina Corso[3,4], Nicolás Lorente[2], and Nacho Pascual[1,3] — [1]CIC nanoGUNE, Donostia-San Sebastián, Spain — [2]Catalan Institute of Nanoscience and Nanotechnology (ICN2), Barcelona, Spain — [3]Ikerbasque, Basque Foundation for Science, Bilbao, Spain — [4]Materials Physics Center, EHU, Donostia-San Sebastián, Spain

In the last decade it has been shown that magnetic properties of a single atom can be probed by inelastic electron tunneling spectroscopy. In addition, magnetic nanostructures have been routinely assembled via atomic manipulation. Spin excitation is induced if the bias voltage exceeds the threshold energy for excitation. This process allows inelastic tunneling that leads to a characteristic change in the conductance. Here we aimed to study the magnetic properties of isolated Cr atoms adsorbed on Cu$_2$N/Cu(100) surface. Different inelastic tunneling spectra were observed over Cr atoms adsorbed on N sites than on Cu sites. In the first case we interpret our spectra as interplay between spin excitation and Kondo screening effect, which appears here at larger biases. However, if Cr atom adsorbs on the Cu site, the Kondo effect does not appear in the spectra, only a spin excitation has a contribution near the Fermi level. Our results suggest that the spin configuration of the Cr atom varies among different adsorption positions. We have performed DFT calculations to better understand the change in spin configuration as well as in the magnetic anisotropy.

O 58.9 Wed 17:00 MA 041

**Fermi surface tomography of the ferromagnetic transition metals Co and Ni by momentum microscopy** — •Martin Ellguth[1], Christian Tusche[1], Alexander Krasyuk[1], Vitaliy Feyer[2], Carsten Wiemann[2], Claus Michael Schneider[2], and Jürgen Kirschner[1,3] — [1]Max-Planck-Institut für Mikrostrukturphysik, Halle — [2]Peter-Grünberg-Institut, Forschungszentrum Jülich — [3]Institut für Physik, Martin-Luther-Universität, Halle

The Fermi surface of a metal represents its electronic structure at one particular energy: the one which separates occupied from unoccupied electronic states. These states are responsible for the electric conductivity and related properties such as the thermoelectric behaviour. As such it is both interesting from a fundamental physics viewpoint as well as for applications. In this study, we have used momentum microscopy as a highly efficient photoemission experiment to probe the Fermi surface of the elemental ferromagnets Co and Ni. The combination of this setup with synchrotron radiation in the energy range from 30 eV to 200 eV allows for scanning the two-dimensional manifold through the perpendicular axis and thus acquire for the first time a volumetric dataset showing the Fermi surface for Co and Ni as photoemission resonances. The majority-spin surface and one of the minority surface sheets of Co are most clearly observed. Our data provides a sensitive test to the energetic position of electronic bands crossing the Fermi level, and therefore to a possible renormalization induced by many-body interactions.

M.E. acknowledges support from the BMBF (05K12EF1).

O 58.10 Wed 17:15 MA 041

**Investigation of the surface of binary metallic alloys using PAES, XPS and STM** — •Samantha Zimnik, Christian Piochacz, Sebastian Vohburger, and Christoph Hugenschmidt — Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department E21, Technische Universität München, Lichtenbergstraße 1, 85748 Garching, Germany

The characterization of the elemental composition of surfaces is of high importance for the understanding of many surface-related processes such as catalysis or oxidation. However, surface segregation causes changes in the elemental constitution of the surface, which affects significantly the macroscopic properties of the system. Therefore, e.g. in the system Fe/Pt, it is of great interest to investigate the theoretically predicted surface segregation process.

Positron annihilation induced Auger Electron Spectroscopy (PAES) is a powerful technique to gather information about the elemental composition of only the topmost atomic layer of a specimen. The positron beam facility NEPOMUC delivers a high intensity positron beam of $10^9$e$^+$/s and enables measurement times of only a few minutes per PAES spectrum. Thus, time-dependent PAES became possible and enables the in-situ observation of surface segregation processes. The upgraded surface spectrometer at NEPOMUC uses the complementary techniques PAES, XPS and STM for a comprehensive surface analysis. First temperature-dependent measurements on binary alloys are presented. Financial support by the BMBF (project no. 05K13WO1) is gratefully acknowledged.

O 58.11 Wed 17:30 MA 041

**Manipulating STM induced light emission by organic adlayers** — •Maren C. Cottin, Ebru Ekici, Rolf Möller, and Christian A. Bobisch — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

Light emitted from the tip-sample junction of a scanning tunneling microscope (STM) carries information about energy transfer processes at surfaces. We use thin layers of bismuth (Bi) on Cu(111) as a substrate for different archetype organic layers, e.g. $C_{60}$ and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). We find that the maximum photon yield may be enhanced if the tunneling tip is placed above the molecules as compared to the bare Bi/Cu(111)-substrate. In a comprehensive study of the light emission characteristics, we present laterally resolved maps of the overall photon intensity measured together with the surface structure. In addition, measurements of the overall photon intensity as a function of the bias voltage, dI/dV-data and spectra of the emitted light allow us to characterize the role of the molecules in the excitation/light emission process.

O 58.12 Wed 17:45 MA 041

**Determination of charge neutrality level in TiO2 films from res-PES measurements.** — •Chittaranjan Das, Massimo Tallarida, and Dieter Schmeisser — Lehrstuhl Angewandte Physik/Sensorik Brandenburgische Technische Universität, Cottbus-Senftenberg Cottbus-03046

Titanium dioxide is one of the metal oxides which have versatile application in different fields. The applications of TiO2 are in the field of cosmetics, electronics (memory resistive switching), dye, photonics and photocatalysis. In the present paper we study the resPES data of TiO2 films prepared by atomic layer deposition. The measurements are done in in-situ system at beam line U49/2-PGM2 in BESSY-II. The density of state in valence band and conduction band is obtained from the resonance photo electron spectroscopy (res-PES) of the O1s and the Ti2p edge. The data allow to determine the position of the VBM and CBM with respect to the Fermi energy. Also the existence of localized O2p and Ti2p derived states is deduced which appear in the gap. In addition we determine the charge neutrality level (CNL).The CNL is the position where the weight of the density of state from valence band and conduction band are equal. This is an important quantity for the discussion of interface properties.

## O 59: Oxide and Insulator Surfaces: Structure, Epitaxy and Growth

Time: Wednesday 15:00–18:15 Location: MA 042

O 59.1 Wed 15:00 MA 042

**Surface phonons of $BaTiO_3$(001) and $BaTiO_3$ ultrathin films on Pt(001) and Au(001)** — •Florian Schumann[1], Klaus Meinel[1], Andreas Trützschler[1], and Wolf Widdra[1,2] — [1]Institute of Physics, Martin-Luther-Universität Halle-Wittenberg — [2]Max-Planck- Institut für Mikrostrukturphysik, Halle

Phonons and their softening are key elements for the understanding of the long-range coupling in ferroelectric and multiferroic materials, which causes, e.g., the paraelectric to ferroelectric phase transition. In thin films, these ferroelectric properties are often controlled by strain from the underlying substrate or heterostructures. Here we study the surface phonons of $BaTiO_3$(001) ultrathin films in comparison with a $BaTiO_3$ single-crystal with high-resolution electron energy loss spectroscopy (HREELS). For all $BaTiO_3$ structures, three well-developed phonon peaks at about 210, 460, and 670 $cm^{-1}$ dominate the HREELS spectra. Calculations of the energy loss spectra within a semi-classical approach identify the three phonons as the A(TO) surface phonon-polaritons (Fuchs-Kliewer modes) of $BaTiO_3$(001). In comparison to the single crystal, the surface phonons of the thin films on Pt(001) and on Au(001) are shifted due to the lattice misfit of +2% and -2%, respectively. Furthermore, the surface phonons show a thickness dependent red shift in the thin films. Calculations identify this shift as phonon-polariton coupling to the metallic substrate.

O 59.2 Wed 15:15 MA 042

**Preparation of $Bi_2Se_3$(0001) surface studied by scanning tunneling microscopy** — •Vasilii Sevriuk, Alberto Cavallin, Safia Ouazi, Dirk Sander, and Jürgen Kirschner — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

Despite the fact that the $Bi_2Se_3$(0001) surface is relatively inert [1], carbon is a common surface contaminant. It is detected by Auger electron spectroscopy (AES) and in scanning tunneling microscopy (STM) it appears as protrusions. Here we report the preparation of $Bi_2Se_3$(0001) by Ar sputtering and annealing and by in vacuo cleavage. We find by STM that sputtering and annealing cycles lead to surface and sub-surface defects, which can be ascribed to Se vacancies [2] and Bi interstitials [3]. After several cycles of sputtering and annealing, a periodic spatial modulation on the length scale of 10–15 nm is observed in STM constant current maps, which we ascribe to a dislocation network [4]. Samples prepared by cleavage do not show this spatial modulation.

[1] V. A. Golyashov, K. A. Kokh, S. V. Makarenko, K. N. Romanyuk, I. P. Prosvirin et al. J. Appl. Phys. 112, 113702 (2012).

[2] Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J. G. Checkelsky, A. Yazdani, M. Z. Hasan, N. P. Ong and R. J. Cava. Phys. Rev. B 79, 195208 (2009).

[3] S. Urazhdin, D. Bilc, S. H. Tessmer, S. D. Mahanti, Theodora Kyratsi, and M. G. Kanatzidis, Phys. Rev. B 66, 161306(R) (2002).

[4] M. Schmid, A. Biedermann, H. Stadler, and P. Varga. Phys. Rev. Lett. 69, 925 (1992).

O 59.3 Wed 15:30 MA 042

**Growth of cuprous oxide on Au(111) and Mo(001) - Role of the support** — •Hanna Fedderwitz, Boris Gross, Hendrik Sträter, and Niklas Nilius — Carl-von-Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Str. 9 - 11, 26129 Oldenburg

Physical vapor deposition of Cu in an oxygen ambience is used to prepare $Cu_2O$ films on two single crystalline supports of different reactivity and lattice symmetry. While on Au(111), the oxide grows in a layer by layer fashion and develops atomically flat films, formation of nanoparticles is observed on a Mo(001) surface. The size and shape of the crystallites can be controlled by varying the temperature and $O_2$ partial pressure during oxide growth. Insight into the atomic configuration of the $Cu_2O$ facets is obtained from low-temperature STM measurements. Whereas Au-supported films expose the ideal (111) termination of cuprous oxide, modified only be a network of dislocation lines, a variety of low-index planes is discernable for deposits on the Mo support. The underlying growth mechanism is analyzed with the Wulff theory for nanoparticles in thermodynamic equilibrium. We discuss consequences of the different growth schemes on the two supports for possible applications of our cuprous-oxide samples in photocatalysis and photovoltaics.

O 59.4 Wed 15:45 MA 042

**Atomic structure and electronic properties of $Cu_2O$(111) films** — •Boris Gross, Hanna Fedderwitz, Hendrik Sträter, and Niklas Nilius — Carl-von-Ossietzky Universität Oldenburg, Carl-von-Ossietzky Str. 9-11, 26129 ,Oldenburg

Atomically flat films of cuprous oxides were prepared by Cu deposition in oxygen onto an Au(111) surface, and analyzed by XPS, electron diffraction and STM. Depending on the preparation conditions, different surface reconstructions are obtained. Whereas the low-temperature structures have no analogy to respective bulk phases and are governed by interactions with the metal support, the high-temperature films have a similar atomic configuration as bulk-cut $Cu_2O$(111). STM conductance spectroscopy reveals the pronounced $2.0\,eV$ band gap of the oxide, in addition to an unoccupied surface state that occurs in the high-temperature phase. Field-emission resonances that govern the high-energy part of the STM spectra are used to monitor local variations in the work function of the system. Given their high crystallographic quality, our $Cu_2O$ films provide an ideal starting point to explore the defect landscape and optical properties for this reference material for photo-catalysis and photovoltaics.

O 59.5 Wed 16:00 MA 042

**Growth of ultrathin Silica films on Ru(0001)** — •Hagen W.

Klemm, Gina Peschel, Ewa Madej, Alexander Fuhrich, Martin Timm, Thomas Schmidt, and Hans-Joachim Freund — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

The SiO$_2$ bilayer on Ru(0001) offers magnificent possibilities for understanding the transition from crystalline to vitreous phase[1], tuning of electronic structure, doping and catalysis[2]. In the thickness range of one to three monolayers we studied the growth of ultrathin Silica films by LEEM, LEED, XPS and XPEEM. We found that the oxidation temperature plays a crucial role for the quality of the resulting film, varying from incomplete oxidation to dewetting of the film. A special focus of our investigation was the transition from crystalline to vitreous phase, as could be clearly seen in LEED. The influence of holes in the film and the morphology of the substrate will be discussed.

[1] Lichtenstein, L. et. al., Angew. Chem. Int. Ed. 51, 404 (2012)
[2] Shaikhutdinov, S. et. al., Chem. Phys. Chem. 14, 71 (2013)

### O 59.6 Wed 16:15 MA 042

**Ultrathin Iron-Silicate films on Ru(0001)** — •Gina Peschel, Hagen Klemm, Thomas Schmidt, and Hans-Joachim Freund — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

Iron silicate can be seen as a model system for zeolites [1], which are important for catalysis and widely used in industry as desiccant, detergent or as molecular sieves. Of special interest is the relation between the specific structure and reactivity. In our case we studied the growth only of a one to two atomic layer thin film on a Ru(0001) support by LEEM, LEED, XPS and XPEEM measurements.

We found the formation of structural domains. The size of these domains increase with temperature and Fe/Si ratio. Futhermore, XPEEM measurements indicate that the domains contain iron and Silica, while in between the domains only Silica is found. The Si2p level shows a chemical shift between Silica bound to FeO and Silica on Ru(0001)only. Beside the (2x2) spots, typical for silica, LEED shows additional spots rotated by 30 ° and a Moiré structure. The unit cell of the new structure is about three percent larger than for ultra-thin silica films.

[1] R. Wlodarczyk, J. Sauer, X. Yu, J. Boscoboinik, B. Yang, S. Shaikhutdinov, H.-J. Freund, J. Am. Chem. Soc. 135 (2013), 19222-19228

### O 59.7 Wed 16:30 MA 042

**First-Principles Embedded Cluster Calculations of Surface Defects at TiO$_2$(110)** — •Daniel Berger, Harald Oberhofer, and Karsten Reuter — Technische Universität München

Bulk and surface defects critically determine many of the properties and functions that make TiO$_2$ such an interesting and widely studied material. Given this importance, it is both surprising and discomforting to see how little is actually known especially about the surface defects of TiO$_2$. For surface oxygen vacancies not even their thermodynamically favored charge state is unambiguously clear. We contribute to this context with first-principles embedded cluster calculations [1] of the rutile TiO$_2$(110) surface. Our approach allows for a numerically particularly efficient application of hybrid density-functional theory inside the quantum mechanic (QM) cluster region. In the extended molecular mechanic (MM) embedding region specifically optimized interatomic potentials provide a quantitative account of the strong TiO$_2$ polarization response. We discuss the advantages of this QM/MM approach against more common periodic supercell calculations especially for charged O vacancies. Over a wide range of electrochemical potentials and oxygen partial pressures our calculations show the $+2$ state to be thermodynamically favored, which can be rationalized by the huge dielectric constant of TiO$_2$.

[1] D. Berger *et al.*, J. Chem. Phys. **141**, 024105 (2014).

### O 59.8 Wed 16:45 MA 042

**Ordered Indium and Iron Adatoms on the Reduced In2O3(111) Surface** — •Margareta Wagner[1], Peter Lackner[1], Steffen Seiler[2], Bernd Meyer[2], Lynn A. Boatner[3], Michael Schmid[1], and Ulrike Diebold[1] — [1]Institut für Angewandte Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10/134, 1040 Wien, Österreich — [2]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstrasse 25, 91052 Erlangen, Deutschland — [3]Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Indium oxide is one of the most important TCOs and commonly used as a contact material in many devices. Recently, In$_2$O$_3$ single crystals, prerequisite for fundamental surface studies, have become available.

The In$_2$O$_3$(111) surface can be transformed from a bulk-terminated surface to one that is covered by single indium adatoms. The transformation and the intermediate stages were followed with Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT). DFT supports the formation of a stable array made of indium adatoms, which is favored over vacancy formation at the given oxygen chemical potential during reduction. The formation of an ordered adatom array is different from any known response of an oxide surface to chemical reduction. Also iron atoms deposited on the oxidized surface arrange as single adatoms in the same (1x1) superstructure. The adatom-covered and oxidized In$_2$O$_3$(111) surfaces are expected to exhibit very different chemical and electronic properties.

### O 59.9 Wed 17:00 MA 042

**Infra-red and Raman frequencies of Co$_3$O$_4$ – an *ab initio* study** — Andrii Titov[1], •Dominik Legut[2,3], and Lucie Obalova[3] — [1]Nanotechnology Centre — [2]IT4Innovations Centre — [3]Inst. Env. Techn., VSB–TU Ostrava, Ostrava, Czech Republic

Among well known catalyst for N$_2$O decomposition belongs Co$_3$O$_4$. Since this reaction has oxidation-reduction mechanism, the electronic properties of Co$_3$O$_4$ represent important feature. We have calculated electronic structure and lattice dynamics, i.e. atomic vibrations using first-principles calculations. We determined Raman and infra-red frequencies of the phonon modes. Our results were calculated using single electron framework within the density functional theory. For the electronic exchange correlation the general gradient approximation as parametrized by Perdew–Burke–Ernzerhof [1] was used. To obtain the correct description of the insulating behaviour the Hubbard U technique was used. The anti-ferromagnetic ordering and spin-orbit interaction were also considered. Lattice vibrations were calculated using Phonopy package [2]. The dependences of the band gap, infra-red and Raman frequencies on the Coulomb interaction (Hubbard U) were revealed and compared with experimental data measured at the VSB-TU Ostrava. The work was supported by the Grant Agency of the Czech Republic, project reg. No. 14-13750S.

**References:**

1. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
2. A. Togo, F. Oba, I. Tanaka, Phys. Rev. B **78**, 134106 (2008).

### O 59.10 Wed 17:15 MA 042

**Surface energy, structure and stability of crystalline corundum surfaces** — •Lilit Amirkhanyan, Torsten Weissbach, and Jens Kortus — Institute of Theoretical Physics, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany

Using first-principles density function theory as implemented in Quantum-ESPRESSO we examined the surface energy of the stable $\alpha$-Al$_2$O$_3$ corundum phase. Corundum is very important for applications due to its outstanding hardness, high melting point, high thermal conductivity and low dielectric constant.

The [001], [100], [110], [112], [114], [113] and [223] crystal planes of $\alpha$-Al$_2$O$_3$ were studied. The surfaces have been modeled using slabs with periodic boundary conditions. We investigated the impact of different termination and the effect of relaxation on surface properties. Further, we discuss possible relations of surface properties to structural elements like number of broken bonds or missing oxygen atoms to complete the coordination.

### O 59.11 Wed 17:30 MA 042

**Surface Adsorbates and Defects on the Subsurface Cation Vacancy Stabilized Surface of Magnetite (001)** — •Eamon McDermott[1], Roland Bliem[2], Gareth Parkinson[2], Ulrike Diebold[2], and Peter Blaha[1] — [1]Institute for Material Chemistry, TU Wien, Vienna, Austria — [2]Institute of Applied Physics, TU Wien, Vienna, Austria

Having proposed a new surface reconstruction for the magnetite (001) surface which is stabilized by a subsurface cation vacancy, we are now studying the extended properties of this reconstruction, including its preferred adsorption sites for various metals, the properties of oxygen vacancies at the structure and the adsorption of CO and OH groups. The surface structure has interesting chemistry, due to the presence of an oxygen site with a $+1$ oxidation state. In particular, we are interested in understanding our database of known magnetite surface defects as observed by STM. Progress on several ongoing investigations will be reported.

O 59.12 Wed 17:45 MA 042

**The Structure of Magnetite(100)-c(2×2) revisited** — •Lutz Hammer[1], Pascal Ferstl[1], M.Alexander Schneider[1], Roland Bliem[2], Ulrike Diebold[2], and Gareth Parkinson[2] — [1]Solid State Physics, FAU Erlangen-Nürnberg — [2]Inst. Appl. Physics, TU Wien

The widely accepted "Distorted-Bulk-Truncation" model [1,2] for the c(2×2) surface reconstruction of $Fe_3O_4(100)$ fails to explain recent STM results for the adsorption and nucleation behaviour of metal adatoms on this surface [3,4]. We have therefore revisited the surface structure by means of a full-dynamical LEED intensity analysis. We tested in particular a new model of subsurface cation vacancies and interstitials [5], which was not yet considered in a former LEED analysis [2]. This new model led to a remarkably better correspondence between experimental and calculated spot intensities expressed by a Pendry R-factor of 0.125 (compared to 0.34 of ref.[2]). The new analysis is based on a very large experimental data base of 11300 eV allowing a safe determination of as much as 59 structural parameters. The atomic coordinates derived from the LEED analysis are in excellent agreement with predictions from DFT for this structure [5]. This study also proves that there are no inherent problems in the LEED I-V methodology to properly determine the structure of oxide surfaces as frequently claimed in literature.

[1] R. Pentcheva et al., PRL 94, 126101 (2005); [2] R. Pentcheva et al., Surf. Sci. 602, 1299 (2008); [3] Z. Novotny et al., PRL 108, 216103 (2013); [4] G.S. Parkinson et al., Nat. Mater. 12, 724 (2013); [5] R. Bliem et al. Science, accepted

O 59.13 Wed 18:00 MA 042

**Surface structure of $Fe_3O_4$ under varying conditions studied by surface x-ray diffraction** — •Björn Arndt[1,2], Roland Bliem[3], Heshmat Noei[1], Oscar Gamba[3], Jessica van der Hoven[3], Gareth Parkinson[3], and Andreas Stierle[1,2] — [1]Deutsches Elektron-Synchrotron (Desy), D-22607 Hamburg, Germany — [2]Fachbereich Physik, Universität Hamburg, D-20355 Hamburg, Germany — [3]Institute of Applied Physics, Vienna University of Technology, 1060 Vienna, Austria

Magnetite ($Fe_3O_4$) exhibits interesting material properties which makes it attractive for industrial applications as a catalyst for the water-gas shift reaction. Therefore, it is important to understand its surface structure under different conditions. The (001) surface of magnetite shows a $(\sqrt{2}x\sqrt{2})R45°$ reconstruction in UHV which gets lifted at around 450°C as well as upon water adsorption at room temperature. To clarify the recent controversy about the atomic structure of the reconstruction and to get insight into it at different conditions, we performed a surface x-ray diffraction experiment on a natural $Fe_3O_4$ (001) single-crystal. The experiment was carried out at the ESRF ID03 beamline using an UHV-ambient pressure flow reaction chamber at 11 keV photon energy. Our data support the recently proposed surface model[1] with overstochiometric oxygen concentration. Upon heating and upon water adsorption, the surface reconstruction vanishes.

[1] R. Bliem et al., submitted

## O 60: Dielectric and Molecular/Water Interfaces

Time: Wednesday 15:00–18:00 Location: MA 043

O 60.1 Wed 15:00 MA 043

**Towards molecular dynamics simulations of electrolytes in water employing neural network potentials** — •Sinja Klees and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

In recent years, artificial neural networks (NNs) have become a promising method to construct reliable and unbiased interatomic potentials for a wide range of systems. By interpolating the energies and forces obtained from first-principles calculations, NN potentials can be constructed systematically and allow to perform large-scale molecular dynamics simulations several orders of magnitude faster than the underlying electronic structure method. Here, we explore the applicability of NN potentials to electrolytes in water. First preliminary results are discussed and compared to density functional theory data.

O 60.2 Wed 15:15 MA 043

**Quantum chemical and quantum dynamical studies of the photocatalytic water splitting on titanium dioxide** — •Jan Mitschker and Thorsten Klüner — Theoretische Chemie, Carl von Ossietzky Universität Oldenburg

We present results from our computer simulations on the photocatalytic water splitting on rutile (110). Our approach consists of a quantum chemical and a quantum dynamical part.

In a first step, we calculated potential energy surfaces (PES) for this system. The surface is made up of a $Ti_9O_{18}$ cluster, saturated by Mg atoms for technical reasons. This cluster is embedded in a large point charge field. This model can describe the adsorption of small molecules successfully on a high level of theory. The bond breaking is a multi-configurational problem. Therefore, CASSCF calculations for the ground state were performed giving a complete (PES) in five dimensions. Furthermore, similar calculations were carried out for an electronically excited state that results from a hole attack on the water. Artificial Neural Networks proofed to be very helpful in fitting these potential energy surfaces without the need of an analytical expression. Both PES are necessary for a real quantum dynamical simulation of photoreactions including quantum effects like tunneling. In the second part of our contribution, we present first results for this kind of simulation based on a jumping wave packet approach. For the first time, the motion of hydrogen after the electronic excitation can be elucidated.

[1] J. Mitschker, T. Klüner, *Phys. Chem. Chem. Phys.*, 2014, DOI: 10.1039/C4CP04593A

O 60.3 Wed 15:30 MA 043

**STM and STS of electric and photocatalytic $H_2O$ dissociation on $TiO_2$ Anatase (101)** — •Christian Dette[1], Miguel A. Pérez[2], Christopher E. Patrick[2], Feliciano Giustino[2], Soon J. Jung[1], and Klaus Kern[1,3] — [1]Max-Planck Institue for Solid State Research, D-70569 Stuttgart — [2]University of Oxford, UK-OX1 3PH Oxford — [3]Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Nanosized $TiO_2$ photocatalytic water-splitting technology has great potential for low-cost, environmentally friendly solar-hydrogen production to support the future hydrogen economy. However, the reaction mechanism and dynamics of the photocatalytic water dissociation on $TiO_2$ anatase (101) have not yet been fully understood. To resolve this ambiguity we first determine fingerprints of O, OH and $H_2O$ on a $TiO_2$ anatase surface by using scanning tunneling microscopy (STM) and spectroscopy (STS) in conjunction with first principle density functional theory (DFT). These fingerprints allow us to investigate the changes in the molecular water structure and its dynamics at the interface during and after the photoreaction. Furthermore, the photon induced dissociation will be compared with the electron induced dissociation.

O 60.4 Wed 15:45 MA 043

**Ultrafast Interfacial Reorientational Dynamics of a Leucine Side Chain** — •Michael Donovan, Mischa Bonn, Ellen Backus, and Tobias Weidner — Max Planck Institute for Polymer Research, Ackermannweg 10 Mainz, Germany 55128

Proteins possess fluctuating structural features which are important for their function. At interfaces, protein motions may be different than in bulk, and this can affect protein function when in contact with surfaces. We utilize surface specific probes to study the interfacial behavior of protein side chains. As a model system we studied the reorientational dynamics of hydrophobic leucine side chains at the air-water interface. We followed ultrafast reorientational motions of excited methyl groups pointing into the hydrophobic phase using femtosecond SFG pump probe methods. Specifically, orthogonally polarized mid IR pump pulses excite molecular vibrations, and interfacial dynamics are followed by watching the temporal evolution of an interface specific sum frequency generation (SFG) probe pulse until the signal recovers to its steady state value. First, the dynamics of a charged Leucine monolayer are followed through time resolved SFG, and later the dynamics of leucine in an alpha helical and beta sheet peptide are followed. It is shown that these fast reorientational motions can act as probes of the local interfacial environment of the side chain.

O 60.5 Wed 16:00 MA 043

**Molecular Ordering at the Bulk Water/TiO2 Rutile (110) Interface** — Giulia Serrano[1], Beatrice Bonanni[1], Marco Di Giovannantonio[1], Tomasz Kosmala[1,2], Ulrike Diebold[3], Aldo Di Carlo[4], Jun Cheng[5], Joost VandeVondele[6], Klaus Wandelt[2], and •Claudio Goletti[1] — [1]Department of Physics, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Rome, Italy — [2]Institut für Physikalische und Theoretische Chemie, Wegeler Str. 12 , 53115 Bonn, Germany — [3]Institute of Applied Physics, Vienna University of Technology, WiednerHauptstrasse 8-10/134, A-1040 Vienna, Austria — [4]Department of Electronic Engineering and CHOSE, Università degli Studi di Roma "Tor Vergata", Via del Politecnico 1, I-00133 Rome, Italy — [5]The School of Natural and Computing Sciences, Weston Building, Weston Walk, Aberdeen CB24 3UE, UK — [6]Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 27, CH-8093 Zürich, Switzerland

Water in direct contact with a solid surface assumes various structures, governed by a delicate relationship between water-surface and water-water interactions. Lateral ordering in the first water monolayer is often observed in UHV, while it is challenging to investigate experimentally if such structures also form when a solid is immersed in the bulk liquid. For the prototypical metal oxide surface TiO2 rutile (110) immersed in high-purity water, density-functional theory (DFT) based molecular dynamics (MD) simulations and high-resolved in-situ Scanning Tunneling Microscopy (STM) results show for the first time that neighboring water molecules form dimers in bulk liquid.

O 60.6 Wed 16:15 MA 043

**Water structure at the TiO2/Water interface** — •Saman Hosseinpour[1], Simon J. Schmitt[1], Kirill M. Bulanin[2], and Ellen H. G. Backus[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Saint-Petersburg State University, Laboratory "Photoactive nanocomposite materials", Saint-Petersburg, Russia

Photocatalytic splitting of water using sun light for production of hydrogen as an environmentally-friendly, storable, transportable, cost efficient and abundant energy source has received much attention in the last decades. Despite the large number of studies focusing on determining and increasing the efficiency of the water splitting process on semiconducting materials especially on TiO2, fundamental questions regarding the exact mechanisms of this process at the molecular level are still not answered. For example, it is unclear what the correlation is between different interfacial structures and the efficiency of the splitting process. The main reason is the absence of an appropriate analytical tool that can specifically probe the electrode/water interface. In this study we utilized sum frequency generation spectroscopy to determine the structure and conformation of interfacial water molecules at the TiO2/bulk water interface. We compared the results with the structure of water molecules adsorbed on the electrode surface from the gas phase. The results showed that there are different water species with different strengths of hydrogen bonding adsorbed to the TiO2 surface. We will use these findings to correlate the water structure on different TiO2 surfaces to the efficiency of the water splitting process.

O 60.7 Wed 16:30 MA 043

**Solid/water interfaces from theory and experiments: the fluorite/water interface** — •Rémi Khatib[1], Ellen H. G. Backus[2], Marie-Pierre Gaigeot[3], and Marialore Sulpizi[1] — [1]Johannes Gutenberg Universität, 55128 Mainz, Germany — [2]Max Planck Institute for Polymer Research, 55128 Mainz, Germany — [3]Université d'Evry val d'Essonne, 91025 Evry, France

Vibration Sum Frequency Generation (VSFG) spectroscopy is a powerful technique which is able to provide information about surfaces and interfaces selectively excluding the centrosymmetric contribution from bulk. The experimental spectra contain information which is crucial to characterize *e.g.* solid/liquid interfaces (including hydrogen bond strength, water dipole orientation) but they call for a microscopic/molecular level interpretation.

Here we present a collaborative theoretical/experimental study which provides a new microscopic understanding of the fluorite ($CaF_2$)/water interface as function of pH. Our interest is twofold: 1) from the theoretical point of view we develop and test new tools to calculate the VSFG spectra including an ab initio description of the models; 2) from the experimental point of view, we move beyond the current state of the art providing the first Phase-Sensitive VSFG spectra for $CaF_2$/water interfaces. The results are encouraging. We provide an atomistic description of the interfaces $CaF_2$/water according to a wide range of pH. We can understand the impact of the surface termination on the water orientation and we can show in particular the importance of the electrical field due to ions in solution on the VSFG response.

O 60.8 Wed 16:45 MA 043

**Reduction of the contact resistance of bipolar plates and foils for fuel cells by atmospheric plasma treatment** — •Tatiana Fedosenko, Nicolas Wöhrl, and Volker Buck — University of Duisburg-Essen and CENIDE, Carl-Benz-Str. 199, 47057, Duisburg, Germany

Proton-exchange membrane fuel cells typically consist of two electrodes - bipolar plates, separated by an electrolyte in a form of a proton exchange membrane. In one specific implementation these bipolar plates are made from a graphite/polypropylene composite. Polypropylene (PP) is unintentionally enriched at the surface of the bipolar plates during the manufacturing, thereby significantly increasing the contact resistance between individual plates. In this study bipolar plates were treated in air plasma at atmospheric pressure while the etching time and the distance between the surface and plasma was varied. It is shown how the plasma etching removes the excess polymer matrix at the surface. Furthermore it was measured by Raman Spectroscopy that the plasma is etching the smaller nanostructured carbon from the surface, leaving larger graphitic structures. Since fewer interfaces are between the crystals, the scattering of electrons is reduced and hence the conductivity of the etched samples is higher than the conductivity of the untreated samples. The etching effect on the surface is correlated with the plasma properties as measured by optical emission spectroscopy. Atmospheric plasma treatment is demonstrated to be an efficient and scalable method to improve the properties of bipolar plates.

O 60.9 Wed 17:00 MA 043

**Substrate induced modifications of the electrocatalytic properties of Pt and Pd monolayers on Au: combined electrochemical and periodic DFT study** — •Jan Kučera[1], Sylvain Brimaud[2], Rolf Jürgen Behm[2], and Axel Gross[1] — [1]Institut für Theoretische Chemie, Universität Ulm — [2]Institut für Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm, Germany

We combine experimental electrochemical approaches with periodic density functional theory (DFT) calculations to elucidate substrate-induced modifications of noble metal electrodes. The systematic utilization of vertical-ligand effects in order to tune electrocatalytic properties of metal electrodes is often hindered by experimental problems in the practical preparation of well defined bimetallic surfaces. As shown recently, smooth and stable Pt monolayer films on Au (Pt-ML) can be realize by using CO as stabilizing agent [1]. Electrocatalytic testing confirmed that the activity of the resulting Pt-ML differs from that of Pt-bulk. Specifically, the electrooxidation of a CO adlayer on Pt-ML is shifted by about 0.2 V to higher potential compared to Pt-bulk. In contrast, comparative examination of Pd-ML and Pd-bulk systems revealed only subtle changes. Theoretical models show that the electronic structure of adsorbed CO remains practically unchanged upon the exchange of the both substrates. However, a variation of the electronic density in the surface metal layer leads to different thermodynamical stabilities of CO adlayers at high-coverages, whose impact on electrocatalyc CO oxidation activity is discussed.

[1] S. Brimaud and R. J. Behm, J. Am. Chem. Soc. **135** (2013) 11716.

O 60.10 Wed 17:15 MA 043

**Nanostructured metal arrays on Si wafers for solar fuel production** — •Simon Filser[1], Robin Nagel[2], Katrin Bickel[1], Qi Li[1], Konrad Schönleber[1], Guiseppe Scarpa[2], Paolo Lugli[2], and Katharina Krischer[1] — [1]TU München, Physik-Department E19a, James-Franck-Str., 85748 Garching, Germany — [2]TU München, Lehrstuhl für Nanoelektronik, Arcisstrasse 21,80333 München, Germany

One approach for the storage of solar energy is the photoelectrochemical conversion of the climate-wrecking $CO_2$ into hydrocarbons. It is well-known that bulk metal electrodes, e.g. gold or copper, reduce $CO_2$ at high overpotentials [1]. The product distributions containing e.g. CO, ethylene and methane sensitively depend on the electrode material and the reaction conditions. Our aim is to integrate such metal catalysts into an electrochemical solar cell to directly transform solar energy into chemical fuels. Conduction band electrons generated by light absorption in the semiconductor are transferred into the metal catalyst where they are used to reduce $CO_2$ to different products in several reaction steps. We realize such a system by structuring a silicon substrate with chessboard arrays of gold structures which can be electrochemically plated by copper which is the only material known to reduce $CO_2$ to methane and ethylene. Silicon is chosen as a substrate because its band gap is well-suited to the solar spectrum. In our experiments, we examine the $CO_2$ reduction efficiency and the product distribution of the $CO_2$ reduction on goldstructures.

[1] Y. Hori, K. Kikuchi, S. Suzuki, Chem. letters, 1985, 1695-1698.

O 60.11 Wed 17:30 MA 043

**Photoelectrochemical $CO_2$ reduction on silicon electrodes functionalized with pyridine** — •Qi Li[1], Sebastian Lindner[1], Anton Tosolini[1], Manuel Windscheid[1], Katrin Bickel[1], Simon Filser[1], Konrad Schönleber[1], Ignaz Höhlein[2], Bernhard Rieger[2], Patrick Zeller[3], Joost Wintterlin[3] und Katharina Krischer[1] — [1]Nonequilibrium Chemical Physics, Physics Department, Technical University Munich, Germany — [2]WACKER-Chair for Macromolecular Chemistry, Chemistry Department, Technical University Munich, Germany — [3]AK Wintterlin, Chemistry Department, Ludwig-Maximilians-University Munich, Germany

Solar driven $CO_2$ reduction to fuels or basic chemicals could provide an exciting new energy conversion pathway. Attempts of creating such a photochemical solar cell have to deal with the large activation barrier of $CO_2$ reduction which tends to lead to low yields and efficiencies.

Based on the reported catalytic effects of dissolved pyridine on the $CO_2$ reduction [1,2] we demonstrate that a functionalized p-Si electrode constitutes a promising interface for the photoelectrochemical $CO_2$ reduction. The interface consists of pyridine molecules which are immobilized on the Si surface via an electrografting process [3]. Modified electrodes have been characterized using electrochemical methods, STM and XPS. The grafted pyridine layer noticeably increases the electrochemical reactivity of the p-Si electrode.

[1] Barton et al., J. Am. Chem. Soc., 2008, 130, 6342-6344 [2] Keets et al., Indian J. Chem., 2012, 51A, 1284-1297 [3] Li et al., Surf. Sci., 2015, 631, 185-189

O 60.12 Wed 17:45 MA 043

**Methanol electrooxidation on UHV prepared Pt modified Ru(0001) model electrodes** — Fabian Argast, •Albert K. Engstfeld, Sylvain Brimaud, and R. Jürgen Behm — Ulm University, Institute of Surface Chemistry an Catalysis, D-89069 Ulm, Germany

The oxidation of methanol (MeOH) on bimetallic PtRu electrodes is described and widely accepted to occur via a bifunctional mechanism, where Pt provides the carbon species and Ru the oxygen species to form $CO_2$. Only recently it has been shown in a model catalyst study that bimetallic PtRu structures do not necessarily enhance the catalytic activity.(A.K. Engstfeld et al., *Angewandte Chemie Int. Ed.* **53** (2014) 12936)

We present results on the MeOH electrooxidation on Pt modified Ru(0001) electrodes. The nanostructured electrodes are prepared under ultra high vacuum (UHV) conditions via physical vapour deposition of Pt on Ru(0001) and are characterized by scanning tunnelling microscopy (STM). Subsequently they are transferred to a flow cell system attached to the UHV system for electrocatalytic investigations. We show that PtRu/Ru(0001) surface alloys and Pt island modified Ru(0001) surfaces are essentially inactive for the electrooxidation of MeOH, despite the presence of bimetallic PtRu interfaces. We discuss the influence of vertical and lateral ligand effects of the Ru(0001) acting on the Pt structures, preventing the initial dissociation of the MeOH. We also show that electrochemically restructured surfaces show an enhanced reactivity and we conclude that defect sites on the rough Pt structures are primarily responsible for the increasing activity.

## O 61: Topological Insulators: Structure and Electronic Structure (HL with DS/MA/O/TT)

Time: Wednesday 15:00–16:30 Location: ER 270

O 61.1 Wed 15:00 ER 270

**New electron states at the Bi/InAs(111) interface** — K Hricovini[1,2], J-M Mariot[3], •L Nicolaï[1,2,7], U Djukic[1], M C Richter[1,2], O Heckmann[1,2], T Balasubramanian[4], M Leandersson[4], J Sadowski[4], J Denlinger[5], I Vobornik[6], J Braun[7], H Ebert[7], and J Minár[7,8] — [1]LPMS, UCP,Cergy, France — [2]DSM-IRAMIS, SPEC, CEA-Saclay, France — [3]LCP-MR, UPMC Univ. Paris 06/CNRS, France — [4]MAX-lab, Lund Univ., Sweden — [5]ALS, Berkeley, USA — [6]EST, Trieste, Italy — [7]LMU Münich, Germany — [8]Univ. of West Bohemia, Plzeň, Czech Republic

The Bi(111) surface is a prototype system to study Rashba-split surface states. Theoretical studies [1] predicted non-trivial topological surface states appearing on a single bi-layer of Bi(111) and a more complex behaviour was suggested for a variable film thickness as a function of layer thickness [2]. This clearly indicates that the electronic properties of thin films of this material are far from being understood. Here we present combined theoretical and ARPES studies of the electronic structure of Bi(111) films grown on InAs(111). Bi growth is epitaxial and a monocrystal of very high quality is obtained after depositing several monolayers. The ARPES experiments on these samples show several new types of electronic states. It is shown that a part of these new states corresponds to novel bulk-like features. These features are well reproduced by the one-step model of photoemission as implemented in the SPR-KKR package [3].[1] M. Wada et al., Phys. Rev. B 83, 121310 (2011). [2] Z. Liu et al., Phys. Rev. Lett. 107, 136805 (2011). [3] H. Ebert, D. Ködderitzsch, J. Minár, Rep. Prog. Phys. 74, 096501 (2011).

O 61.2 Wed 15:15 ER 270

**Ultrafast currents at the surface of the topological insulator $Bi_2Se_3$** — •Lukas Braun[1], Luca Perfetti[2], Gregor Mussler[3], Markus Münzenberg[4], Martin Wolf[1], and Tobias Kampfrath[1] — [1]Fritz-Haber-Institut Berlin (MPG) — [2]Ecole Polytechnique Palaiseau — [3]Forschungszentrum Jülich — [4]Universität Greifswald

Optical excitation of topological insulators (TIs) can launch electron currents along the TI surface whose direction can be controlled by varying the polarization of the driving light [J. W. McIver *et al.*, Nat. Nanotech. **7**, 96]. So far, photocurrents have been detected with a time resolution from DC to picoseconds [C. W. Luo *et al.*, Adv. Opt. Mat. **1**, 804]. Since electrons moving through a solid typically undergo scattering on a 100fs time scale, it is highly desirable to generate and detect TI photocurrents with femtosecond time resolution in a contact-free manner. For this purpose, we excite n-doped $Bi_2Se_3$ (Fermi energy at 300meV) crystals with a femtosecond laser pulse (10fs, 1.55eV). The resulting photocurrent gives rise to the emission of a broadband terahertz (THz) electromagnetic pulse (1 to 20THz) whose transient electric field is detected by means of electro-optic sampling. We present a method that allows us to extract the transient current $j(t)$ from the measured field $E(t)$. The AC photocurrents are found to be dominated by shift currents along the surface and photo-Dember injection currents into the bulk. We finally discuss the origin of $j(t)$ and implications for the dynamics of photoexcited TI electrons.

O 61.3 Wed 15:30 ER 270

**Observation of the photon drag effect in epitaxially grown $(Bi_{1-x}Sb_x)_2Te_3$ based topological insulators** — •H. Plank[1], L. E. Golub[2], P. Olbrich[1], T. Herrmann[1], S. Bauer[1], V. V. Bel'kov[2], G. Mussler[3], J. Kampmeier[3], D. Grützmacher[3], and S. D. Ganichev[1] — [1]University of Regensburg, Regensburg, Germany — [2]Ioffe Institute, St. Petersburg, Russia — [3]Jülich Aachen Research Alliance (JARA-FIT), Jülich, Germany

We report on the observation of a terahertz (THz) radiation induced photon drag effect in epitaxially grown $(Bi_{1-x}Sb_x)_2Te_3$ three-dimensional topological insulators. We demonstrate that the excitation with polarized radiation results in a dc electric photocurrent. While at normal incidence a current arises due to the photogalvanic effect in the surface states, caused by asymmetrical scattering of Dirac fermions [1], at oblique incidence it is overweighted by the trigonal photon drag effect. The currents are generated in $n$- and $p$-type $(Bi_{1-x}Sb_x)_2Te_3$ samples with various composition applying linearly and circularly polarized THz radiation. Results are analysed in terms of phenomenological theory and microscopic model based on transfer of photon momentum to free carriers resulting in an asymmetric distribution of electrons (holes) in k-space. Our analysis describes well all experimental findings including e.g. variation of the angle of incidence, radiation polarization and frequency. The observed trigonal photon drag and photogalvanic effect provide an opto-electronic method to study high frequency transport of Dirac fermions even at room temperature.

[1] P. Olbrich *et al.*, Phys. Rev. Lett. **113**, 096601(2014)

O 61.4 Wed 15:45 ER 270

**Cyclotron Resonance Induced Spin Polarized Photocurrents in Surface States of a 3D Topological Insulator** — •K.-M. Dantscher[1], D.A. Kozlov[2], Z.D. Kvon[2], P. Faltermeier[1], M. Lindner[1], P. Olbrich[1], C. Zoth[1], G.V. Budkin[3], S.A. Tarasenko[3], V.V. Bel'kov[3], N.N. Mikhailov[2], S.A. Dvoretskii[2], D. Weiss[1], and S.D. Ganichev[1] — [1]University of Regensburg, Regensburg, Germany — [2]Institute of Semiconductor Physics, Novosibirsk, Russia — [3]Ioffe Institute, St. Petersburg, Russia

We report on the observation of cyclotron resonance (CR) induced photocurrents excited by cw radiation, with frequencies of 2.54, 1.62 and 0.69 THz in a 3D topological insulator based on 80 nm strained HgTe films. To support the complex study, including optical, optoelectronic and electron transport experiments, various sample designs have been used. The measurements were done in a wide range of temperatures (1.6 to 120 K). We demonstrate that the photocurrent is generated in the topologically protected surface states. Studying the resonance response in the gated samples we examined the behaviour of the photocurrent and Dirac fermions cyclotron mass upon variation of Fermi energy. For large gate voltages we also detected CR in the bulk HgTe with the mass about two times larger than that obtained for the surface states. Based on this data we develop a microscopic theory of the effects and show that the asymmetry of light-matter coupling in the system of Dirac fermions subjected to an external magnetic field causes the electric current to flow. We show that the current is spin polarized.

O 61.5 Wed 16:00 ER 270

**Response of the topological surface state to surface disorder in $TlBiSe_2$** — Florian Pielmeier[1], •Andreas Eich[2], Gabriel Landolt[3,4], Bartosz Slomski[3,4], Julian Berwanger[1], Alexander A. Khajetoorians[5], Jens Wiebe[2], Roland Wiesendanger[2], Jürg Osterwalder[3], Franz J. Giessibl[1], and J. Hugo Dil[3,4,6] — [1]Institute of Experimental and Applied Physics, Universität Regensburg, D-93040 Regensburg, Germany — [2]Department of Physics, University of Hamburg, Jungiusstrasse 11, D-20355 Hamburg, Germany — [3]Physik-Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland — [4]Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland — [5]Institute of Molecules and Materials, Radboud University, 6500 GL Nijmegen, Netherlands — [6]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

By a combination of experimental techniques we show that the topmost layer of the topological insulator $TlBiSe_2$ as prepared by cleavage is formed by irregularly shaped Tl islands. No trivial surface states are observed in photoemission, which suggests that these islands can not be regarded as a clear surface termination. The topological surface state is, however, clearly resolved in photoemission experiments. This is interpreted as a direct evidence of its topological self-protection and shows the robust nature of the Dirac cone like surface state.

O 61.6 Wed 16:15 ER 270

**Wet etch process for HgTe nanostructure fabrication** — •Kalle Bendias[1], Erwann Bocquillon[1], Alex Hughes[2], Christoph Brüne[1], Hartmut Buhmann[1], and Laurens W. Molenkamp[1] — [1]EP3, Physikalisches Institut, Universität Würzburg — [2]Department of Physics, Stanford University

Topological insulators (TI) are a new class of material with outstanding spin properties. Grown in 2d quantum wells HgTe does not only host Quantum Spin Hall edge channels [1][2], but also a giant Rashba splitting [3]. Both could lead to numerous applications in spintronic devices. In order to perform experiments such as spininjection, -probing [3] or quantum point contact collimation [4] a high carrier mobility and i.e. a long ballistic mean free path is essential.

The conventional processing method using ion milling to define the structure strongly affects these surface properties on small microstructures. In this talk the development and results of an alternative lithography etch method using KI:I:HBr as wet etchant are presented. Measurements on microstructures will be shown, indicating comparable mobilities on big and small structures.

[1] Markus König et al., Journal of the Physical Society of Japan 77.3 (2008), S. 031007.

[2] C. Brüne et al., Nature Physics 6.6 (2010), S. 448-454.

[3] J. Hinz et al., Semiconductor science and Technology 21.4 (2006), S 501-506.

[4] L.W. Molenkamp et al., Phys. Rev. B 41, 1274 (1990)

## O 62: Graphene: Applications, Luminescence and Spin Relaxation (HL with O/TT)

Time: Wednesday 16:45–18:45 Location: ER 270

O 62.1 Wed 16:45 ER 270

**Fabrication and Growth of Three-dimensional Graphene Electrodes with Controllable Pore Size** — •Simon Drieschner, Michael Weber, Evangelos Makrygiannis, and Jose A. Garrido — Walter-Schottky-Institut, Physik Department, TU München, Am Coulombwall 4, 85748 Garching

Three-dimensional graphene-based electrodes combine graphene's unique properties like high conductivity, chemical inertness, and mechanical stability with a high surface to volume ratio, which could be of great interest for energy applications. However, tuning the pore size of 3D graphene networks is a non-trivial challenge, since the growth of graphene depends on the shape and structure of the metal substrate. Here we demonstrate the fabrication of 3D electrodes by using metal powder providing an interconnected scaffold which serves as substrate for the growth of graphene by chemical vapor deposition. The pore size distribution is shown to be controlled by the used metal particles and the growth temperature. After wet chemical etching of the metal catalyst, a freestanding and stable graphene foam of low mass and high crystalline crystal quality as confirmed by Raman spectroscopy is obtained. Cyclic voltammetry and electrochemical impedance spectroscopy measurements are used to confirm its excellent electrochemical properties. Our work highlights the great potential of these 3D graphene electrodes for energy storage and sensing applications.

O 62.2 Wed 17:00 ER 270

**Graphene microelectrode arrays for the electrochemical detection of neurotransmitters** — •Martin Lottner[1], Luis Batista-Pires[2], and Jose A. Garrido[1] — [1]Walter Schottky Institut, TU München, München, Deutschland — [2]Catalan Institute of Nanoscience and Nanotechnology, ICN2, Barcelona, Spain

Graphene has great potential for use as stimulation and sensing material in neural and cardiac implants. Its flexibility and chemical stability anticipate a good biocompatibility, which cytotoxicity studies have underlined. It is transparent to visible light and non-magnetic, which allows for unperturbed optical stimulation and post-implantation MRT imaging. In this contribution, we present graphene microelectrode arrays for the electrochemical detection of neurotransmitters. Vacancy defects were introduced by ozone exposure and growth conditions were varied to increase double layer content of the electrodes. The modifications were validated using Raman spectroscopy. Cyclic voltammetry studies show an electrochemical window of about 1V. Ferricyanide redox studies have been performed upon increasing defect density and double layer content, to investigate the transition from macro- to microelectrode behaviour. Further, a sensitivity for the detection of norepinephrine and dopamine below 1nM is demonstrated. This study shows that modified CVD graphene microelectrodes can be used for highly sensitive detection of neurotransmitters. Taking advantage of the high interfacial capacitance and large electrochemical window of graphene electrodes, we will discuss their use for safe extracellular stimulation.

O 62.3 Wed 17:15 ER 270

**Structural study of mono- and bilayer graphene nanoribbons directly grown on SiC(0001)** — •Lauren A. Galves, Timo Schumann, João Marcelo J. Lopes, and Henning Riechert — Paul-Drude-Institut für Festkorperelektronik, 10117 Berlin, Germany

Graphene nanoribbons (GNR) are very promising for nanoelectronics, since they possess unique electronic properties which are dependent on their width, edges, as well as number of graphene layers [1-2]. Therefore, achieving the controlled and high-quality synthesis of GNRs is anticipated to be of great importance. One of the methods which show great potential is the growth of GNRs on surface facets of SiC(0001) by the graphitization method [3]. In this contribution we report on the controlled growth and characterization of epitaxial mono- and bilayer GNRs on SiC(0001) surfaces. They were synthesized by utilizing the surface graphitization method at high temperatures and a straightforward air annealing (for bilayer GNRs) [4]. The influence of the surface step heights (i.e. facet sizes) on the ribbon growth and properties was analyzed. A correlation between steps heights and ribbons width was established. The nanostructures were analyzed by AFM height and phase contrast images. This allowed the determination of the SiC surface morphology as well as ribbons width. Raman spectroscopy was employed to gain information about the thickness of the GNRs (i.e. mono- or bilayer graphene) and their preferential edge type.

[1] V. Barone et al., Nano Lett. 6, 2748 (2006); [2] T.S. Li et al., Eur. Phys. J. 64, 73 (2008); [3] M. Sprinkle et al. Nat. Nanotechnol. 5, 727 (2010); [4] M.H. Oliveira Jr. et al., Carbon 52, 83 (2013).

O 62.4 Wed 17:30 ER 270

**Correlation of the crystallite sizes and D band frequency of non-graphitic carbons** — •Dominique B. Schuepfer[1], Kristin Faber[2], Bernd M. Smarsly[2], Roman V. Yusupov[3], and Peter J. Klar[1] — [1]Institute of Experimental Physics I, Justus-Liebig-University Giessen, Germany — [2]Institute of Physical Chemistry, Justus-Liebig-University Giessen, Germany — [3]Institute of Physics, Kazan Federal University, Russia

Raman spectroscopy is often used to determine the crystallite size $L_a$ of non-graphitic carbons by taking into account the intensity ratio of the defect-induced D band and the G band. We present an analysis of soft pitches via Raman spectroscopy in comparison to wide-angle X-ray spectra revealing discrepancies for $L_a$. Significant errors can be caused by known issues, for example the superposition of certain bands while estimating the intensities. Therefore, we introduce an alternative approach: An analysis of the D band revealed a correlation between its position and the crystallite size in the range of crystallite sizes less than 2 nm. The Raman shift significantly increases for smaller $L_a$ using an excitation wavelength in the visible range. UV light yields the opposite behavior of the D band position, probably because of resonant absorption processes. To further characterize the samples in different $L_a$-ranges ($L_a < 2\,\mathrm{nm}$ and $L_a > 2\,\mathrm{nm}$) electron paramagnetic resonance spectroscopy (EPR) has been carried out. Isotropic shaped EPR spectra are observed up to a crystallite size of 2 nm and samples containing crystallite sizes larger 2 nm show anisotropic signals. This behavior correlates with the detected Raman shift.

O 62.5 Wed 17:45 ER 270

**Ultrafast photocurrents in back-gated graphene** — •Felix Schade, Andreas Brenneis, Jose A. Garrido, Simon Drieschner, and Alexander W. Holleitner — Walter Schottky Institut and Physik-Department, Technische Universität München, Am Coulombwall 4a, Garching, Germany

We present picosecond time-resolved photocurrent measurements of back-gated CVD grown graphene on sapphire substrates. We examine the optoelectronic dynamics with respect to (i) the thermal coupling of graphene to its environment [1], (ii) different doping levels by tuning the back-gate voltage with respect to the Dirac point, and (iii) thermoelectric, photovoltaic as well as bolometric contributions. To this end, the graphene sheets are contacted by a THz-stripline circuit, and the ultrafast response is read-out by an Auston-switch [2]. The back-gate is separated from the graphene by the help of ALD-grown sapphire.

The ERC grant NanoREAL is acknowledged.

[1] A. Brenneis, et al., Nature Nanotechnology, DOI: 10.1038/NNANO.2014.276 (2015). [2] L. Prechtel, et al. Nature Comm. 3, 646 (2012).

O 62.6 Wed 18:00 ER 270

**Coherent and Incoherent Photoluminescene from Photoexcited Graphene** — •Torben Winzer[1], Richard Ciesielski[2], Matthias Handloser[2], Alberto Comin[2], Achim Hartschuh[2], and Ermin Malic[1] — [1]Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Germany — [2]Department Chemie, Ludwig Maximilians Universität München, Germany

Based on a microscopic theory and experimental measurements we investigate the ultrafast photoluminescence arsing from photo-excited graphene. Our calculations, performed within the density matrix formalism, allow for energy- and time-resolved insights into the radiative processes where two distinct microscopic mechanisms are distinguished: Beside the incoherent photoluminescence, which is driven by recombination of excited carriers, we find a coherent contribution induced by the microscopic polarization [1]. The incoherent spectrum mainly depends on the excitation strength. In contrast, the coherent photoluminescence spectrally shifts with the excitation energy, which is demonstrated for the first time and confirmed by our measurements. [1] T. Winzer, R. Ciesielski, M. Handloser et al., arXiv:1411.0531v1 (2014)

O 62.7 Wed 18:15 ER 270

**Polarised Hot Carrier Photoluminescence in Graphene** — •Thomas Danz, Andreas Neff, Reiner Bormann, Sascha Schäfer, and Claus Ropers — 4th Physical Institute, University of Göttingen, Göttingen, Germany

The thermalisation of photogenerated hot charge carriers in graphene leads to photoluminescence at wavelengths far away from that of the exciting pump laser [1,2]. To date, no polarisation properties of the photoluminescence have been reported, although recent numerical simulations show a strong anisotropy of the underlying relaxation processes in graphene [3]. This is in agreement with the results of transient pump-probe measurements showing a dependence of the transmissivity on the angle between pump and probe polarisations [4]. Here, we present polarisation- und time-resolved two-pulse excitation photoluminescence measurements with sub-30fs ultrashort laser pulses. We demonstrate an anisotropic nature of the emitted photoluminescence and use these findings to discuss complementary insights into the ultrafast carrier response in graphene.

[1] C. H. Lui *et al.*, Phys. Rev. Lett. **105**, 127404 (2010)
[2] W. Liu *et al.*, Phys. Rev. B. **82**, 081408 (2010)
[3] E. Malic *et al.*, Appl. Phys. Lett. **101**, 213110 (2012)
[4] M. Mittendorff *et al.*, Nano Lett. **14**, 1504 (2014)

O 62.8 Wed 18:30 ER 270

**Spin Relaxation in Graphene** — •Frank Ortmann[1], Dinh. V. Tuan[2], David Soriano[2], Sergio O. Valenzuela[2,3], and Stephan Roche[2,3] — [1]Institute for Materials Science and Dresden Center for Computational Materials Science, TU Dresden, Germany — [2]ICN2 Barcelona, Spain — [3]ICREA, Barcelona, Spain

Spin polarization of electrons in graphene has been under great attention in recent years due to intrinsically small spin-orbit coupling and hyperfine interaction and high carrier mobilities. However, experimental spin-relaxation times are 3-4 orders of magnitude too short compared to theoretical predictions. Such discrepancy, together with contradictory proposals for spin-relaxation mechanisms, triggered a debate about its behavior in clean and/or defective graphene.

We observe an intrinsic spin-dephasing mechanism in graphene that is most strongly impacting the Dirac point, which can be enhanced by the adsorption of heavy ad-atoms.[1] The extracted spin relaxation times ($\tau_s$) from our simulations show good agreement with experimentally observed energy dependencies of $\tau_s$.

[1] D. V. Tuan, F. Ortmann et al. Nature Phys. 10, 857 (2014).

# O 63: 2D Materials beyond Graphene

Time: Wednesday 18:15–21:00 Location: Poster A

O 63.1 Wed 18:15 Poster A

**XPS study of mecanical exfoliated molybdenum disulphide** — •Philipp Espeter, Dominique Handschak, Christoph Keutner, Peter Roese, Ulf Berges, and Carsten Westphal — Experimentelle Physik I/DELTA, TU Dortmund, Otto-Hahn-Straße 4, 44221 Dortmund, Germany

The transition metal dichalcogenide molybdenum disulphide ($MoS_2$) belongs to the layered materials with a strong in-plane and weak out-of-plane bonding. Thinning bulk $MoS_2$ down to monolayer thickness influences its electronic proporties. $MoS_2$ monolayer with direct bandgap of about $1,9$ eV is a promising candidate for applications in electronic and opto-electronic devices. We report on the results of XPS investigations of mechanical exfoliated molybdenum disulphide conducted at the PGM undulator beamline 11 of Dortmund's synchrotron source DELTA. Vacancy formation due to the exfoliation process is monitored as well as the occupation of sulfur lattice sites and vacancies by oxygen.

O 63.2 Wed 18:15 Poster A

**Unoccupied electronic states in silicene nanoribbons on Ag(110)** — •Luca Bignardi[1], Fabian Kleimeier[1], Mohammed Rachid Tchalala[2], Hamid Oughaddou[2,3], and Helmut Zacharias[1] — [1]Physikalisches Institut, Westfälische Wilhems-Universität, Wilhlem-Klemm-Str. 10, 48149 Münster, Germany — [2]Institut des Sciences Moléculaires d'Orsay, ISMO-CNRS, Bâtiment 210, Université Paris-Sud, 91405 Orsay, France. — [3]Département de Physique, Université de Cergy-Pontoise, 95000 Cergy-Pontoise, France

In the last few years, silicene, a honeycomb 2D lattice of Si atoms, has emerged as a potential candidate for new-generation electronic devices, with the advantage of being compatible with existing semiconductor technologies. A full technological exploitation of this material requires a comprehensive characterisation of its occupied and unoccupied electronic structure.

Deposition of silicon on Ag(110) single-crystals is known to result in the formation of self-assembled silicene nanoribbons, showing a (2x5) overlayer. In this contribution, we present an investigation of the unoccupied electronic states of this interface. By means of inverse photoemission spectroscopy (IPE), we identify the electronic empty states due to the silicene nanoribbons. Moreover, we provide a description of the modifications induced by the Si overlayer on the unoccupied states of the metallic substrate.

O 63.3 Wed 18:15 Poster A

**Structural Analysis of $MoS_2$ on Au(111) by X-ray Standing Waves** — •caio silva[1], ferdinand farwick zum hagen[1], wouter jolie[1], christoph schlueter[2], tien-lin lee[2], and carsten busse[1] — [1]II. Physikalisches Institut, Universität zu Köln, Germany — [2]Diamond Light Source, United Kingdom

The present work clarifies important aspects of the structure of $MoS_2$ epitaxially grown on Au(111) by physical vapor deposition. The results are very significant to understand the interaction between transition-metal dichalcogenides (TMDCs) and metallic substrates. TMDCs present fascinating electronic, optical and catalytic properties. Remarkable differences are found in the single-layered TMDCs in contrast to the bulk material, e. g. transition from indirect to direct band gap and spin-orbit-induced spin splitting due to the symmetry loss. Determination of the structure down to the atomic level is crucial in understanding the correlation between these properties and the morphology.

X-ray standing waves (XSW) has been used to study the average distances between the single-layer S-Mo-S to substrate surface. Chemical analysis was performed by means of high-resolution x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) was used to elucidate the sample quality and the in-plain structure of $MoS_2$/Au(111).

O 63.4 Wed 18:15 Poster A

**Epitaxial growth of $MoS_2$ monolayers on graphene/SiC** — •Maciej Dendzik[1,2], Jill Miwa[1,2], Soren Ulstrup[1,2], Signe Gronborg Sorensen[2], Antonija Grubisic Cabo[1,2], Marco Bianchi[1,2], Matteo Michiardi[1,2], Jeppe Vang Lauritsen[2], and Philip Hofmann[1,2] — [1]Aarhus University, Department of Physics and Astronomy, Aarhus, Denmark — [2]Aarhus University, Interdisciplinary Nanoscience Center, Aarhus, Denmark

Monolayers of transition metal dichalcogenides (TMDCs) are a novel class of materials which recently attracted considerable attention due to their interesting physical properties and possible applications in fields of electronics and spintronics. Nevertheless, the growth of high quality single-layered films of TMDCs still remains a challenge. Here we present an in situ physical vapour deposition approach of growing $MoS_2$ monolayers. Intermediate stages of the process are characterised by means of scanning tunneling microscopy, providing an insight into the growth mechanism. Grown samples are further investigated by angle resolved photoemission and compared with $MoS_2$ monolayers grown on Au(111). The results indicate high quality and large coverage of the monolayer.

O 63.5 Wed 18:15 Poster A

**Growth and characterization of thin MoS2 layers by CVD** — •Gregor Nordheim, Martina Wanke, Adrian Schütze, Florian Speck, and Thomas Seyller — Institut für Physik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany

MoS2 is a two-dimensional layered material like graphene, with a hexagonal structure and weak van der Waals forces between the layers. In contrast to graphene, MoS2 has a band gap which makes it an interesting material for electronic and optoelectronic applications. Chemical vapor deposition (CVD) is a promising approach to synthesize uniform, high quality monolayer and few layer MoS2 films on various substrates such as silicon oxide, sapphire [1-3].

We report on the growth and characterization of MoS2 using a custom build CVD setup. Epitaxial monolayer graphene and the buffer layer on SiC(0001) synthesized by sublimation growth in Ar [4] were used as substrates. The samples were analyzed by X-ray photoelectron spectroscopy (XPS) in order to obtain information about their chemical composition and the thickness of the layers. In addition, the MoS2 layers were studied by atomic force microscopy (AFM).

[1] Y. Yu et al., Scientific Rep. 3 (2013) 1866. [2] M.R. Laskar et al., Nat. Mater. 102 (2013) 252108. [3] Y.-H. Lee et al., Nano Lett. 13 (2013) 1852. [4] K.V. Emtsev et al., Nat. Mater. 8 (2009) 203.

## O 64: New Methods

Time: Wednesday 18:15–21:00 Location: Poster A

O 64.1 Wed 18:15 Poster A

**Transfer chamber from electrochemical cell to UHV** — •Georgijs Bakradze[1], Reiner Krause[1], Dirk Vogel[2], Beibei Pang[2], Andreas Erbe[2], Martin Stratmann[2], Michael Rohwerder[2], and Karina Morgenstern[1] — [1]Ruhr-University in Bochum, Faculty of Chemistry and Biochemistry, Bochum — [2]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

We describe a custom-built transfer chamber dedicated to the transfer of electrodes from the liquid phase into the UHV. The transfer chamber allows to combine several surface analytical techniques, and, thus, to obtain valuable insights into structure and microscopic properties of the electrochemical double layer region on electrodes. The transfer chamber can be coupled to an experimental cluster having facilities for: (i) electrochemical preparation (allowing emersion from electrolyte solution under a constant potential into a controlled humid atmosphere), (ii) in situ electrochemical measurements (Kelvin probe), (iii) surface analysis (ambient-pressure XPS), and (iv) optical characterisation (FTIR spectroscopy). The transfer chamber allows the sample transfer without breaking the UHV conditions directly into a UHV chamber having facilities for microstructural characterisation (low-temperature STM). Efficiency and performance of the setup will be tested on the Au(111) surface, which will be prepared under controlled electrode potentials and relative humidity conditions, revealing the influence of ions on the structure of condensed water layers in realistic electrochemical environments.

O 64.2 Wed 18:15 Poster A

**Space Charge Corrected Electron Momentum Microscope for Time-Resolved Hard X-ray Photoemission at the European XFEL** — •Markus Scholz[1], Gerd Schönhense[2], Yves Acremann[3], Katja Medjanik[2], Nils Gerken[1], and Wilfried Wurth[1,4] — [1]Physics Department and Center for Free-Electron Laser Science, Universität Hamburg, D-22761 Hamburg, Germany — [2]Institut für Physik, Johannes Gutenberg-Universität, D-55099 Mainz, Germany — [3]Department Physik, ETH Zürich, CH-8093 Zürich, Switzerland — [4]DESY Photon Science, D-22607 Hamburg, Germany

Photoelectron spectroscopy at synchrotron radiation sources is a well-established technique to study static electronic properties of materials. To overcome limitations in information depth recently hard x-ray photoemission (HAXPES) has been developed as a powerful tool to study electronic structure of the bulk or of buried interfaces. With the new hard x-ray free-electron lasers time-resolved HAXPES will enable dynamic studies of bulk and interface electronic structure down to the femtosecond regime. We will set up a HAXPES endstation for European XFEL, which will be based on a novel electron momentum microscope. To utilize the high-brilliance and ultrashort pulses, we developed new strategies to minimize space-charge induced effects in photoelectron spectroscopy experiments. This project is funded by FSP 302 - FEL, 05K13GU3 and 05K13UM2.

O 64.3 Wed 18:15 Poster A

**Setup for time-resolved STM-induced luminescence** — •Michael Mohr and Richard Berndt — IEAP, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

Scanning tunneling microscopy (STM) can be used to induce light emission. The correlation between the arrival times of different STM-induced photons at a detector can be measured with time-correlated single photon counting (TCSPC). These correlation-measurements can provide information about the time scale of rapid processes in the tunnel-junction that influence the STM-induced light emission. These can be, e. g., charge fluctuations on molecules or the fluorescence of molecules themselves. We present a setup for such TCSPC-measurements with a resolution down to the sub-nanosecond range.

O 64.4 Wed 18:15 Poster A

**Surface properties of $CeO_2$(111) within kinetic Monte Carlo simulations** — •Stefano Mattiello[1], Stefan Kolling[1], Marvin Lee Gusen[2], Christian Heiliger[2], and Herbert Oven[3] — [1]Technische Hochschule Mittelhessen, Gießen, Germany — [2]I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Germany — [3]Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Germany

Recently Kullgren and coworkers claim a incompatibility between density functional theory (DFT) and experimental results of Esch about the density and structure of the vacancies for the surface (111) of $CeO_2$ under UHV condition and they assume that the claimed oxygen vacancies are in fact fluorine impurities. In order to examine the possibility of a significant fluorine contamination we perform a twice investigation of the ceria surface within kinetic Monte Carlo simulations. Firstly, assuming the formation of vacancies and neglecting fluorine impurities we find that this possibility is not totally incompatible with the relevant DFT results, if microscopic dynamics is considered. Secondly, we investigate the competition between fluorine and oxygen vacancies finding a direct correlation between fluorine and vacancies concentration. This may suggest, that the absence of vacancies and the presence of fluorine only should be unlikely.

O 64.5 Wed 18:15 Poster A

**An approximative method to tackle the modeling of thin film IR spectra** — •Jochen Vogt — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

A vibrational analysis of molecular adlayers based on the calculation of the full Hessian within DFT or other *ab initio* theory is frequently a computationally expensive task. In order to tackle the modeling of IR spectra of thin films with large unit cells, an approximative method is investigated. It is based on the first principles calculation of the Hessians and dipole derivative tensors of individual molecular entities or small clusters using large basis sets. These partial Hessians are used in the second step to reconstruct the full Hessian. The off-diagonal elements representing the intermolecular vibrational coupling are built from the partial dipole derivative tensors assuming that dipole-dipole interaction is the leading coupling term. The inclusion of other types of interaction, however, is possible. First results indicate that calculated Davydov splittings due to dynamic dipole-dipole coupling are larger than observed in experiments and thus require the inclusion of a suitable scheme of electrostatic damping [1].

[1] J. Salas et al., J. Chem. Phys. 133 (2010), 234101

O 64.6 Wed 18:15 Poster A

**Characterizing Measurements at the U55-Beamline at DELTA** — •Ulf Berges[1,2], Christoph Keutner[1,2], and Carsten Westphal[1,2] — [1]DELTA/ZfSy, TU Dortmund, Maria-Goeppert-Mayer Str. 2, 44221 Dortmund — [2]Experimentelle Physik Ib, TU Dortmund, Otto-Hahn-Str.4, 44221 Dortmund

A VUV-Beamline for linearly polarized synchrotron radiation within the energy range between 55 eV and 1500 eV is operated at DELTA, a synchrotron radiation facility at the University of Dortmund, Germany. The beamline is mostly used to perform XPS- and XPD-experiments with an energy resolution of about $\frac{E}{\Delta E} = 3000$ and a photon flux of about 1e13 photons/s/100mA in the routine mode. New measurements characterizing the present status concerning energy resolution and photon flux of this beamline will be presented. The improved instrumentation of the beamline will be discussed, too.

O 64.7 Wed 18:15 Poster A

**Investigation of glass degradation by X-ray Photoelectron spectroscopy** — •Stephanie Reiss[1], Stefan Krischok[1], Sabine Urban[2], and Edda Rädlein[2] — [1]Institut für Physik and Institut für Mikro- und Nanotechnologien, TU Ilmenau, PF 100565, 98684 Ilmenau, Germany — [2]Institut für Werkstofftechnik, TU Ilmenau, Postfach 100565, 98684, Ilmenau, Germany

Changes in the surface chemical composition during glass degradation were studied by X-ray photoelectron spectroscopy. The samples were manufactured in a float process in which the glass melt is formed on a liquid tin bath leading to a surface with tin enrichment (bath side) and one without (air side). Both sides of fresh and aged glasses were analyzed. The evaluation of the measured O1s core level spectra reveals two components: one at 532eV related to bridging oxygen (BO) linking two silicons and one at 530.3eV related to negatively charged non-bridging oxygen (NBO) where one silicon is substituted by a positive alkali ion. The changes in the ratio of these O1s components give insight in the progress of network dissolution. For the bath side the BO/NBO-ratio decreases from 10.8 to 2.2 after aging. While the fresh sample's air side shows clearly the BO and NBO component with a ratio of 4.9, the seasoned air side exhibits only one signal. Its FWHM is wider than for each single component of the fresh sample and its binding energy lies with 531.6eV in between them leading to the conclusion that both components are almost equal in intensity and hence superimpose to each other. The stronger degradation of the air side hence points to an anticorrosive effect of tin.

## O 65: Oxides and Insulators

Time: Wednesday 18:15–21:00 Location: Poster A

O 65.1 Wed 18:15 Poster A

**Adsorption behaviour of 2H-Tetraphenylporphyrin on rutile TiO2(110): a room temperature STM investigation** — •Martin Drost, Fan Tu, Florian Vollnhals, Hans-Peter Steinrück, and Hubertus Marbach — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The controlled fabrication of well-defined nanostructures can be addressed by the self-assembly of functional molecules on surfaces. In this regard, we investigate the adsorption behavior of 2H-tetraphenylporphyrin (2HTPP) as a prototype functional molecule on rutile TiO2(110) with scanning tunneling microscopy (STM) mainly at room temperature. A coverage dependent study reveals that at low coverages the 2HTPPs are mainly observed as isolated individual molecules in registry with the Ti-rows of the substrate. With increasing coverage, more and more loosely ordered molecular domains are found. Interestingly, upon moderate heating a significant restructuring of the adsorption system is observed, which yield to the formation of well-ordered supramolecular assemblies of the porphyrins. The specific contributions of molecule-substrate and molecule-molecule interactions will be discussed.

This work was funded by the DFG through grant MA 4246/1-2, research unit FOR 1878/funCOS; and the Excellence Cluster "Engineering of Advanced Materials" granted to the FAU Erlangen-Nürnberg.

O 65.2 Wed 18:15 Poster A

**The Role of H-Termination on the ZnO (10$\bar{1}$0) Surface** — •Maria E. Stournara[1], Oliver T. Hoffman[1,2], Patrick Rinke[1,3], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Institut für Festkörperphysik, Technische Universität Graz, Graz, Austria — [3]COMP/Department of Applied Physics, Aalto University School of Science, Aalto, Finland

The optical and electronic properties of H-terminated ZnO surfaces play a significant role for the electronic and excitonic states in hybrid inorganic/organic semiconductor technologies. As the intrinsic presence of H affects the properties of the ZnO surface even at infinitesimally low concentrations, a careful evaluation of the stable H-surface configurations is necessary to understand the effect of H adsorption on the surface electronic structure. To elucidate the role of the latter we perform density-functional theory PBE-vdW$^{MBD}$ calculations for various H-concentrations. We find that H adsorption results in a complex behavior with a competition between hydrogen adsorption on surface O and surface Zn atoms, even at low H concentrations. This is responsible for a diverse surface electronic structure, where OH-bonding leads to a metallic behavior, whereas a semiconducting state is restored for adsorption on Zn-sites. Our results indicate that the former is favored at infinitesimally low coverage, whereas the latter is displayed for half-monolayer concentrations where H is adsorbed on neighboring Zn- and O- sites, forming ZnO-"stripes". In light of this, we evaluate intermixed site-motifs via a lattice gas hamiltonian (LGH) to describe H adsorption for a wide range of concentrations.

O 65.3 Wed 18:15 Poster A

**adsorption of PTCDA on KCl and NaCl(100) surfaces** — Hazem ALdahhak, •Wolf Gero Schmidt, and Eva Rauls — Universität Paderborn, Warburger Str. 100, 33098 Paderborn

The adsorption of PTCDA (C24H8O6) on metal substrates has for a long time been used as model system for understanding molecular self-assembly. Ionic crystals as substrate provide the additional possibility to study the molecular properties with little perturbation by substrate screening or strong substrate-adsorbate bonds [1]. Here, we present density-functional theory calculations on the adsorption and adsorbate-substrate interaction between PTCDA and planar and as well as stepped NaCl as well as KCl surfaces. The adsorption is dominated by van-der-Waals and electrostatic forces. This lead to a site-specific adsorption of the molecule on the surface, possibly resulting in commensurate long-range ordered structures [2]. The influence of the substrate and bonding mechanism on the molecular electronic structure as well as the molecular vibrations is investigated in detail and compared with the experimental data available [3-5]. Our calculations for different kinds of step-edge defects show the importance of these surface defects for initiating the adsorption of organic molecules on ionic surfaces.

[1] V. W. Henrich, P.A Cox, The surface of metal Oxides, vol.1, Cambridge University Press, 1996 [2] H. Aldahhak et al, Surf. Sci. 617, 242-248, 2013. [3] Que et al., J. Phys. Chem. C (in Press). [4] H Karacuban et al. Nanotechnology, 22 (29), 295305, 2011. [5] A. Paulheim et al., Phys. Chem. Chem. Phys.15 (2013) 4906.

O 65.4 Wed 18:15 Poster A

**Improving ceramic–polymer interface stability: Ab-initio study of benzoic acid on TiO$_2$** — •Wolfgang Heckel, Axel Dreyer, Gerold A. Schneider, and Stefan Müller — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

In order to prepare functional hybrid composites with desired mechanical properties, the control of the interface stability is crucial. For a strong binding, carboxylic acids (CA) as a linker between ceramics and polymer are often used and extensively studied in the past.

Our results of a thermogravimetric analysis give rise to the assumption, that CA with an aromatic side chain can still improve the binding energy compared to CA with simple aliphatic ones. We present a corresponding DFT analysis of benzoic acid on both, anatase and rutile TiO$_2$ surfaces. To describe properly the attractive interaction of adsorbing molecules among each other, our results show clearly the requirement of applying an exchange correlation functional with van der Waals correction. On all surfaces, the resulting binding energies increase up to about 0.2 eV per molecule compared to CA with aliphatic side chains.

Supported by DFG, SFB 986, projects A4 and A6.

O 65.5 Wed 18:15 Poster A

**Fine structure in infrared spectra of high quality CO$_2$ ultrathin films on the NaCl(100) surface** — •Jochen Vogt — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

The splitting of the $\nu_3$ asymmetric stretch mode into a longitudinal optical (LO) and a transverse optical mode (TO) is a well known feature of CO$_2$ ice thin films [1]. In new experiments, high quality ultrathin films were grown by exposure of a saturated monolayer CO$_2$-p(2×1)/NaCl(100) to additional CO$_2$ at 40 K. Films prepared in this way appear to be highly ordered over a wide spatial range and show additional fine structure between the TO and LO modes. A mode at 2348.9 cm$^{-1}$ is observed in p- and s-polarized spectra and does not shift with increasing film thickness. According to a simulation of the film spectra based on vibrational exciton theory, this mode can be assigned to a collective vibrational excitation of molecules near the interface with the substrate. Additional peaks e. g. at 2359.1 cm$^{-1}$ and 2363.8 cm$^{-1}$ show up and disappear again during film growth. These modes can be assigned to resonant excitation of domains with unique film thickness. [1] O. Berg, R. Disselkamp, G. E. Ewing, Surf. Sci. 277 (1992), 8.

O 65.6 Wed 18:15 Poster A

**Adsorption of H$_2$O at Cleaved Sr$_{n+1}$Ru$_n$O$_{3n+1}$ and Ca$_3$Ru$_2$O$_7$ (001) Surfaces** — •Daniel Halwidl[1], Bernhard Stöger[1], Florian Mittendorfer[1], Wernfried Mayr-Schmölzer[1], Zhiming Wang[1], David Fobes[2], Jin Peng[2], Zhiqiang Mao[2], Michael Schmid[1], Josef Redinger[1], and Ulrike Diebold[1] — [1]Institute of Applied Physics and Center for Computational Materials Science, Vienna University of Technology, Vienna, Austria — [2]Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

Complex ternary perovskite oxides are increasingly used in solid oxide fuel cells and catalysis [1]. Therefore it is highly desirable to obtain a better understanding of their surface chemical properties. We use low-temperature scanning tunneling microscopy and DFT to investigate the adsorption of $H_2O$ on $Sr_{n+1}Ru_nO_{3n+1}$ (n=1,2) and $Ca_3Ru_2O_7$. Dosing water at 105 K on the clean surfaces leads to dissociation of the molecule forming an $(OH)_{ads}$ group and an $O_{surf}H$ group. While no long-range diffusion was observed at 78 K on neither $Sr_{n+1}Ru_nO_{3n+1}$ or $Ca_3Ru_2O_7$, we observe a locally restricted movement of the $(OH)_{ads}$ around the $O_{surf}H$ on $Sr_{n+1}Ru_nO_{3n+1}$. Annealing to room temperature leads to diffusion, enabling interactions and the formation of 1D chains. Adsorbed water forms various superstructures with long-range order depending on the coverage, dosing temperature and annealing time. This work was supported by the Austrian Science Fund (FWF project F45) and the ERC Advanced Grant "OxideSurfaces".

[1] M. A. Pena, and J. L. G. Fierro, Chem. Rev. 101, 1981 (2001).

O 65.7 Wed 18:15 Poster A

**Methanol Adsorption on CeO2(111) Single Crystal Surface** — Chengwu Yang, Fabian Bebensee, •Alexei Nefedov, and Christof Woell — Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Due to the oxygen mobility and the reducibility of cerium ions, ceria and related materials have extensive catalytic applications [1]. Studying the interaction of methanol with ceria surfaces taking the so-called surface science approach is of crucial importance to gain a fundamental understanding of the oxidation of alcohols to aldehydes [2]. Here, we used a novel apparatus [3] combining a state-of-the-art FT-IR spectrometer with a dedicated UHV-chamber to monitor the adsorption of methanol on CeO2(111) surfaces. The system allows acquiring spectra in both reflection at grazing incidence on single crystals and in transmission geometry on polycrystalline powders. From the comparison to data obtained on well-defined single crystals, a precise interpretation of the complicated infrared spectra for adsorbates on powders can be reached. Methanol adsorbs dissociatively at 120 K at defective CeO2(111) surfaces to yield a surface methoxy species. The IR spectra of this methoxy species, in particular the C-O stretch frequency, provide information about their coordination to the oxide surface and the presence of surface oxygen vacancies.

[1] A. Trovarelli, P. Fornasiero (Ed.), Catalysis by Ceria and Related Materials (2nd edition), Imperial College Press, London, 2013.

[2] J. M. Vohs, Chemical Reviews, 2013, 113, 4136.

[3] C. Yang, et al., Phys. Chem. Chem. Phys, 2014, 16, 24165.

O 65.8 Wed 18:15 Poster A

**$CO_2$ adsorption on $CeO_2$(110) single crystal surface** — Chengwu Yang, •Alexei Nefedov, Jun Chen, Fabian Bebensee, and Christof Woell — Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Interest in the adsorption of carbon dioxide on oxide surfaces arises not only from the need to mitigate emission of this greenhouse gas, but but also its potential use as a feedstock for the chemical industry [1]. Ceria, one of the most reducible metal oxide, has proven to be a highly active catalyst for $CO_2$ reduction to methanol [2]. For a fundamental understanding of processes occurring on high surface-area $CeO_2$ catalysts under reaction conditions, adsorption studies on well-defined single crystal surfaces in ultrahigh vacuum (UHV), i.e. the surface-science approach, is indispensable [3, 4]. Here we report results on $CO_2$ adsorption onto pristine and defective $CeO_2$(110) single crystal surfaces characterized using x-ray photoelectron spectroscopy, UHV infrared spectroscopy, and near edge x-ray absorption fine structure spectroscopy. Our data indicate that $CO_2$ adsorbes predominantly as a carbonate on this ceria surface.

[1] M. Aresta (Ed.), Carbon Dioxide as Chemical Feedstock, Wiley-VCH, New York, 2010.

[2] J. Graciani, et al., Science, 2014, 345, 546.

[3] H.-J. Freund, M. W. Roberts, Surface Science Reports, 1996, 25, 225.

[4] Uwe Burghaus, Progress in Surface Science, 2014, 89, 161.

O 65.9 Wed 18:15 Poster A

**DFT modeling of diatomic molecules physisorbed on the NaCl(100) surface** — •Jochen Vogt — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

Computational schemes to treat van der Waals interaction within density functional theory (DFT) are currently a field of vivid research and rapid development. Recent quantitative LEED studies have provided detailed experimental structure information on the low temperature geometries of CO, $N_2$, and $O_2$ adsorbed on the NaCl(100) surface [1-3]. For the modeling of these classical physisorption systems based on PBE functionals and pseudopotentials, different schemes to treat van der Waals interaction were used and compared with respect to binding energy, molecule-surface distance, and potential energy curves.

[1] Jochen Vogt, Birgit Vogt, J. Chem. Phys. 2014, in press

[2] Jochen Vogt, J. Chem. Phys. **137** (2012), 174705

[3] Anne Möller, diploma thesis, Magdeburg 2012

O 65.10 Wed 18:15 Poster A

**Using CO as a probe molecule for exploring rutile $TiO_2$ surface structures** — •Hannah Schlott[1], Maria Buchholz[2], Fabian Bebensee[2], Christof Wöll[2], and Bernd Meyer[1] — [1]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — [2]Institut für Funktionelle Grenzflächen (IFG),Karlsruher Institut für Technolgie (KIT)

Using density-functional theory (DFT) we investigated the adsorption of CO molecules on various structural models of the reconstructed rutile $TiO_2$(011) surface. While the adsorption of CO on rutile $TiO_2$(110), the most thoroughly studied oxide surface in surface science, is well understood [1,2], the situation is less clear for the reconstructed $TiO_2$(011) surface. Thermal treatment and infrared spectroscopy indicate a similar stability of the CO molecules as on $TiO_2$(110), albeit with the molecules lying flat on the surface. In the DFT calculations, however, we find for the recently proposed structural models of the reconstructed $TiO_2$(011) surface only adsorption sites either with horizontal CO orientation and lower binding energy or with similar binding energy as on $TiO_2$(110) and vertical CO orientation. Implications of this observation will be discussed.

[1] P.M. Kowalski, B. Meyer, D. Marx, Phys. Rev. B **79**, 115410 (2009).

[2] M. Kunat, F. Traeger, D. Silber, H. Qiu, Y. Wang, A.C. van Veen, Ch. Wöll, P.M. Kowalski, B. Meyer, C. Hättig, D. Marx, J. Chem. Phys. **130**, 144703 (2009).

## O 66: Electronic Structure of Surfaces

Time: Wednesday 18:15–21:00 Location: Poster A

O 66.1 Wed 18:15 Poster A

**XMCD of 3d adatoms on $Bi_2Te_3$ and $Bi_2Te_2Se$: experiment and ab initio theory** — Martin Vondracek[1], •Jan Honolka[1], Cinthia Piamonteze[2], Jonas Warmuth[4], Matteo Michiardi[3], Philip Hofmann[3], Khajetoorians Alexander Ako[4], Jens Wiebe[4], Roland Wiesendanger[4], Tim Wehling[5], Jan Minar[6], Hubert Ebert[6], Jian-Li Mi[3], Bo B. Iversen[3], and Markus Dunst[6] — [1]Inst. of Physics ASCR, Prague, Czech Republic — [2]PSI, Switzerland — [3]iNano, Aarhus University, Denmark — [4]INF, University of Hamburg, Germany — [5]Inst. of Theo. Physics, University of Bremen, Germany — [6]LMU München, Germany

The chalcogenide 3D topological insulator $Bi_2Te_3$ obeys time-reversal symmetry, and hosts a linear dispersive, topological surface state around the Gamma point[1]. It is predicted, that magnetic adatoms can break time-reversal symmetry, thereby generating an energy gap at the Dirac point of the otherwise topologically protected surface states[2]. Here we summarize experimental XAS and XMCD results of single $3d$ adatoms Ni, Fe, and Cu on $Bi_2Te_3$ and $Bi_2Te_2Se$ surfaces. While Cu shows a $d^{10}$ electronic configuration, we find a significant resonant Ni $L_{2,3}$ intensity in XAS, however no magnetic dichroism within the detection limit. The results are compared to ab initio theory. Calculated equilibrium positions of adatoms and their host structure show strong relaxation effects. $d$-shell occupancies and magnetic properties are extracted. Moreover, we present simulated resonant spectral shapes. [1] M. Z. Hasan and C. L. Kane, Reviews of Modern Physics 82, 3045 (2010). [2] Y. L. Chen et al., Science 329, 659 (2010).

O 66.2 Wed 18:15 Poster A

**STM study on the electronic properties of the Vanadium (100) (1x5) surface reconstruction** — •Andreas Topp[1], Berthold Jäck[1], Matthias Eltschka[1], Markus Etzkorn[1], Christian Ast[1], and Klaus Kern[1,2] — [1]Max-Planck Institute for Solid State Research, D-70569 Stuttgart — [2]Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Vanadium has recieved comparibly little attention in surface science, despite the interesting superconducting properties, since its superconducting phase offers a high critical temperature with moderate critical fields [1]. The (1×5) reconstuction of the Vanadium (100) surface has been studied by means of AES, ARPES, STM topography, LEED and DFT [2, 3]. The influence of oxygen in forming this reconstuction has been of special interest. Here, we use scanning tunneling microscopy to investigate the local electronic structure of the (1×5) reconstruction with atomic scale precision. By reporting on conductance measurements between $0 - 1\,\mathrm{V}$, we can show that the local density of states strongly varies within the reconstruction.

[1] S.Sekula and R.Kernohan, Phys. Rev. B **5**, 904 (1972)
[2] R.Koller *et al.*, Surf. Sci. **480**, 11 (2001)
[3] M.Kralj *et al.*, Surf. Sci. **526**, 166 (2013)

O 66.3 Wed 18:15 Poster A

**Force and Kelvin Probe Measurements on Confined Electronic States inside Quantum Resonators** — •Fabian Queck[1], Florian Albrecht[1], Alastair McLean[2], and Jascha Repp[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — [2]Department of Physics, Engineering Physics and Astronomy, Queen's University, Kingston, Ontario, Canada, K7L 3N6

On closed-packed surfaces of noble metals such as Cu(111) surface state electrons form a nearly free electron gas in two dimensions. The electrons are scattered from step-edges, point defects and adsorbates giving rise to standing wave patterns, which can be engineered by so-called quantum corrals [1]. The standing wave patterns gives rise to long range interactions between adsorbates [2] and should therefore be associated with measurable forces between scatterers.

Here we make an attempt to directly measure these forces with atomic force microscopy and to measure the possible changes of the local contact potential difference generate by the modulation of the surface local density of states associated with the standing wave patterns.

[1] M. F. Crommie, C. P. Lutz, and D. M. Eigler. Confinement of Electrons to Quantum Corrals on a Metal Surface. Science, 262(5131), 218-220, 1993.

[2] J. Repp. Rastertunnelmikroskopie und -spektroskopie an Adsorbaten auf Metall und Isolatoroberflaechen. PhD thesis, Freie Universitaet Berlin, 2002.

O 66.4 Wed 18:15 Poster A

**Three-dimensional band mapping and spin-polarized states in the phase change material $Ge_2Sb_2Te_5$** — •Marcus Liebmann[1], Christian Pauly[1], Jens Kellner[1], Jos Boschker[2], Rui Ning Wang[2], Evangelos Golias[3], Jaime Sanchez-Barriga[3], Oliver Rader[3], Raffaella Calarco[2], and Markus Morgenstern[1] — [1]II. Inst. Phys. B, RWTH Aachen University — [2]Paul-Drude-Institut für Festkörperelektronik, Berlin — [3]Helmholtz-Zentrum für Materialien und Energie, BESSY, Berlin

We present an angle-resolved photoemission (ARPES) study of the ternary phase change material $Ge_2Sb_2Te_5$, epitaxially grown on Si(111) in the metastable cubic phase, transferred in-situ in ultrahigh vacuum from the molecular beam epitaxy system to the analysis chamber. This material serves, e.g., in DVDs as a fast switchable material (1 ns) between the metallic cubic and an insulating amorphous phase. Recently, the observation of an inverted valence band provided evidence of non-tivial $\mathbb{Z}_2$ topology [1], opening up the perspective of ns-switching between a topological crystalline and an insulating amorphous phase. We performed a three-dimensional mapping of the band structure by variation of the photon energy (15-31 eV) and found the center of the bulk valence band about 130 meV below the Fermi energy and away from the center of the Brillouin zone. A spin polarization of nearly 100% close to the Fermi energy has been observed by spin-polarized ARPES. We show a detailed analysis of the involved states near the Fermi energy contributing to the transport.

[1] C. Pauly *et al.*, Appl. Phys. Lett. **103**, 243109 (2013).

O 66.5 Wed 18:15 Poster A

**Manipulation and control of electronic properties of Si:P $\delta$-layers** — •Federico Mazzola[1], Craig Polley[3], Jill Miwa[2], Michelle Simmons[4], and Justin Wells[1] — [1]NTNU, Norwegian University of Science and Technology — [2]Department of Physics and Astronomy, Aarhus University — [3]MAX-IV Laboratory, Lund, Sweden — [4]Centre for Quantum Computation & Communication Technology School of Physics The University of New South Wales

Many body interactions play a fundamental role for material properties such as conductivity, scattering and transport of carriers. In particular, electron-phonon- coupling (EPC) has been attracting interest because is thought to be a prerequisite for superconductivity.

$\delta$-doping in Si, which consists in placing a highly conductive P layer just beneath the Si surface, constitutes an important step for quantum computer architectures allowing for the possibility of shrinking the scale of devices down to the atomic scale, with a single atom transistor and atomic scale nanowire having been demonstrated.

Here I will introduce ARPES and Resonant-PES characterization and explain how such a technique can be used to understand many-body interactions in the electronic band-structure of Si:P $\delta$-layers and to characterize the dimension of this new hybrid system. In particular, we will introduce a characterization of the electronic confinement of a sub-surface state and we will study how such a state is affected by many-body interactions.

O 66.6 Wed 18:15 Poster A

**Elementary contributions to the resistivity of a thin $Bi_2Se_3$ film** — •Sebastian Bauer, Paul Graf, and Christian A. Bobisch — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

We present scanning tunneling potentiometry (STP) measurements on a 14 QL $Bi_2Se_3$ film on Si(111) using a multiprobe STM [1]. STP gives us simultaneously microscopic information about the topography and the electrochemical potential of the topological insulator (TI) $Bi_2Se_3$ while a lateral current flows through the $Bi_2Se_3$ film. The microscopic (nm-scale) sheet conductance of the $Bi_2Se_3$ film is evaluated by STP yielding a value of 1.8 mS. This is very close to the value of our macroscopic ($\mu$m-scale) measurements (2.1 mS) also found by other groups [2]. Despite the topological protection of the $Bi_2Se_3$ surface state [3], we observe sharp voltage drops on the $Bi_2Se_3$ surface, located at $Bi_2Se_3$ step edges. The step edges contribute to the total resistance of the surface by a resistivity of 0.9 Ω·cm at each step edge of a quintuple layer, reducing the sheet conductance of the TI film [4].

[1] A. Bannani, C. A. Bobisch, and R. Möller, Rev. Sci. Instrum. 79, 083704 (2008). [2] A. Taskin et al., Phys. Rev. Lett. 109, 066803 (2012). [3] M. Hazan and C. L. Kane, Rev. Mod. Phys. 82, 3045-3067 (2010). [4] S. Bauer and C. A. Bobisch, in revision.

O 66.7 Wed 18:15 Poster A

**Manipulating the surface conductivity of $Bi_2Se_3$ by Bi ad-islands** — •Paul Graf, Sebastian Bauer, and Christian A. Bobisch — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

We studied the microscopic (nm-scale) electron transport on the surface of thin films of the topological insulator $Bi_2Se_3$ [1],[2] by scanning tunneling potentiometry (STP) [3] using a multiprobe STM [4]. Especially, we analyzed the impact of Bi ad-islands to the electron transport, i.e. the electrochemical potential of the $Bi_2Se_3$ film. In addition, the macroscopic ($\mu$m-scale) conductivity was determined by a two point measurement. Since the surface state of $Bi_2Se_3$ is topologically protected, small defects on the surface like the bismuth bilayer islands are predicted not to disturb the current flow through the $Bi_2Se_3$ film significantly. We find that both, the microscopic and the macroscopic conductivity of the $Bi_2Se_3$ film increases after adding bismuth bilayer islands to the surface. This effect can be explained by electron donation from the bismuth ad-islands to the $Bi_2Se_3$ film [5]. The impact of scattering of conduction electrons at the Bi ad-islands to the local surface potential will be discussed.

[1] C. L. Kane und E. J. Mele, Phys. Rev. Lett. 95, p. 146802 (2005). [2] H. Zhang et. al., Nat. Phys. 5, p. 438 (2009). [3] P. Muralt et. al., Appl. Phys. Lett. 48, p. 514 (1986). [4] A. Bannani, C. A. Bobisch and R. Möller, Rev. Sci. Instrum. 79, 083704 (2008). [5] M. Chen et. al., Appl. Phys. Lett. 101, p. 081603 (2012)

O 66.8 Wed 18:15 Poster A

**Core-resonant double photoemission from palladium films** — •Ilya Kostanovskiy, Frank Schumann, Zheng Wei, Yuri Aliaev, and Jürgen Kirschner — Max Planck Institute of Microstructure Physics, Halle, Germany

We present a core-resonant double photoemission study from palladium films with synchrotron radiation. In an MVV Auger process a 3d (M) core level electron is excited and the subsequent decay involves two 4d (V) valence electrons. This process provides access to the electron-electron interactions in the valence band. We measured Pd 3d photoelectrons in coincidence with the Auger MVV electrons by means of linear polarized light. We selected two polarization directions perpendicular to each other. In contrast to single electron photoemission we observe a polarization dependence not only for the photo electrons, but also for the Auger line. This effect can be quantitatively explained within a simple model.

Additionally, we present the sum energy spectra which display a simple triangular-like line shape. It resembles a self convolution of a constant density of states. Our results will be compared with theoretical descriptions of the Auger decay. These either implement an electron-electron interaction within the valence band or use atomic multiplet theory.

O 66.9 Wed 18:15 Poster A

**Rashba-splitting in thin Bi-films on a Au(111)-surface** — •Dominik Jungkenn[1], Sebastian Jakobs[1,2], Stepan Tsirkin[3], Andreas Ruffing[1], Eugene Chulkov[3], Mirko Cinchetti[1], Stefan Mathias[1], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, 67663 Kaiserslautern, Germany — [2]Graduate School Materials Science in Mainz, Erwin Schroedinger Straße 46, 67663 Kaiserslautern, Germany — [3]Donostia International Physics Center (DIPC), Depto. de Fisica de Materiales and Centro Mixto CSIC-UPV/EHU, Facultad de Ciencias Quimicas, UPV/EHU, 20018 San Sebastian, Spain

The combination of large spin-orbit coupling and a broken inversion symmetry at the surface or interface of a crystal leads to a spin-dependent splitting of the band structure (Rashba-effect [1]), which is of great interest in the growing field of spintronics. The Rashba-effect was observed in different systems with varying splitting magnitudes, e.g surface states, quantum-well states and topological insulators. Here, we investigate the strongly Rashba-type spin-orbit split system Bi/Au(111) using low energy electron diffraction (LEED) and angle resolved photoemission spectroscopy (ARPES). Our results exhibit a spin-split band structure with a so far unrivaled large Rashba parameter ($\alpha_R = 4.78$ eVÅ) for a coverage below 1 monolayer (ML). The results are supported by DFT calculations that reproduce our observations in good agreement.

[1] Yu. A. Bychkov, E. I. Rashba. JETP, 39(2), 78-81 (1984)

O 66.10 Wed 18:15 Poster A

**Analysis of the Band Dispersions of the Bilayer Ruthenate $Sr_3Ru_2O_7$ around the High Symmetry Points** — •Arlette S. Ngankeu[1,2], Emanuela Carleschi[1], Bryan P. Doyle[1], Volodymyr B. Zabolotnyy[3], Timur K. Kim[4], Ivana Vobornik[5], Manju Unnikrishnan[5], Rosalba Fittipaldi[6], Mario Cuoco[6], Antonio Vecchione[6], and Sergey V. Borisenko[3] — [1]University of Johannesburg (South Africa) — [2]Aarhus University (Denmark) — [3]IFW Dresden (Germany) — [4]Diamond Light Source ( United Kingdom) — [5]IOM-CNR TASC Laboratory Trieste (Italy) — [6]CNR-SPIN and Department of Physics, University of Salerno (Italy)

We have investigated the formation of heavy d electron quasiparticles in $Sr_3Ru_2O_7$ by analysing the dispersion of the low-energy states around the high symmetry points Γ and X of the first Brillouin zone. This study was performed at the BESSY $1^3$ ARPES endstation. We report the existence of flat bands giving rise to van Hove singularities (vHS) in the DOS in closed proximity to the Fermi level, associated to the $\gamma_2$, $\alpha_2$ and $\delta$ Fermi surface sheets. These vHS are deemed to be responsible for the appearance of the multiple metamagnetism observed in the system. Our results also show signatures of strong correlation effects characterised by the peak-dip-hump line shape of the dispersive states. Finally, we have noted the presence of bands not predicted by electronic structure calculations, which might be band replicas ascribed to the reconstruction of the sample surface.

O 66.11 Wed 18:15 Poster A

**Low temperature scanning tunneling microscopy investigation of the phase change material Ge2Sb2Te5** — •Jens Kellner[1], Christian Pauly[1], Marcus Liebmann[1], Jos Boschker[2], Volker Deringer[3], Raffaella Calarco[2], Richard Dronskowski[3], and Markus Morgenstern[1] — [1]II. Physikalisches Institut B, RWTH Aachen University and JARA-FIT, Germany — [2]Paul Drude Institut für Festkörpelektronik, Berlin, Germany — [3]Institute of Inorganic Chemistry, RWTH Aachen University, Germany

We present a scanning tunneling microscopy (STM) study of the phase change material GST-225 (GST), epitaxially grown on Si(111) in the metastable cubic phase, transferred in-situ in ultrahigh vacuum from the molecular beam epitaxy system to the STM. Despite the fact that GST is already commercially used, there is still no complete understanding of the ultra fast switching speed, the strong resistance change and the high endurance of the Ge-Sb-Te alloys. One contribution to such a theory is an atomic scale understanding of the electronic properties of GST. V. Deringer modeled the surfaces by cutting slabs from the hexagonal bulk cells of GST followed by relaxation. The relaxed structure features a number of octahedral and tetrahedral Ge bonds which can be distinguished in the density of states (DOS) projections. We detected the differential conductivity of such states by scanning tunneling spectroscopy at 0.4 K leading to an identification of different bonding configurations.

O 66.12 Wed 18:15 Poster A

**Tuning the Fermi energy to the Dirac point in the ternary topological insulator $(Bi_{1-x}Sb_x)_2Te_3$** — •Jens Kellner[1], Markus Eschbach[2], Jörn Kampmeier[3], Martin Lanius[3], Gregor Mussler[3], Lukasz Plucinski[2], Markus Liebmann[1], Detlev Grützmacher[3], Claus Schneider[2], and Markus Morgenstern[1] — [1]II. Physikalisches Institut B, RWTH Aachen University and JARA-FIT, Germany — [2]Forschungszentrum Jülich GmbH, Peter Grünberg Institut (PGI-6), Germany — [3]Forschungszentrum Jülich GmbH, Peter Grünberg Institut (PGI-9), Germany

A topological insulator (TI) has a bulk energy gap but conducting helical surface states. In order to make use of these states, e.g. in transport devices or for creating exotic quasiparicles like Majorana Fermions, one has to tune the Fermi energy ($E_F$) close to the Dirac point ($E_D$) within the band gap. However, currently used TI materials e.g. $Bi_2Te_3$ and $Sb_2Te_3$ have major drawbacks. For $Bi_2Te_3$, $E_D$ is buried in the bulk valence band (BVB) and $E_F$ is located in the bulk conduction band (BCB). Whereas with $Sb_2Te_3$, $E_D$ is in the bulk energy gap and $E_F$ is located in the BVB. Mixing the two compounds leads to a ternary system $(Bi_{1-x}Sb_x)_2Te_3$ where charge compensation is achieved and the position of $E_D$ can be tuned [1].We were able to synthesize $(Bi_{1-x}Sb_x)_2Te_3$ thin films for $0.94<x<0.96$ by molecular beam epitaxy (MBE), transferred in-situ in ultrahigh vacuum from the MBE system to the photoemission setup. Angle resolved photoemission spectroscopy shows that $E_F$ and $E_D$ are congruent and no bulk bands intersect $E_F$. [1] J. Zhang, Nat. Comm. 2, 574 (2011)

O 66.13 Wed 18:15 Poster A

**Two-photon photoemission from $GeSb_2Te_4$** — •Sebastian Otto, Philipp Rosenzweig, and Thomas Fauster — Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

Time- and angle-resolved, polarization-dependent two-photon photoemission is used to study the electronic structure and dynamics at the surface of $GeSb_2Te_4$. The topological surface state is centered at 0.45 eV above the Fermi level due to intrinsic p-doping. The valence band, the two lowest conduction bands and an image-potential state are identified. Measurements with circularly polarized light show the expected change of sign in the circular-dichroism asymmetry at the Dirac point. The dichroism depends only on the circular polarization of the probe pulse, which indicates an indirect filling from the conduction band. The second conduction band shows a negative dispersion similar to $SnSb_2Te_4$ [1] and $Sb_2Te_3$ [2].

[1] D. Niesner, S. Otto, V. Hermann and Th. Fauster, Phys. Rev. B **89**, 081404(R) (2014)

[2] J. Reimann, J. Güdde, K. Kuroda, E. V. Chulkov and U. Höfer, Phys. Rev. B **90**, 081106(R) (2014)

O 66.14 Wed 18:15 Poster A

**Double photoemission from surfaces: intensity relations** — •Yuri Aliaev, Frank Oliver Schumann, Ilya Kostanovski, Gianluca Di Filippo, Zheng Wei, and Jürgen Kirschner — Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

The emission of an electron pair upon single photon absorption requires a finite electron-electron interaction. This makes double photoemission a particulary sensitvie tool to study the electron correlation in matter.

This is supported by a recent theoretical work which predicts that the pair intensity is a direct reflection of the correlation strength.[1] In order to explore the validity of this we performed a study on a variety of materials. Among them are noble metals, transition metals and insulators. The latter include transition metal oxides like CoO and NiO which are also termed highly correlated. We find an increased pair emission rate of NiO and CoO compared to the metals which reaches factor of 10. This enhancement is photon energy depedent. It is highest at 23.7 eV and decreases monotonically as a function of the photon energies. At 60 eV the intensity levels for the oxides and metals are largely identical.

We also discovered that an increase of the coincidence intensity is accompanied by an increase in the singles count rate. This demonstrates that the pair emission is an efficient process at surfaces contributing up to 15% to the single electron emission. Our experimental results demonstrates that the correlation strength can be accessed by double photoemission.

[1] B.D. Napitu, J. Berakdar, Phys. Rev. B **81**, 195108. (2010)

O 66.15 Wed 18:15 Poster A

**Electronic structure of spintronic materials investigated with laser-based high-resolution angle-resolved photoemission** — •Pika Gospodaric, Markus Eschbach, Lukasz Plucinski, Ewa Mlynczak, Mathias Gehlmann, Sven Döring, and Claus Michael Schneider — Forschungzentrum Jülich GmbH, Peter Grünberg Institute (PGI-6), 52425 Jülich, Germany

In this contribution we will present the first experimental results obtained with the new setup for high resolution angle resolved photoemission spectroscopy (ARPES) operated with laser light. The existing lab-based ARPES system was upgraded with a 6 eV photon source based on the fourth harmonic generation of fundamental 1.5 eV ultrashort pulsed laser beam from a commercial Ti:Sa oscillator. A small spot size of 100 microns can be achieved on the sample, whereas the short pulses allow time-resolved measurement as a future application. The system offers electronic structure investigation of surfaces with possibility to control the polarization of light and thus enables detection of differential absorption of left and right circular polarized light, i.e. circular dichroism (CD), which can be observed in spin polarized energy bands. Calibrations were performed on Au(111)and Cu(111) single crystal surfaces which exhibit clear parabolic surface states in the center of their Brillouin zone. Investigation of the spin texture of the Dirac cone in the 3D topological insulator Sb2Te3 was performed using CD.

O 66.16 Wed 18:15 Poster A

**Subsurface contributions in epitaxial rare-earth silicides** — •Olaf Lübben[1], Jorge I. Cerdá[2], Alexander N. Chaika[3], and Igor V. Shvets[1] — [1]Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College, Dublin 2, Ireland — [2]Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Cantoblanco, 28049 Madrid, Spain — [3]Institute of Solid State Physics RAS, Chernogolovka, Moscow district 142432, Russia

Metallic thin films of heavy rare-earth silicides epitaxially grown on Si(111) substrates have been widely studied in recent years because of their appealing properties: unusually low values of the Schottky barrier height, an abrupt interface, and a small lattice mismatch. Previous studies also showed that these silicides present very similar atomic and electronic structures. Here, we examine one of these silicides ($Gd_3Si_5$) using scanning tunneling microscopy (STM) image simulations that go beyond the Tersoff-Hamann approach. These simulations strongly indicate an unusual STM depth sensitivity for this system.

O 66.17 Wed 18:15 Poster A

**Ultrafast time and angle resolved photoemission spectroscopy measurements using high harmonic radiation above 70eV photon energy and sub-1eV resolution at 10kHz repetition rate** — •Jürgen Schmidt[1], Alexander Guggenmos[1,2], Soo Hoon Chew[1], and Ulf Kleineberg[1,2] — [1]LMU München, Fakultät für Physik, Am Coulombwall 1, 85748 Garching — [2]MPQ, Hans-Kopfermann-Str. 1, 85748 Garching

High harmonic generation has established as the standard tool for ultrafast time resolved photoelectron spectroscopy experiments to study electron dynamics on gases and solids. Angle resolved measurements additionally give insight into the momentum space of the electrons and provide full information about the band structure dynamics. These measurements benefit from sources with high repetition rate on the one hand and high photon energies on the other hand in order to be able to also address core-like electron states which revealed insight into the temporal dynamics of the photoemission process [1]. Here we show that our source produces harmonic radiation between 70 and 100eV at a repetition rate of 10kHz with sufficient flux for angle resolved photoemission experiments [2] and we report about time resolved measurements on various metal surfaces excited by few-cycle NIR pulses. [1] Cavalieri et al., Nature 449, 1029 (2007) [2] Schmidt et al., Rev. Sci. Instrum., to be submitted

## O 67: Electronic Structure Theory: General, Method Development

Time: Wednesday 18:15–21:00 Location: Poster A

O 67.1 Wed 18:15 Poster A

**Electron-phonon coupling in the KKR formalism** — •Carsten Eberhard Mahr, Christian Franz, Marcel Giar, and Christian Heiliger — Justus-Liebig University, Giessen, Germany

Electron-phonon coupling is one of the main incoherent inelastic scattering mechanisms in a wide variety of crystalline material systems at room temperature. Therefore, it is necessary to incorporate those effects in any realistic calculation of thermoelectric properties. We do so by extending our density functional theory (DFT) based Korringa-Kohn-Rostocker (KKR) Green's function formalism code.

By adding a Fröhlich-type interaction to the Kohn-Sham Hamiltonian which corresponds to the previously calculated Green's function $G_{\text{ee}}$ containing the electron-electron interaction in e.g. local density approximation (LDA), we can compute the dressed propagator through Dyson's equation as $G = G_{\text{ee}} + G_{\text{ee}} \cdot \Sigma_{\text{eph}} \cdot G$. The self-energy $\Sigma_{\text{eph}}$ is treated in Self-Consistent First Born Approximation (SCFBA), which may be obtained using a perturbative diagrammatic approach within Keldysh NEGF formalism.

We give transformed representations of the beforementioned relations and quantities for bulk calculations in the KKR 'basis' set. Based thereupon, central formulas for non-equilibrium transport in our calculational scheme are presented.

O 67.2 Wed 18:15 Poster A

**SEMT: An Orthogonal and Localized Basis-Set for All-electron Density Functional Theory** — •Andrea Nobile and Stefan Blügel — Peter Grünberg Institute (PGI-1) and Institute for Advanced Simulation (IAS-1), Forschungszentrum Jülich GmbH and JARA, Jülich, Germany

Employing all-electron methods for simulations by density functional theory (DFT) allows for unbiased, highly accurate solutions of the Kohn-Sham equations. Current popular all-electron schemes like FLAPW+LO and APW+LO use a basis set that is not localized in real space and as a consequence the resulting Hamiltonian is dense. These basis sets are non-orthogonal thereby posing constraints on the choice of the eigensolver and on the usage and development of alternative, less than cubic scaling convergence schemes.

We tackle the localization and orthogonality problem by combining spectral elements with muffin-tin spheres. The introduced method, that we call spectral-element-muffin-tin (SEMT), produces a basis set that is localized and numerically orthogonal by construction.

When compared to pure spectral element methods, our basis needs a substantially smaller number of degrees of freedom per atom. The strength of the SEMT method is in the combination of all-electron, real space, sparsity and orthogonality. We demonstrate the method with our implementation (Velvet) on some elemental materials by comparing the results with FLAPW+LO calculations.

O 67.3 Wed 18:15 Poster A

**Electron-phonon relaxation times from first principle calculations** — •Florian Rittweger[1,2], Nicki F. Hinsche[1], and Ingrid Mertig[1,2] — [1]Martin-Luther-Universität, Institut für Physik, Von-Seckendorff-Platz 1, DE-06120 Halle — [2]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, DE-06120 Halle

Electron-phonon interaction (EPI) is usually related to the phenomenon of superconductivity. Besides these studies the influence of the EPI on transport properties became popular in the last years.

While ARPES measurements offer experimental access to the EPI, theoretical approaches are based on the calculation of the electron-phonon matrix elements. The latter leads either to the calculation of the complex electron-phonon self-energy and therefore the renormalization of the electronic band structure or to the estimation of the electron-phonon coupling strength $\lambda$ and the state-dependent relaxation time $\tau_{\mathbf{k}}$. The k-dependence of $\tau$ enters the Boltzmann equation for the computation of transport properties like the electrical conductivity, thermal conductivity and the thermopower beyond the relaxation time approximation typically used.

We calculate the EPI using linear response density functional perturbation theory and present first results and discussions for simple metals.

O 67.4 Wed 18:15 Poster A

**How Molecules Interact Through Nanostructures** — •Mausumi Chattopadhyaya and Alexandre Tkatchenko — Fritz Haber Institut der MPG, Berlin, Germany

Molecules often interact and assemble in the presence of environments, such as solvents, surfaces, or nanostructures. While in the gas phase intermolecular interactions are fairly well understood, much less is known about intermolecular interactions in polarizable environments. To shed some light into this matter, we have investigated the interaction between aromatic molecules through a range of nanostructures, including graphene, h-BN, fullerenes, carbon nanotubes, and phosphorene. In each of these cases, we have computed the non-additive interaction terms by using density-functional theory with many-body dispersion interactions (DFT+MBD method [1,2]). We found that in most of the cases the intermolecular interaction energy decreases due to the presence of a nanostructure, as expected from classical electrodynamics. However, for sufficiently polarizable nanostructures, we observe a regime in which the interaction energy increases due to non-trivial quantum-mechanical fluctuations of electric dipoles. [1] Phys. Rev. Lett. 108, 236402 (2012); [2] J. Chem. Phys. 140, 18A508 (2014).

O 67.5 Wed 18:15 Poster A

**Precise dynamical response functions in all-electron methods: application to the RPA correlation energy** — Markus Betzinger, •Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, Germany

The main obstacle in calculating dynamical response functions in practice is their slow convergence with respect to the basis-set size and the number of unoccupied bands. We showed in Refs. [1,2] for the static Kohn-Sham (KS) density response in the all-electron FLAPW method that an incomplete-basis-set correction (IBC) gives rise to a much better convergence behavior. The IBC contains a basis response term that provides response contributions that lie outside the Hilbert space spanned by the original basis. These contributions, therefore, incorporate to some extent an infinite number of states. We present an extension of the IBC to the frequency domain and demonstrate that precise RPA response functions can be obtained already with small basis-set sizes and few numbers of unoccupied states. As an example, we apply the correction to the RPA correlation energy of KS density-functional theory, whose central ingredient is the RPA response function.

[1] M. Betzinger *et al.*, Phys. Rev. B **85**, 245124 (2012).

[2] M. Betzinger *et al.*, Phys. Rev. B **88**, 075130 (2013).

O 67.6 Wed 18:15 Poster A

**RPA spectra from a combination of tetrahedron method and Wannier interpolation** — •Johannes Kirchmair, Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The polarization function within the random-phase approximation (RPA) describes the response of the electron density due to perturbations of the effective potential and is one of the key quantities in many-body perturbation theory. For example, it is employed in the calculations of *GW* quasiparticle energies, the RPA correlation energy, the Hubbard $U$ parameter, but also in phonon calculations. Very often, practical calculations of the polarization function suffer from severe convergence problems. The convergence with respect to unoccupied states has recently been discussed a lot in literature and correction schemes have been proposed. Another problem is the summation over, in principle, infinitely many k points. The standard method, the so-called tetrahedron method, uses a geometrical interpolation in the three dimensions of reciprocal space that can be understood as the analog of linear interpolation in one dimension. This fast and reliable method, however, shows slow convergence of the spectral properties especially for small frequencies. In this work, we propose to take these low-energy virtual excitations from a Wannier-interpolated band structure. The Wannier interpolation is seamlessly combined with the tetrahedron method, which then takes care of the high-energy virtual excitations. We show test calculations and first results for RPA spectra.

O 67.7 Wed 18:15 Poster A

**Calculation of electron energy loss spectra for resistive switching oxides from first principles** — •Roman Kováčik[1,2] and Marjana Ležaić[2] — [1]I. Physikalisches Institut, RWTH Aachen and JARA, 52056 Aachen, Germany — [2]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Calculation of the energy-loss near-edge structure (ELNES) of electron energy loss spectra (EELS) is implemented within the density functional theory framework using the full potential linearized augmented planewave (FLAPW) approach in the FLEUR code (`www.flapw.de`). The double differential cross-section is evaluated using the full relativistic treatment of incoming electrons and the transition matrix elements allowing arbitrary transitions (beyond the dipole approximation) following the formalism of Jorissen (PhD thesis, 2007). We present ELNES calculations of EELS on complex oxides with a promising application in resistive switching, such as Sr-rich phases in $SrTiO_3$. Support from the DFG (SFB917-Nanoswitches) is gratefully acknowledged.

## O 68: Electronic Structure Theory: Many-Body Effects

Time: Wednesday 18:15–21:00 Location: Poster A

O 68.1 Wed 18:15 Poster A

**Spin Entanglement in Atoms and Molecules** — •Stefano Pittalis[1], Filippo Troiani[1], Carlo Andrea Rozzi[1], and Giovanni Vignale[2] — [1]Istituto Nanoscienze, Consiglio Nazionale delle Ricerche, Modena, Italy — [2]Department of Physics, University of Missouri, Columbia, Missouri, USA

We investigate spin entanglement in many-electron systems within the framework of density functional theory. We show that the entanglement length of a Kohn-Sham system, which is extracted from the spatial dependence of the local concurrence, is a sensitive indicator of atomic shells, and reveals the character, covalent or metallic, of chemical bonds. These findings shed light on the remarkable success of modern density functionals, which tacitly employ the entanglement length as a variable. This opens the way to further research on entanglement-based functionals.

O 68.2 Wed 18:15 Poster A

**The role of the quantum well states in the oscillating behavior of the magnetic anisotropy energy and the orbital moment anisotropy** — •Leonid Sandratskii — Max Planck Institute of Microstructure Physics, Halle, Germany

We report detailed first-principles theoretical study of the correlated behavior of the magnetic anisotropy energy and the orbital moment anisotropy as a function of the thickness of the ferromagnetic films. The role of the quantum well states in the formation of the oscillations is discussed. The analysis of the contributions of different points in the 2D Brillouin zone is performed. The special role of the surface layer is considered. The symmetry of the quantum mechanical problem is studied. It is shown that the electronic states possess transversal components of the orbital moment that compensate each other after summation over the Brillouin zone.

O 68.3 Wed 18:15 Poster A

**Ab initio calculation of the first order Raman spectrum of graphene and graphite** — •Albin Hertrich, Caterina Cocchi, Pasquale Pavone, and Claudia Draxl — Department of Physics, Humboldt-Universität zu Berlin, Germany

Raman scattering produced by fluctuations of the dielectric function caused by phonons is an important non-destructive method for characterizing carbon-based materials. By adopting a fully ab initio approach, we compute the first order Raman spectrum of graphene and graphite using the full-potential all-electron density-functional-theory (DFT) package exciting [1]. This code is based on the augmented plane-waves approach and allows for the calculation of both phonon-dispersion curves, within the frozen-phonon approximation, and frequency-dependent dielectric tensors, from time-dependent DFT and the Bethe-Salpeter equation. Starting from these ingredients, the first-order Raman scattering intensity (G peak) within the adiabatic approximation is obtained from the derivative of the dielectric function with respect to the normal coordinates of the optical phonons at the Γ point of the Brillouin zone and the vibrational matrix element. Our results are interpreted and discussed in comparison with the existing literature.

[1] A. Gulans *et al.* J. Phys.: Condens. Matter **26** (2014) 363202

O 68.4 Wed 18:15 Poster A

**Thermoelectric clathrates: stability of the $\mathbf{Ba_8Al_xSi_{46-x}}$ and $\mathbf{Sr_8Al_xSi_{46-x}}$ compounds** — •Maria Troppenz, Santiago Rigamonti, and Claudia Draxl — Humboldt-Universität zu Berlin

On the search for high-efficiency thermoelectric materials, promising candidates are clathrate compounds. Their cage-like structure, capable of containing guest atoms, allows for exploiting the idea of the phonon-glass electron-crystal, proposed as a way to reach a large figure of merit.

In this work, we focus on the clathrates $Sr_8Al_xSi_{46-x}$ and $Ba_8Al_xSi_{46-x}$ . In contrast to the well-studied Ga-Ge based clathrates, Al-Si clathrates are of technological interest in terms of price, weight, and low environmental impact. The use of Sr and Ba as guests is motivated by the glass-like conductivity of $Sr_8Ga_{16}Ge_{30}$ and the high thermoelectric efficiency of $Ba_8Ga_{16}Ge_{30}$. The electronic transport properties are optimized at the Zintl composition, corresponding to $x = 16$. However, it has not been possible to synthesize samples with $x > 10$ for Sr or $x > 15$ for Ba [1].

We explore the structural stability of the compositional range $0 \leq x \leq 16$ as well as the stability against competing phases that are observed in experiments (e.g. $SrAl_2Si_2$). Due to the large number of substitutional configurations we resort to a cluster expansion based on accurate calculations of a subset of substitutional configurations.

[1] J.H. Roudebush, N. Tsujii, A. Hurtando, H. Hope, Y. Grin, and S.M. Kauzlarich, *Inorg. Chem.* **51**, 4161 (2012).

O 68.5 Wed 18:15 Poster A

**Atomistic Modeling of Optical Coefficients in Layered Materials** — •Christian Vorwerk, Caterina Cocchi, and Claudia Draxl — Humboldt Universität zu Berlin and IRIS Adlershof, 10099 Berlin, Germany

The optical properties of a material are fully determined by the complex dielectric tensor. Comparison with measured data however, requires accounting for the experimental setup. This is in particular important for molecular materials, owing to their anisotropic nature.

We apply a 4x4-matrix formalism [1] to calculate optical coefficients of layered anisotropic materials, combining *ab initio* calculations of the dielectric tensor with the solution of Maxwell's equations. This approach [2] allows us to investigate the impact of polarization and incidence angle of the incoming light beam on the spectra of layered materials, having a specific orientation with respect to the substrate. We apply the formalism to optical as well as to X-ray absorption spectra, computing the full dielectric tensor with the all-electron full-potential code `exciting` [3] by means of many-body perturbation theory. Our prototypical target systems are different polymorphs of sexithiophene, crystals of functionalized pentacenes, self-assembled monolayers of azobenzenes, and more.

[1] P. Yeh, Surf. Sci. 96, 41 (1980). [2] P. Puschnig and C. Ambrosch-Draxl, Adv. Eng. Mater. 8, 1151 (2006). [3] A. Gulans et al., J. Phys.: Condens. Matter 26, 363202 (2014).

O 68.6 Wed 18:15 Poster A

**The Novel Materials Discovery (NoMaD) Repository** — •Evgeny Blokhin[1], Fawzi Mohamed[2], Karsten Hannewald[1], Luca Ghiringhelli[2], Pasquale Pavone[1], Christian Carbogno[2], Johann-Christoph Freytag[3], Matthias Scheffler[2], and Claudia Draxl[1] — [1]Humboldt-Universität zu Berlin, Institut für Physik und IRIS Adlershof, Zum Großen Windkanal 6, 12489 Berlin — [2]Fritz Haber Institute of the Max Planck Society, Theory Department, Faradayweg 4-6, 14195 Berlin — [3]Humboldt-Universität zu Berlin, Institut für Informatik, Rudower Chaussee 25, 12489 Berlin

Since many years our community is producing an enormous amount of data by CPU-intensive calculations. Most of these data are not used, although the information content is significant. We propose to change our scientific culture following the idea of open access. The NoMaD Repository (https://nomad-repository.eu) was established to host, organize, and share materials data. NoMaD also copes with the increasing demand of storing scientific data and making them available for longer periods. NoMaD facilitates research groups to share and exchange their results. Upload of data is possible without any barrier. Results are accepted in their raw format as produced by the underlying electronic-structure package. At present, the repository is being filled with results for inorganic and organic semiconductors, catalysis and corrosion, optoelectronics, thermoelectrics, and biophysics. These areas will be continuously complemented by others.

O 68.7 Wed 18:15 Poster A

**Acoustic magnons in the long-wavelength limit: resolving the Goldstone violation in many-body perturbation theory** — •Mathias C.T.D. Müller, Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Ferromagnetic materials exhibit a spontaneously broken global rotation symmetry in spin space leading to the appearance of massless quasiparticles (zero gap) in the long-wavelength limit. These magnons are formed by the correlated motion of electron-hole pairs with opposite spins, which we describe from first principles employing the $T$-matrix formalism in the ladder approximation within the FLAPW method [1]. Due to approximations used in the numerical scheme, the acoustic magnon dispersion exhibits a small but finite gap at Γ. We analyze this violation of the Goldstone mode and discuss possible correction schemes. One of the correction schemes, which involves an adjustment of the Kohn-Sham (KS) exchange splitting, is motivated by the spin-wave solution of the one-band Hubbard model. The new exchange splittings turn out to be closer to experiment. We present corrected magnon spectra for Co, Ni, and Fe. In addition, we discuss an approach that implements the magnetic susceptibility using a renormalized Green function instead of the KS one. The latter, much more expensive approach is expected to fulfill the Goldstone condition without correction.

[1] E. Şaşıoğlu *et al.*, Phys. Rev. B **81**, 054434 (2010); C. Friedrich *et al.* Top. Curr. Chem. **347**, 259 (2014).

O 68.8 Wed 18:15 Poster A

**Electronic Structure of Hybrid Materials by Means of Self-Consistent** ***GW*** — •Nora Salas-Illanes and Claudia Draxl — Humboldt-Universität zu Berlin, Institut für Physik, Theoretische Festkörperphysik, Zum Großen Windkanal 6, 12489 Berlin

Nano-structured hybrid materials, typically consisting of two or more components that exhibit different nature, are very promising for optoelectronic applications. Unexpected new electronic properties can arise in these systems, which are absent in either of the building blocks. Unfortunately, state-of-the-art electronic-structure methods are not well suited or can even badly fail for such interfaces.

For a large number of materials, DFT provides accurate results for most ground-state properties. However, in order to obtain realistic results of electronic excitations, we have to go beyond DFT, using many-body perturbation theory (MBPT). State-of-the-art MBPT calculations are performed using the quasiparticle approach in the $GW$ approximation.

In principle, the $GW$ approach requires the self-consistent solution of the Hedin equations. However, most of the up-to-date calculations are performed using the results of the first iteration (one-shot $GW$). Unfortunately, this procedure cannot be used for obtaining accurate results for hybrid materials where, instead, some kind of self-consistent $GW$ needs to be employed.

We implemented the quasi-particle self-consistent $GW$ scheme in the all-electron full-potential code **exciting**. We present here the first results of our implementation for selected prototype materials.

O 68.9 Wed 18:15 Poster A

**Size-dependent optical gaps of Cu chalcogenide nanocrystals from *GW* and the Bethe-Salpeter equation** — •Sabine Körbel[1,2], Miguel Alexandre Lopes Marques[1,2,3], and Silvana Botti[4,2,3] — [1]Martin-Luther-Universität Halle-Wittenberg, Germany — [2]Université Claude Bernard Lyon 1, France — [3]European Theoretical Spectroscopy Facility — [4]Friedrich-Schiller-Universität Jena, Germany

In semiconductor nanocrystals, quantum confinement, which opens the optical gap with decreasing nanocrystal size, allows to tune the optical absorption edge. Hence, nanoparticles of different sizes may be used in multilayer thin-film solar cells, with each layer consisting of nanocrystals of a different size, absorbing light at a different frequency, therefore enhancing the overall efficiency of the solar cell, all the while using one and the same photovoltaic absorber material. Here we present size-dependent optical gaps of nanocrystals of $Cu_2ZnSn(S,Se)_4$ [CZTS(e)], an earth-abundant semiconductor with a direct optical gap suitable for solar-cell absorbers, calculated with *GW* and the Bethe-Salpeter equation, and compared to experimental data, where available.

O 68.10 Wed 18:15 Poster A

**2D Metal Dichalcogenides and Oxides for Hydrogen Evolution: A Computational Approach** — •Mohnish Pandey[1], Aleksandra Vojvodic[2], Kristian S. Thygesen[1], and Karsten W. Jacobsen[1] — [1]Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK - 2800 Kongens Lyngby, Denmark — [2]SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

We explore the possibilities of hydrogen evolution by basal planes of 2D metal dichalcogenides and oxides in the 2H and 1T phases using the hydrogen binding energy as a computational descriptor. The binding energies are calculated using density functional theory with the BEEF-vdW functional which includes uncertainty estimates on the calculated binding energies. For some groups of systems like the Ti, Zr, and Hf dichalcogenides the hydrogen bonding the bonding to the 2H structure is stronger than to the 1T structure while for the Cr, Mo, and W dichalcogenides the behavior is opposite. This is rationalized investigating shifts in the chalcogenide *p*-levels comparing the two structures.

## O 69: Ultrafast Electron and Spin Dynamics

Time: Wednesday 18:15–21:00 Location: Poster A

O 69.1 Wed 18:15 Poster A

**Influence of linkers on electron dynamics in dye-functionalized SiC** — •Nils Fabian Kleimeier[1], Deb Kumar Bhowmick[1], Linda Stegemann[1,2], Cristian Alejandro Strassert[1,2], and Helmut Zacharias[1,2] — [1]Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster — [2]Center for Nanotechnology (CeNTech), Universität Münster, Heisenbergstrasse 11, 48149 Münster

Functionalized SiC surfaces have gained wide interest in the field of biosensors, transistors and OLEDs due to the bio-inertness, high stability and large, tunable band gap of SiC. The interaction between the organic dye and the SiC surface can be tuned by using different linker molecules. To investigate the effect of the linkers, benzo[ghi]perylene dye was attached to the surface using p-aminophenyltrimethoxysilane (p-APTMS), aminopropyl-triethoxy-silane (APTES) and aminoundecyltriethoxysilane (AUDTES). Fluorescence images and confocal microscopy were used to determine the distribution of the dyes on the surface and the radiative lifetimes which are in the range of 1-10 ns [1]. To determine the efficiency of electron injection into the SiC, non-radiative lifetimes of about 100 fs were measured using time-resolved two-photon photoemission (TR-2PPE).

[1] Deb Kumar Bhowmick, Steffen Linden, André Devaux, Luisa De Cola, Helmut Zacharias, Small 8, 592 (2012)

O 69.2 Wed 18:15 Poster A

**Femtosecond time- and angle-resolved photoemission spectroscopy of $1T$-$TaSe_2$** — •Florian Diekmann, Christian Sohrt, Ankatrin Stange, Michael Bauer, and Kai Rossnagel — Institut für Experimentelle und Angewandte Physik Universität Kiel, D-24098 Kiel

According to previous angle-resolved photoemission spectroscopy and scanning tunneling microscopy studies, the surface of $1T$-$TaSe_2$ displays combined Peierls-Mott insulating behavior for temperatures below about 260-300 K, while bulk sensitive resistivity measurements show metallic character and no indication for a Mott transition [1]. Here, we use time- and angle-resolved extreme ultraviolet photoemission spectroscopy to directly determine the momentum-dependent electronic structure dynamics of this surface phase on the femtosecond time scale [2]. The extracted spectroscopic order parameters reveal a global two-time-scale dynamics indicating a quasi-instantaneous loss of the Mott and charge-density-wave electronic orders and a subsequent coherent suppression of the lattice distortion on a time scale related to the frequency of the charge-density-wave amplitude mode. Specifically after one half-cycle of coherent amplitude-mode vibration, a crossover state between insulator and metal with partially filled-in and partially closed Mott and Peierls gaps is reached.

[1] L. Perfetti *et al.*, Phys. Rev. Lett. **90**, 166401 (2003).
[2] C. Sohrt *et al.*, Faraday Discuss. **171**, 243 (2014).

O 69.3 Wed 18:15 Poster A

**Spectroscopy and dynamics of unoccupied electronic statesof the topological insulators $Sb_2Te_3$ and $Sb_2Te_2Se$** — •Johannes Reimann, Jens Güdde, Kenta Kuroda, and Ulrich Höfer — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg

The electronic structure and ultrafast electron dynamics of the *p*-doped topological insulator $Sb_2Te_3$ and its derivative $Sb_2Te_2Se$ was investigated by means of time- and angle-resolved two-photon photoemission (2PPE). Our experiment reveal that the massless Dirac-cone like energy dispersion of topological surface states is realized above the Fermi energy in both materials. In agreement with theoretical predictions we find that the unoccupied bands of $Sb_2Te_2Se$ are shifted to higher energies as compared to $Sb_2Te_3$. The observed electron dynamics in the topological surface state (TSS) of both materials is, however, very similar, which is a signature that the decay is dominated by the number of unoccupied states in the valence band. At lower temperatures at which the electron mobility in the bulk is enhanced, the decay becomes surprisingly faster, which strongly indicates that transport perpendicular to the surface into the bulk conduction band is important for the decay of the TSS.

O 69.4 Wed 18:15 Poster A

**Towards ultrafast X-ray condensed matter physics with MHz repetition rate HHG sources** — •R. Klas[1,2], S. Hädrich[2,3], J. Rothhardt[2,3], S. Eich[1], M. Barkowski[1], J. Urbancic[1], M. Aeschlimann[1], J. Limpert[2,3,4], and S. Mathias[1] — [1]TU Kaiserslautern and Research Center OPTIMAS, Kaiserslautern — [2]Friedrich Schiller University Jena, Abbe Center of Photonics, Institute of Applied Physics, Jena — [3]Helmholtz-Institute Jena, Jena — [4]Fraunhofer Institute for Applied Optics and Precision Engineering, Jena

In recent years, an increasing number of ultrafast material science experiments are based on the use of table-top high-harmonic generation (HHG) lightsources [1,2]. Despite the huge success of these first experiments, a major drawback has been the limited repetition rate of these lightsources, in particular with respect to all types of photoemission experiments. Here, we combine newly developed high-repetition rate HHG sources [3,4] with state-of-the-art element-specific magneto-optical Kerr experiments. The chances and prospects for future ultrafast materials science experiments with these lightsources will be discussed.

[1] S. Mathias et al., Springer, chapter in "Ultrafast Nonlinear Optics", Editors R. Thomson, C. Leburn, D. Reid (2013)
[2] S. Mathias et al., JESRP 189, 164 (2014)
[3] J. Rothhardt et al., Opt. Lett. 39, 5224 (2014)
[4] S. Hädrich et al., Nat Phot 8, 779 (2014)

O 69.5 Wed 18:15 Poster A

**Coherent and incoherent electronic excitations in the Mott insulator $1T$-TaS$_2$** — •Manuel Ligges[1], Isabella Avigo[1], Simon Freutel[1], Matthias Kalläne[2], Ping Zhou[1], Lutz Kipp[2], Kai Rossnagel[2], and Uwe Bovensiepen[1] — [1]Fakultät für Physik und Zentrum für Nanointegration, Universität Duisburg-Essen — [2]Institut für Experimentelle und Angewandte Physik, Universität Kiel

Using femtosecond time- and angle-resolved photoemission spectroscopy we study the partial quench of charge order in the prototypical Mott insulator $1T$-TaS$_2$ after optical excitation. An unoccupied electronic state is observed in the correlated (spectrally gapped) commensurate and nearly-commensurate charge density wave (CDW) phases of the material that is found to be abscent in the (almost metallic) incommensurate CDW phase and, thus, appears to be a direct measure of short range correlations. From its energetic position ($E$-$E_F$=170 meV), this state might be identified as the upper Hubbard band. The population of this coherent feature follows the temporal laser pulse profile and differs significantly from the incoherent electronic population dynamics in the same energetic window and $\boldsymbol{k}$-region ($\bar{\Gamma}$) that shows clear life time effects ($\tau \approx 150$ fs). We conclude that this state directly reflects the presence of charge order in the system which promptly collapses in the presence of the laser field, leaving the system behind in a state similar to the high-temperature metallic phase.

O 69.6 Wed 18:15 Poster A

**2D RABBITT spectroscopy for the investigation of attosecond dynamics** — •Martin Piecuch, Martin Aeschlimann, and Stefan Mathias — University of Kaiserslautern and Research Center OPTIMAS, TU Kaiserslautern, 67663 Kaiserslautern, Germany

Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) is a powerful and well-established method for attosecond pulse characterization [Paul et al., Science 292,1689 (2001)]. Additionally, the RABBITT technique has been very useful to measure and understand basic dynamics in the high-harmonic generation process itself in the past. Here, we present theoretical calculations of an extension of the RABBITT scheme by combining it with modern techniques derived from 2D spectroscopy: excitation with multiple laser pulses, and phase cycling to select specific coherence pathways. We show that these methods open up new and powerful routes to study attosecond dynamics in atoms, molecules, and materials in the future.

O 69.7 Wed 18:15 Poster A

**Electronic Structure and Excitation Dynamics of the CuPc/PTCDA/Ag(111) Heterointerface** — •Jonas Zimmermann, Andreas Namgalies, Nico Armbrust, and Ulrich Höfer — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg

We grow well-defined monolayers of copper(II)phthalocyanine (CuPc) on top of monolayers of perylene-tetracarboxylic acid dianhydride (PTCDA) on Ag(111) as model systems for organic donor-acceptor heterointerfaces. We employ time-resolved two-photon photoemission (2PPE) to examine the dynamics of charge transfer processes at these interfaces. An optical parametric oscillator (OPO) enables us to tune the pump photon energy to the HOMO-LUMO transition of CuPc. The time-resolved 2PPE spectra reveal the subsequent decay of the excitation. In case of the PTCDA monolayer the excited electron cannot be transferred from the LUMO of CuPc to unoccupied PTCDA orbitals because the former LUMO of PTCDA is shifted below the Fermi level by chemisorption. Instead, we observe an electron transfer into the interface state of PCTDA/Ag(111). This metal-organic hybrid state arises from the Shockley surface state of clean Ag(111) and is located at 0.6 eV above the Fermi level. The electron transfer from CuPc shows up as resonantly enhanced and temporarily delayed 2PPE intensity of the interface state when the pump photon energy is tuned through the CuPc HOMO-LUMO transition at 1.8 eV.

O 69.8 Wed 18:15 Poster A

**Influence of the density of states on nonequilibrium dynamics in metals** — •Sebastian Weber[1], Benedikt Y. Mueller[2], and Baerbel Rethfeld[1] — [1]Technische Universität Kaiserslautern, Germany — [2]Max-Planck-Institut für Intelligente Systeme, Germany

After excitation with an ultrashort laser pulse, the electrons in a metal are in a strong nonequilibrium state. During thermalization, they interact also with the lattice, transferring energy to the phonons. On the basis of complete Boltzmann-type collision integrals, a method allowing to treat materials with an arbitrary density of states has been developed [Phys. Rev. B 87, 035139 (2013)]. This method provides insights into the response of different material classes to ultrafast laser excitation. Note that this approach also opened the way to describe ultrafast magnetization dynamics, see [Phys. Rev. Lett. 111, 167204 (2013)].

Here, we study the microscopic relaxation processes, in particular thermalization and the electron-phonon coupling strength under nonequilibrium conditions. Results for gold [Appl. Surf. Sci. 302, 24 (2014)] are compared to those obtained for other metals like copper and silver.

O 69.9 Wed 18:15 Poster A

**Time-resolved photoelectron spectroscopy in a back-pump/front-probe geometry** — •Gerrit Horstmann, Simon Lange, Claus Ropers, and Sascha Schäfer — IV. Physical Institute, Friedrich-Hund-Platz 1, University of Göttingen, Germany

The combination of ultrafast pump-probe techniques with angle-resolved photoelectron spectroscopy (ARPES) has enabled the detailed investigation of ultrafast electron dynamics in condensed matter. However, the influence of fundamental transport processes such as electron scattering in bulk material or at interfaces as well as propagation through functional layers is difficult to access in time-resolved photoelectron spectroscopy (tr-PES). Here, we present a flexible tr-PES setup allowing for optical sample excitation at the backside of an ultrathin film combined with time- and angle-resolved photoelectron probing at the film's front surface. In a first step, we study the photoemission from back-pumped homogeneous metal films on sapphire substrates, characterizing the delay-dependent spectral and angular distributions of photoemitted electrons. Possible future applications are discussed, e.g., for the investigation of optically-triggered conductivity changes in correlated materials.

O 69.10 Wed 18:15 Poster A

**Correlation of Chirp and Delay in Attosecond Streaking Measurements from W Surfaces** — •Andreas Kim[1], Johannes Barth[1], Peter Feulner[1], Konrad Hütten[1], Reinhard Kienberger[1], Ferenc Krausz[2], and Stefan Neppl[3] — [1]TU-München, Physikdepartment, Garching, Germany — [2]MPI für Quantenoptik, Garching, Germany — [3]LBNL, Berkeley, USA

Attosecond streaking, i.e., the momentum-modulation of photoelectrons emitted by ultrashort XUV pulses into the strong field of a synchronized IR laser [R. Kienberger et al., Nature 427, 817], enables chronoscopy on the attosecond timescale. It has been used to explore time delays between the release of photoelectrons from different electronic levels with unprecedented resolution, from isolated particles [e.g. M. Schultze et al., Science 328, 1658] and condensed matter [A. Cavalieri et al., Nature 449, 1029; S. Neppl et al., PRL 109, 087401]. This method also provides information on characteristic parameters of the ultrashort XUV pulses like duration, central energy and chirp, i.e., the temporal variation of the photon energy across the pulse. We measure a direct correlation between the wave-packet chirp and relative time delay between conduction band and W4f core-level photoemission, with different chirp values for conduction band and W4f electrons. We show that reliable information on the excitation pulse, the electronic transport and screening processes can only be derived from such attosecond streaking data, if detection and evaluation artifacts are identified and accounted for. Supported by the Deutsche Forschungsgemeinschaft (Munich Centre for Advanced Photonics; MAP B.1.3 & B.1.4)

# O 70: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses

Time: Wednesday 18:15–21:00 Location: Poster A

O 70.1 Wed 18:15 Poster A

**Lattice dynamics in few-layer Molybdenum disulfide investigated by Ultrafast Electron Diffraction** — •Marlene Adrian, Christian Gerbig, Silvio Morgenstern, Christian Sarpe, Arne Senftleben, and Thomas Baumert — University of Kassel, Institute of Physics (CINSaT), D-34132 Kassel, Germany

Molybdenum disulfide (MoS2) is a prototype example for transition metal dichalcogenides (TMDs), which form a group of van der Waals bound two-dimensional layered materials [1]. Due to their unique electronic and optical properties such as circular dichroism, a strong spin-orbit coupling and a shift from indirect to direct band gap semiconductor with decreasing film thickness from bulk to monolayer, TMDs are interesting for both fundamental research and industrial applications such as electronic devices [2].

We study dynamical processes following optical excitation in few-layer MoS2 by means of time-resolved Ultrafast Electron Diffraction (UED), which has become a promising technique to directly provide insights into dynamics in crystalline solids at the microscopic level with a sub-picosecond temporal resolution [3, 4]. Our highly compact UED-setup is fully characterized by experiments and many-body simulations [5].

[1] S. Z. Butler et al., ACS Nano 7, 2898 (2013).
[2] G. Berghäuser and E. Malic, arXiv:1311.1045 (2014).
[3] A. H. Zewail, J. Phys. Chem. 98, 2782-2796 (1994).
[4] B. Siwick and D. Miller, Science 302, 1382-1385 (2003).
[5] C. Gerbig et al., in preparation (2014).

O 70.2 Wed 18:15 Poster A

**Resolution studies on a compact femtosecond transmission electron diffractometer and phonon decay in single crystalline graphite** — Christian Gerbig[1], •Silvio Morgenstern[1], Marlene Adrian[1], Christian Sarpe[1], Arne Senftleben[1], Matthias Wollenhaupt[2], and Thomas Baumert[1] — [1]University of Kassel, Institute of Physics (CINSaT), D-34132 Kassel, Germany — [2]University of Oldenburg, Institute of Physics, D-26111 Oldenburg, Germans

Time-resolved diffraction, using x-ray or electron probes, has become a promising technique to directly provide insights into dynamics at the molecular level with ultrafast precision [1]. We study dynamical processes in single crystalline graphite by means of ultrafast electron diffraction in order to expand the understanding of phonon generation and decay mechanisms being essential for future carbon based electronic devices [2].

Our highly compact DC electron diffractometer is fully characterized by experiments and N-body simulations. At balanced conditions a temporal resolution of 200 fs along with high-definition diffraction is achieved for dynamical studies on graphite single crystals in a maintainable measurement time [3]. We further present generation and decay processes of incoherent as well as coherent phonons in graphite as a function of film thickness down to few-layer graphene.

[1] M. Chergui & A. H. Zewail, Chem. Phys. Chem. 10, 28 (2009).
[2] T. Kampfrath et al., Phys. Rev. Lett. 95, 187403 (2005).
[3] G. Sciaini & R. J. D. Miller, Rep. Prog. Phys. 74, 096101 (2011).

O 70.3 Wed 18:15 Poster A

**Laser-induced heating of nano-crystalline graphene monitored by Ultrafast Electron Diffraction** — •Silvio Morgenstern, Christian Gerbig, Marlene Adrian, Xaver Holzapfel, Arne Senftleben, Matthias Wollenhaupt, and Thomas Baumert — Universität Kassel, Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), D - 34132 Kassel, Germany

Ultrafast Electron Diffraction (UED) has lately become one of the most promising techniques to directly provide insights into fundamental dynamics in solids at the microscopic level and on the pico- to sub-picosecond timescale [1,2]. In this contribution we present our UED setup to reach a high spatial and temporal resolution below 200 fs [3]. Additionally we present first results of time-resolved diffraction experiments on nano-crystalline graphene (NC graphen) [4] and discuss the possibility of time-resolved observations of out-of-plane dynamics in such materials [5]. Finally we compare our results to results from CVD graphene [6].

[1] A. H. Zewail, J. Phys. Chem. 98, 2782-2796 (1994), [2] B. Siwick & D. Miller, Science 302, (5649), 1382-1385 (2003), [3] C. T. Hebeisen, Opt. Letters Vol. 31, No. 23, 3571 (2006) [4] A. Truchanin, ACS Nano Vol. 5, No. 5, 3896 (2011), [5] J. C. Meyer, Nature 446, 60-63 (2007), [6] M. Schäfer, New J. Phys. 13, 063030 (2011)

O 70.4 Wed 18:15 Poster A

**Laser-induced ultrafast phenomena in Ge** — •Tobias Zier, Eeuwe S. Zijlstra, and Martin E. Garcia — University of Kassel, Germany

The extreme non-equilibrium state in a solid induced by an intense femtosecond laser pulse excitation, in which the electrons have a temperature of several 10 000 K and the atoms remain nearly unaffected, allows to access pathways that are not accessible in thermodynamic equilibrium and therefore gives rise to interesting effects. Prominent phenomena are thermal phonon squeezing, nonthermal melting and solid-to-solid phase transitions. We performed ab initio Molecular-Dynamics simulations of laser-excited germanium in order to study the structural response of this semiconducting material as a function of the fluence and compared our results to recent experimental findings [1].

[1] Trigo, M et al., Nature Phys. 9, 790 (2013)

O 70.5 Wed 18:15 Poster A

**Delayed surface phonon excitation in Bi(111) films** — Verena N. Tinnemann, Tim Frigge, •Boris Krenzer, Bernd Hafke, Annika Kalus, Carla Streubühr, Ping Zhou, Manuel Ligges, Dietrich von der Linde, Uwe Bovensiepen, and Michael Horn-von Hoegen — Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg

We used ultra-fast reflection high energy electron diffraction to follow the excitation of surface phonons on an epitaxial Bi(111) film on Si(111) upon impulsive excitation with a femtosecond laserpulse. The thermal motion of the atoms is determined from the transient intensity drop described through the Debye-Waller effect. The excitation of vibrational motion of the surface atoms occurs with a time constant of 12 ps. For strained Bi(111) films grown on Si(001) we observe a bi-exponential behaviour with a fast (< 6 ps) and slow, temperature dependent (12 to 60 ps) component for the vibrational excitation of the surface. We attribute the different response to the presence of an electronic surface state for relaxed 4.5 nm thick Bi films on Si(111) while this state is absent on the strained 4.5 nm thick Bi films grown on Si(001). In the first case the excited carriers populate the surface state without heating the bulk and weak electron phonon coupling excite surface phonons on a timescale of 12 ps. On Si(001) the excited carriers remain in the bulk of the film, couple to phonons on a much faster time scale < 6 ps, and surface phonons are then excited only by anharmonic coupling between bulk and surface phonon modes.

O 70.6 Wed 18:15 Poster A

**Sub 400 fs temporal resolution in reflection high energy electrondiffraction at surfaces** — •Tim Frigge, Bernd Hafke, Boris Krenzer, Carla Streubühr, Ping Zhou, Manuel Ligges, Dietrich von der Linde, Uwe Bovensiepen, and Michael Horn-von Hoegen — Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg

In time resolved reflection high energy electron diffraction at surfaces an ultra short electron pulse probes the surface at grazing incidence. At energies of 30 keV the electrons travel at 1/3 of the speed of light and require 20 ps to traverse a typical sample width of 2 mm. For pump-pulses at normal incidence the sample surface is excited simultaneously. This resulting geometric velocity mismatch limits the overall experimental temporal resolution. Employing a tilted pulse front scheme for the laser excitation we are able to overcome this limitation and obtain a temporal resolution of 600 fs when probing the entire sample width. Reduction of the electron number per pulse and probing only a narrow part of the sample further improves the temporal resolution to less than 400 fs without electron pulse compression. Temporal broadening due to vaccum dispersion on the 8 cm distance between photocathode and sample is minimized by the narrow initial electron energy spread of only 100 meV of the back illuminated Au photocathode. Additionally, a new electron gun design ensures a vertical coherence length of more than 30 nm. An integration time of 10 s is sufficient for good statistics for one diffraction image, i.e. a diffraction movie with 100 frames at 50 fs delay steps is recorded in less than 30 min.

O 70.7 Wed 18:15 Poster A

**Quantum coherent interaction of electrons with optical near-fields in an ultrafast electron microscope** — Armin Feist, •Katharina E. Echternkamp, Jakob Schauss, Sergey V. Yalunin, Sascha Schäfer, and Claus Ropers — 4th Physical Institute, University of Göttingen, Göttingen, Germany

Harnessing the coherent interaction of light and matter is expected to play a key role for future quantum computation, communication and metrology. Here, we present the coherent quantum state manipulation of free electrons in an ultrafast electron microscope [1]. Ultrafast transmission electron microscopy (UTEM) is a laser pump/electron probe technique, enabling the investigation of ultrafast processes on the nanometer length scale [2]. We have recently implemented an UTEM by modifying a commercial Schottky field emission TEM (JEOL JEM-2100F). In our experiments, the electron beam is focused to a spot close to a surface of a conical gold tip. The high spatial confinement of the optically excited near-field of the nanostructure allows for an otherwise forbidden dipolar coupling between the free electrons and photons. In the electron kinetic energy spectra, we observe the creation of spectral sidebands, stemming from the absorption and emission of multiple photons [3]. The field dependent sideband populations reveal the quantum coherence of the process.

[1] A. Feist *et al.*, submitted (2014).

[2] A.H. Zewail, Science, **328**, 187 (2010).

[3] B. Barwick *et al.*, Nature, **462**,902 (2009).

O 70.8 Wed 18:15 Poster A

**Classical potential for femtosecond-laser excited silicon** — •Bernd Bauerhenne, Tobias Zier, Eeuwe S. Zijlstra, and Martin E. Garcia — Theoretische Physik - Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Using femtosecond-laser pulses it is possible to manipulate solids in unconventional ways, which can, for example, be used to write structures on surfaces. In order to understand and predict such processes an effective classical potential is a key tool. Here we developed a new potential for laser-excited silicon starting from known classical potentials by fitting realistic density functional theory simulations of nonthermal melting of silicon [1]. We also optimized the potential function. As first results, we found, that our new potential describes accurately the fractional diffusion during ultrafast melting of silicon and that we can reproduce both the time-resolved pair correlation function and the angular distribution function.

[1] E. S. Zijlstra, A. Kalitsov, T. Zier, and M. E. Garcia, Fractional diffusion in silicon, Adv. Mater. 25, pp. 5605-5608, 2013.

O 70.9 Wed 18:15 Poster A

**Imaging, diffraction, and interferometry with ultrabright electron pulses** — •Robert Bücker[1], Albert Casandruc[1], Chiwon Lee[1], Philipp Pelz[1], Haider Zia[1], Günther Kassier[1], and R. J. Dwayne Miller[1,2] — [1]Max Planck Institute for the Structure and Dynamics of Matter, CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany — [2]Departments of Chemistry and Physics, University of Toronto, Toronto Ontario, M5S 3H6, Canada

High-brightness electron pulses in the ns to $\mu$s regime promise to be the optimal probe for determination of structure and irreversible dynamics in biological systems. Combined with the favorable elastic-to-inelastic ratio of electron scattering, the large transverse coherence length achievable with nanometric emitters allows maximizing the information content per scattering event, hence keeping radiation damage at a minimum and allowing to extract sufficient structural information even from small samples, such as nanocrystals. In this contribution, we present the concept, implementation, and first results of experiments tailored to these goals. This comprises both field emission-based electron diffraction beam lines in the range from few to hundreds of kilovolts, as well as transmission electron microscopes enhanced with pulsed sources and high-speed imaging detectors.

Particular attention will be paid to a compact 12 kV apparatus, designed for interferometric characterization of various kinds of pulsed electron sources, as well as proof-of-principle demonstrations of coherent diffractive schemes with bright many-electron pulses.

O 70.10 Wed 18:15 Poster A

**Characterization of a picosecond electron gun for diffraction experiments** — •Nele L. M. Müller[1], Sebastian Trippel[1], Terence G. Mullins[1], Karol Długołecki[1], and Jochen Küpper[1,2,3] — [1]Center for Free-Electron Laser Science, DESY, Hamburg — [2]The Hamburg Center for Ultrafast Imaging, Hamburg — [3]Department of Physics, University of Hamburg

The aim of the presented work is to investigate the structure and dynamics of molecules in the gas-phase by electron diffraction experiments. The contribution presents our newly set-up electron gun that will be combined with an existing controlled-molecules apparatus [1]. The developed DC electron gun can produce up to 10 million electrons per pulse and uses an electro-static lens for focusing. The expected pulse durations are tens of picoseconds. The focusing electrodes are arranged in a configuration similar to a Velocity Map Imaging spectrometer. Besides focusing this can be used to measure the spatial and velocity distribution of the electron pulse when emitting from the cathode. In combination with electron trajectory simulations this allows for further characterization of the electron beam, as for example the determination of pulse duration and coherence length. Electron diffraction data from solid state and gaseous samples will be presented.

[1]Trippel et al., *Mol. Phys.* **111**, 1738-1743 (2013)

O 70.11 Wed 18:15 Poster A

**UED@SLAC: Structural dynamics in laser-excited solids studied by MeV electron diffraction** — •Klaus Sokolowski-Tinten[1], Renkai Li[2], Alex H. Reid[2], Stephen P. Weathersby[2], Garth Brown[2], Martin Centurion[3], Tyler Chase[2], Ryan Coffee[2], Jeff Corbett[2], Josef C. Frisch[2], Markus Guehr[2], Nick Hartmann[2], Carsten Hast[2], Ling Ho[2], Michael Horn von Hoegen[1], David Janoschka[1], Keith Jobe[2], Erik Jongewaard[2], James R. Lewandowski[2], Justin E. May[2], Dough McCormick[2], Frank Meyer zu Heringdorf[1], Xiaozhe Shen[2], Christian Witt[1], Juhao Wu[2], Jie Yang[2], Dürr Hermann[2], and Xijie Wang[2] — [1]Faculty of Physics and Centre for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Lotharstraße 1, 47048 Duisburg, Germany — [2]SLAC National Accelerator Laboratory, Menlo Park, USA — [3]University of Nebraska-Lincoln, Lincoln, USA

With the aim to provide synergistic and complementary experimental capabilities for the study of ultrafast processes at their fundamental length and time scales SLAC National Laboratory, operator of the world's first hard X-ray free electron laser, the Linear Coherent Light Source, has recently started an initiative for ultrafast electron scattering and microscopy. This contribution will discuss the setup for femtosecond time-resolved MeV electron diffraction, which has been brought into operation over the last few months at SLAC's Accelerator Structure Test Area (ASTA), as well as results from first user experiments addressing the ultrafast lattice response in laser-excited thin Bismuth-films.

O 70.12 Wed 18:15 Poster A

**Miniaturized photoelectron gun for ultrafast low-energy electron diffraction** — •Gero Storeck, Simon Schweda, Max Gulde, Sebastian Schramm, Sascha Schäfer, and Claus Ropers — IV. Physical Institute, University of Göttingen, 37077 Göttingen, Germany

Probing structural dynamics at surfaces with high temporal resolution provides insights into a rich class of phenomena, which are unique to quasi-two-dimensional systems [1,2]. Utilizing a laser-pump/electron-probe scheme, ultrafast low-energy electron diffraction (ULEED) promises direct access to such processes, provided that the generation of well-collimated ultrashort low-energy electron pulses is achieved. Recently, nanometric photocathodes were shown to minimize spatial and temporal pulse broadening at low electron energies, resulting in a first ULEED experiment [3]. Using this experimental setup, laser-driven dynamics in a polymer/graphene bilayer were resolved with a temporal resolution of 2 ps in a transmission geometry. In a further development, we present the design of a compact pulsed electron gun allowing for ultrafast low-energy electron experiments in backscattering diffraction. First applications to graphene on silicon carbide are shown.

[1] A. Hanisch-Blicharski et al., Ultramicroscopy 127, 2-8 (2013). [2] J. M. Kosterlitz et al., J. Phys. Chem. 6, 1181-1203 (1973). [3] M. Gulde et al., Science 354, 200 (2014).

O 70.13 Wed 18:15 Poster A

**Lattice response with respect to the orientation of the crystal to the femtosecond laser excitation observed by time-resolved electron diffraction** — Carla Streubühr, •Ping Zhou, Manuel Ligges, Klaus Sokolowski-Tinten, Thomas Payer, Frank Meyer zu Heringdorf, and Michael Horn-von Hoegen — Fakultät für Physik und Zentrum für Nanointegration, Universität Duisburg-Essen

One of the fundamental questions in the field of ultrafast structural dynamics is the time scale for the energy transfer between the electron and phonon subsystem of a solid after femtosecond optical excitation. For crystalline materials, especially for layered materials like graphite or most of superconductors, the material properties depend strongly on the symmetries of the crystals. The excitation and relaxation of the lattice cannot be treated as symmetrical. The advantage of electron diffraction is the ability to map many diffraction orders at the same time and, thus, obtain rich structural information. We present here results of time resolved electron diffraction experiments on Bismuth and Nickel membranes to demonstrate the difference of the energy transfer of hot electrons to the lattice depending on the direction of the displacements. Besides the disordered thermal displacement, strain waves can be generated. They propagate between the surfaces and influence on the diffraction intensity in different way depending on the materials and the diffraction geometries. By using a simple model we could extracted strain wave information from the disordered thermal displacement and get the frequency and damping of the strain wave.

O 70.14 Wed 18:15 Poster A

**Observation of heat transport by time-resolved x-ray diffraction using a conventional microfocus x-rax tube** — •Mathias Sander[1], Peter Gaal[2], and Matias Bargheer[1] — [1]Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Str. 24-25,14476 Potsdam,Germany — [2]Institut für Nanostrukturen und Festkörperphysik, Universität Hamburg, Jungiusstr. 11 20355 Hamburg, Germany

We demonstrate a table top setup for real-time observation of heat transport in crystalline layered structures via time-resolved x-ray diffraction on timescales from nanoseconds to milliseconds. The sample is excited either by an electronically heated microchip or by short laser pulses depending on the relevant timescale. The x-rays are generated by a conventional microfocus x-ray tube, focused by a polycapillary x-ray optic and monochromatized by a single reflection, e.g. from a Si or HAPG crystal. X-rays diffracted by the sample are detected in a fast x-ray phosphor and a photomultiplier and fed into a time-correlated single-photon counting module, which records histograms of events along the entire pump-probe delay. The resulting data shows time-dependent angular shifts of Bragg reflections which are interpreted as thermal diffusion dynamics on nano- and micrometer length scales.

O 70.15 Wed 18:15 Poster A

**Inelastic scattering of low-energy electrons by optical near-fields** — •Lars Drögemüller, Sascha Schäfer, and Claus Ropers — IV. Physical Institute, University of Göttingen, 37077 Göttingen, Germany

Ultrafast low-energy electron diffraction (ULEED) is a new tool in ultrafast surface science [1], which utilizes a laser-pump/electron-probe scheme to study the structural dynamics at surfaces and ultrathin films. For the future development of ULEED, a reliable and quantitative temporal characterization of the employed low-energy electron pulses is required. While inelastic near-field scattering was successfully applied for pulse characterization at high-energies [2, 3], its extension to the low-energy regime is challenging.

In this study, numerical simulations based on the finite-element-method were performed to investigate near-field electron scattering at low energies. Plasmonic effects and optical resonances in tailored nanostructures were considered to optimize the electron-photon scattering cross section.

[1] M. Gulde et al., Science 345, 200-4 (2014). [2] B. Barwick, D. J. Flannigan A. H. Zewail, Nature 462, 902-6 (2009). [3] F. O. Kirchner, A. Gliserin, F. Krausz, P. Baum, Nature Photonics 8, 52-57 (2013).

O 70.16 Wed 18:15 Poster A

**Cooperative atomic motion probed by femtosecond electron diffraction** — Maximilian Eichberger[1] and •Jure Demsar[2] — [1]Department of Physics, University of Konstanz — [2]Institute of Physics, Johannes Gutenberg-University Mainz

Recently, several studies of light-induced suppression or quenching of charge density wave order were performed using ultrafast diffraction methods. This coherent process, which takes place on a 100 femtosecond timescale (a fraction of a period of the corresponding amplitude mode), is accompanied by a rapid sub-picosecond energy transfer to the lattice via strong electron-phonon and phonon-phonon scattering. Both processes, the coherent order parameter dynamics and the incoherent redistribution of energy among different subsystems, affect the diffraction pattern. For their comparable timescales they are hard to distinguish based on the dynamics alone.

Using ultrafast electron diffraction in transmission we show, that by simultaneous tracking the intensities of lattice and super-lattice diffraction peaks for multiple diffraction orders (this being one of the main advantages of ultrafast electron diffraction against femtosecond X-ray methods) the two processes can be effectively disentangled.

O 70.17 Wed 18:15 Poster A

**Coherent and incoherent electron-phonon coupling in graphite observed with radio-frequency compressed ultrafast electron diffraction** — •Bradley Siwick, Robert Chatelain, Vance Morrison, Bart Klarenaar, and Jean-Phillipe Boisvert — McGill University, Center for the Physics of Materials, Montreal, Canada

Radio-frequency compressed ultrafast electron diffraction has been used to probe the coherent and incoherent coupling of impulsive electronic excitation at 1.55 eV (800 nm) to optical and acoustic phonon modes directly from the perspective of the lattice degrees of freedom. A bi-exponential suppression of diffracted intensity due to relaxation of the electronic system into incoherent phonons is observed, with the 250 fs fast contribution dominated by coupling to the E2g2 optical phonon mode at the $\Gamma$-point ($\Gamma$-E2g2) and A1 optical phonon mode at the K-point (K-A1). Both modes have Kohn anomalies at these points in the Brillouin zone. In addition, electronic excitation leads to both in-plane and out-of-plane coherent lattice responses in graphite whose character we are able to fully determine based on spot positions and intensity modulations in the femtosecond electron diffraction data. The in-plane motion is specifically a $\Gamma$-point shearing mode of the graphene planes with an amplitude of approximately 0.06 pm and the out-of-plane motion an acoustic breathing mode response of the film.

O 70.18 Wed 18:15 Poster A

**Structure and Dynamics with Ultrafast Electron Microscopes** — •Bradley Siwick[1], Mark Stern[1], Lily Nikolova[2], Federico Rosei[2], Jennifer McLeod[2], Tom Lagrange[3], and Bryan Reed[3] — [1]McGill University, Center for the Physics of Materials, Montreal, Canada — [2]Institut National de la Recherche Scientifique, Centre Énergie, Matériaux, Télécommunications, Varennes, Canada — [3]Condensed Matter and Materials Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, USA

This poster will describe a series of recent experiments on explosive crystallization in amorphous germanium, where we have directly "watched" the nano-micro structural evolution in the material using dynamic transmission electron microscopy (DTEM). Direct visualization of the crystallization front allows for time-resolved snapshots of the initiation and roughening of dendrites on sub-microsecond time scales and a rapid transition to a ledge-like growth mechanism at longer times. Direct observations of the speed of the explosive crystallization front as it evolves along a laser-imprinted temperature gradient have been used to experimentally determine the complete interface response function (i.e., the temperature-dependent front propagation speed) for this process, which reaches a peak of 16m/s. These result suggests a modification to the liquid-mediated mechanism commonly used to describe this process that replaces the phase change at the leading amorphous-liquid interface with a change in bonding character (from covalent to metallic) occurring in the hot amorphous material.

# O 71: Surface Dynamics

Time: Wednesday 18:15–21:00 Location: Poster A

O 71.1 Wed 18:15 Poster A

**Femtosecond Laser-induced Desorption of Atomic and Molecular Hydrogen Isotopes from Graphite** — •Robert Frigge, John D. Thrower, and Helmut Zacharias — Physikalisches Institut, Universität Münster, Germany

In the interstellar cycle of matter the formation of molecular hydrogen by recombination of adsorbed atoms on dust particles is an important process. In photon dominated regions this process is likely to be induced by radiation. Here, we examine the desorption of H and $H_2$ from HOPG following surface excitation with fs-laser pulses at $\lambda = 400$ nm. Desorbed neutral species are analyzed by state-selective ionization and a time-of-flight detector. The desorbing H atoms show three different kinetic energy distributions, while for $H_2$ only a very low energy distribution with $<E_{kin}> = 60$ meV is found. Electron scattering calculations [1] have been performed, taking into account different H-graphite adsorption potentials appropriate for different adsorption sites(para-, ortho- configuration) [2]. A nonlinear fluence dependence of the atomic desorption yield allows two-pulse correlation measurements. For the para-sites a FWHM of 600 fs can be explained by coupling the desorption to electrons, while the ortho-sites yield a distribution with a dip at 1 ps which cannot be explained by this model. We consider the possibility that the excitation of optical phonons, which occurs within 1 ps [3], is responsible for this dip.

[1]R. Frigge et al., Phys. Rev. Lett., **104**, 256102 (2010)
[2]L. Hornekær et al., Phys. Rev. Lett., **97**, 186102 (2006)
[3]M. Breusing et al., Phys. Rev. Lett., **102**, 086809 (2009)

O 71.2 Wed 18:15 Poster A

**Thermal desorption studies of ammonia from single crystal and polycrystalline forsterite** — •Tushar Suhasaria, John Thrower, and Helmut Zacharias — Physikalisches Institut, WWU Münster, Germany

Olivine [$Mg_{2x}Fe_{2-2x}SiO_4$] is an abundant silicate mineral that constitutes a major component of interstellar dust grains [1]. Forsterite [$Mg_2SiO_4$], the magnesium rich member of the olivine family, is the most abundant of crystalline silicates as suggested by the infrared space observatory (ISO) mission [2]. In cold, dense molecular clouds, various molecules collide with and stick to these dust grains and form icy mantles. Forsterite can thus be used as chemically simple dust grain model to understand the interaction between these adsorbed molecules and the grain surface. In the present work we use temperature programmed desorption (TPD) to investigate the desorption kinetics of ammonia ($NH_3$) ices on both single crystal and polycrystalline forsterite surfaces. A desorption energy of 25.8 $kJmol^{-1}$ was obtained for multilayer $NH_3$ desorption from both surfaces. For the low coverage regime, a distribution of binding energy sites on the forsterite surface was revealed, depending on the nature of the surface. These desorption kinetics parameter are useful to be incorporated into chemical models [3] to understand the gas-grain interaction in more details.

1.Campins, H., & Ryan, E. V. 1989, Astrophys. J., 341, 1059.
2.Molster, F. J., Waters, L. B. F. M., & Tielens, A. G. G. M. 2002, Astron. Astrophys., 382, 222.
3.Garrod, R. T., 2013, Astrophys. J., 765, 60

O 71.3 Wed 18:15 Poster A

**The role of non-equilibrium dynamics in photo-induced phase transitions of correlated materials** — •S. Eich[1], S. Mathias[1], J. Urbancic[1], A.V. Carr[2], A. Stange[3], S. Michael[1], T. Popmintchev[2], T. Rohwer[3], M. Wiesenmayer[1], A. Ruffing[1], S. Jakobs[1], S. Hellmann[3], P. Matyba[2], C. Chen[2], L. Kipp[3], M. Bauer[3], M.M. Murnane[2], H.C. Schneider[1], K. Rossnagel[3], H.C. Kapteyn[2], and M. Aeschlimann[1] — [1]TU Kaiserslautern and Research Center OPTIMAS, 67663 Kaiserslautern, Germany — [2]JILA, University of Colorado and NIST, Boulder, Colorado 80309-0440, USA — [3]Institute of Experimental and Applied Physics, University of Kiel, 24098 Kiel, Germany

We use femtosecond extreme-ultraviolet time- and angle-resolved photoelectron spectroscopy to study the ultrafast photo-induced suppression of the charge-density wave (CDW) in 1T-$TiSe_2$. In the following non-equilibrium electron dynamics after femtosecond laser excitation, we see that hot-carrier multiplication is the primary driver for the ultrafast CDW suppression. As soon as the optically excited carriers have relaxed to a quasi-equilibrium hot Fermi-distribution electron gas, the CDW suppression stops. Theoretical calculations of the hot-carrier scattering processes and the screening properties further link the carrier multiplication to the observed CDW gap dynamics.

O 71.4 Wed 18:15 Poster A

**Switching single azobenzene-based molecules by STM** — •Simon Jaekel[1], Knud Seufert[1], Christophe Nacci[1], Stefan Hecht[2], and Leonhard Grill[1] — [1]Department of Physical Chemistry, University of Graz, Austria — [2]Department of Organic Chemistry, Humboldt Universität zu Berlin, Germany

Molecular switches, i.e. molecules that exhibit at least two stable states * each with characteristic physical/chemical properties * that can be achieved reversibly by an external stimulus, represent an interesting class of functional molecules since they allow to get detailed insight in a basic chemical process, which is also relevant in biological processes. Furthermore, they are key in the field of Molecular Electronics that is based on the ultimate miniaturization of electronic devices down to the level of single molecules. Various molecular switches have been studied in the last years, many of them based on azobenzene, a prototype of a molecular switch that exhibits a trans and a cis isomer with different electronic structure and absorption behavior. The switching process can be induced either by light, by the tunneling electrons or the electric field in the junction of a scanning tunneling microscope (STM) [1,2]. Here, we present new results on a new type of azobenzene derivatives that are strongly decoupled from the metallic surface by additional side groups. Accordingly, we find a very different adsorption behavior since the molecule-surface interaction is strongly reduced and successfully observe switching processes.

[1] Choi et al., Phys. Rev. Lett. 96, 156106 (2006); [2] M. Alemani et al., J. Am. Chem. Soc., 128 (45), 14446 (2006);

O 71.5 Wed 18:15 Poster A

**The optical pump - X-Ray probe option of the LISA Liquid Surface Diffractometer** — •Jonas Warias[1], Christoph Lemke[1], Matthias Greve[1], Bridget Murphy[1,2], and Olaf Magnussen[1,2] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Germany — [2]Ruprecht Haensel Laboratory, Christian-Albrechts-Universität zu Kiel, Germany

The study of liquid surfaces and interfaces is of crucial importance for understanding many physical, chemical and biological phenomena. The LISA diffractometer [1], installed at the P08 beamline at the PETRA III synchrotron radiation source Hamburg, is a specialized instrument for hard X-ray scattering studies of liquid surfaces and interfaces. In the poster we describe ongoing work on extending this instrument's capabilities by an optical pump - X-ray probe option, which allows investigations of ultrafast processes at liquid interfaces. This includes installation of a 200 $\mu$J pulse energy fs-laser providing wavelengths from 210 nm to 2600 nm and optics for directing the laser pulse on the sample surface. The setup takes advantage of the specific design of LISA, where all scattering studies in the range from 6.5 keV to 29 keV can be performed without moving the sample. It will allow structural studies of non-equilibrium nanoscale processes at liquid interfaces and langmuir films. We thanks the BMBF (05K13FK2) for funding this project. [1] B.M. Murphy et al. J. Synchrotron Rad. 21 (2014) 45-46

# O 72: Graphene: Adsorption, Intercalation and Doping

Time: Wednesday 18:15–21:00 Location: Poster A

O 72.1 Wed 18:15 Poster A

**Defects and oxygen adatoms on graphene** — •Jan Gesenhues and Michael Rohlfing — Institut für Festkörpertheorie, Universität Münster, 48149 Münster, Germany

Oxygen adatoms on graphene are one of the ingredients of graphene oxide and are being discussed as building blocks to open a band gap in the Dirac cone of graphene. In our work we study graphene and oxygen adatoms within the theoretical framework of Tight-Binding and Density Functional Theory (DFT). The SIESTA program was used to carry out the DFT calculations.

In order to study defects in the graphene-layer a supercell approach is used. We take a closer look at the 5-7 defect and its effect on the electronic structure, in particular on the local density of states near the Fermi level. Furthermore we investigate the absorbtion of a single oxygen atom on the graphene-layer. Structure optimisations for various unit-cell sizes show that the oxygen atom equilibrium position is approximatly 2 Å above the layer, also resulting in a perpendicular displacement of the surrounding carbon atoms of a few 0.1 Å. The effetcs on the electronic structure are studied in comparison with the undisturbed system via the (local) density of states.

O 72.2 Wed 18:15 Poster A

**High Energy Ion Irradiation of Graphene** — Philipp Ernst[1], •Tobias Foller[1], Oliver Ochedowski[1], Roland Kozubek[1], Johannes Hopster[1], Jan Weber[2], Thorsten Balgar[2], and Marika Schleberger[1] — [1]Fakultät für Physik and CeNIDE, Universität Duisburg-Essen, 47048 Duisburg, Germany — [2]Fakultät für Chemie and CeNIDE, Universität Duisburg-Essen, 45117 Duisburg, Germany

In this presentation we show that single high energetic ions can be used as a tool to locally modify the properties of graphene. For this graphene samples are irradiated with swift heavy ions (typical kinetic energies in the rage of 100 MeV) and slow highly charged ions (potential energies up to 45 keV). By combining various analytical techniques like AFM, TEM, and Raman spectroscopy it is shown that depending on the irradiation parameters (ion energy, angle of incidence, choice of substrate for graphene) various modifications like local defective areas, pores in form of origami-like foldings and even doping can be introduced into the graphene sheet. Remarkably graphene field-effect measurements revealed that irradiation with swift heavy ions under perpendicular incidence with small fluences doubles the mobility of holes compared to the unirradiated sample. In contrast to this, irradiation with highly charged ions decrease the mobility. In this case defects are created which are subsequently hydrogenated as strongly suggested by sum frequency generation spectroscopy.

O 72.3 Wed 18:15 Poster A

**Initial stages of hydrogen intercalation of epitaxial graphene studied by XPS and LEEM** — •Julia Krone, Florian Speck, Felix Fromm, Martina Wanke, and Thomas Seyller — TU Chemnitz, Institut für Physik, Reichenhainer Straße 70, 09126 Chemnitz, Germany

During graphitization of SiC(0001) surfaces, a buffer layer (BL) is formed at the interface between graphene and the substrate. The BL is a graphene-like layer covalently bound to the SiC [1]. Hydrogen intercalation underneath the BL has been shown to decouple it from the substrate, thus converting it into quasi-freestanding monolayer graphene (QFMLG) [2]. This modification of the interface results in improved charge carrier mobility as compared to regular epitaxial graphene on SiC [3], making it an interesting material for electronic applications. Investigation of short-time annealing of the BL in molecular hydrogen could help to elucidate the initial stages of hydrogen intercalation and BL decoupling. In this work, we employ a combination of X-ray photoelectron spectroscopy, low-energy electron microscopy and low-energy electron diffraction to study the onset of QFMLG formation.

[1] K. V. Emtsev *et al.*, Phys. Rev. B **77**, 155303 (2008).
[2] C. Riedl *et al.*, Phys. Rev. Lett. **103**, 246804 (2009).
[3] F. Speck *et al.*, Appl. Phys. Lett. **99**, 122106 (2011).

O 72.4 Wed 18:15 Poster A

**XPS-investigation of the interaction of Lanthanides with epitaxial graphene** — •Sarah Roscher, Martina Wanke, and Thomas Seyller — Institut für Physik, TU Chemnitz, Reichenhainer Saße 70, D-09126 Chemnitz, Germany

Large-scale epitaxial graphene on silicon carbide is promising for electronic applications. Recently, interface engineering by intercalation of various elements underneath the buffer layer has been studied by several groups and it was demonstrated that elements of the Lanthanides are able to intercalate through epitaxial graphene [1-3]. In this study, erbium was deposited onto different graphene layers epitaxially grown on SiC(0001) and subsequently annealed in a temperature range of 300-950°C. X-ray photoelectron spectroscopy (XPS) was employed to determine the chemical composition of the sample, the intercalation, and the amount of doping. The XPS data indicate that subsequent heating to 850°C results in partial intercalation of the buffer layer. Because of erbium's high reactivity the influence of oxygen on the sample preparation demanded particular attention.

[1] S. Schumacher et al., Nano Lett. 13 (2013) 5013.
[2] S. Watcharinyanon et al., Graphene 2 (2013) 66.
[3] L. Huang et al., Appl. Phys. Lett. 99 (2011) 163107.

O 72.5 Wed 18:15 Poster A

**Structure and thermodynamic stability of graphene oxide** — •Sebastian Gsänger and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

A large set of possible atomic configurations of graphene oxide with different composition and coverage were investigated by density functional theory. The adsorption of hydroxyl groups and the formation of epoxides and endoperoxides was systematically evaluated. In a first series of calculations the mutual interaction and the preferred relative position of pairs of adsorbates was determined. Based on these results, promising low-energy adsorption pattern at high coverage were derived and their thermodynamic stability was analyzed in terms of a surface phase diagram. Finally, the possibility for formation of 1,4-endoperoxides on graphene oxide was investigated in detail.

O 72.6 Wed 18:15 Poster A

**Investigation of the molecular doping of graphene on 6H-SiC(0001)** — •Christian Raidel[1], Christian Heidrich[1], Julia Krone[1], Florian Speck[1], Peter Wehrfritz[1], Felix Fromm[1], Roland J. Koch[1], Peter Robaschik[2], Francisc Haidu[2], Ovidiu Gordan[2], Zoran Mazej[3], Dietrich R. T. Zahn[2], Thomas Seyller[1], and Martina Wanke[1] — [1]Technische Physik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany — [2]Halbleiterphysik, TU Chemnitz, Reichenhainer Str. 70, D-09126 Chemnitz, Germany — [3]Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Graphene is characterized by two linear bands crossing each other at the K-point of the hexagonal Brillouin zone. In neutral graphene, the Fermi level lies exactly at the crossing point where the density of states is zero. For certain applications, it is desirable to choose both charge carrier type and density which can be accomplished by electrostatic gating or doping. While substitutional doping alters the graphene lattice, charge transfer doping using adsorbates keeps the lattice intact.

In this work, we investigate charge transfer doping of graphene on 6H-SiC(0001) by organic molecules. Angle-resolved photoelectron spectroscopy (ARPES) was used to determine the position of the Dirac point and thus charge carrier type and density. It was observed that fluorinated fullerenes, mainly C60F48 can effectively induce p-type doping [1]. Thereby, the charge transfer is influenced by electron affinity of the adsorbed molecule and by the work function of the graphene, which was investigated in these studies. A model for the doping efficiency [1] of the various adsorbates was tested.

[1] Tadich, et al., APL 102, 241601 (2013)

O 72.7 Wed 18:15 Poster A

**Theoretical NMR signatures of water and ice on graphene** — •Achraf Jaadouni, Eva Rauls, Wolf Gero Schmidt, and Uwe Gerstmann — University of Paderborn, Paderborn Germany

Since the discovery of graphene the adsorption of water has been discussed as a possibility for doping [1], while changing the electron mobility surprisingly little. Theoretical studies have shown that the electronic properties of the resulting system strongly depends on the microscopic details of the substrate [2].

In this theoretical work we investigate the influence of thin layers of ice using density functional theory (DFT) whereby van-der-Waals interaction has been taken into account. We demonstrate that an adsorption of at least two layers of ice on free standing graphene results in a charge transfer between the ice and graphene layers and, thus, can lead to a doping of graphene. The sign of the charge transfer and by this the type of doping, however, depends on the orientation of the water molecules. As a consequence, a mixture of two phases can result in a cancellation of the doping effect. Whereas the two configuration differ only slightly in total energies, the NMR chemical shifts calculated for both types of nuclei, O as well as H, are significantly different. Hence, a control of the orientation of the ice layers should be experimentally possible via nuclear magnetic resonance (NMR).

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306, 666 (2004).

[2] T.O. Wehling, A.I. Lichtenstein, and M.I. Katsnelson, Appl. Phys. Lett. 93, 202110 (2008).

## O 73: Nanostructures at Surfaces: 1D and 2D Structures

Time: Wednesday 18:15–21:00 Location: Poster A

O 73.1 Wed 18:15 Poster A

**Fabrication of ultrathin metallic nano-contacts for molecular electronics** — •Atasi Chatterjee, Frederik Edler, Christoph Tegenkamp, and Herbert Pfnür — Leibniz Universität Hannover, Institut für Festkörperphysik, 30167, Hannover, Germany

Molecular electronics, where single molecules can be used as active electronic components, is the maximum miniaturisation of electronic devices that one can achieve by the bottom up approach. To interface single molecules with the existing macroscopic electronic devices and to understand the functionalities of the molecules, metallic nano-contacts are required. Our aim is to create flat silver nano-contacts by angle deposition, which are ultrathin (few monolayers) at the centre and robust at the ends. We use a combination of electron beam lithography on a silicon substrate, and an electro-migration process to fabricate these nano-contacts, and create nanometer separation at the centre in a controllable manner. This helps the molecules to be adsorbed on an atomic and molecular scale and makes the bonding between molecule and metallic leads better. Such laterally open contact structures together with the adsorbed molecules allow direct access to the STM tips for local control, characterisation of the gap and imaging the molecules. The final aim is to study the electrical conduction properties of single molecules inside the gap which are chemically bound to these fabricated metallic contacts.

O 73.2 Wed 18:15 Poster A

**Massive Formation of Highly Oriented Metal-Acetylide Chains Investigated by Scanning Tunneling Microscopy** — •Jing Liu, Qiwei Chen, and Kai Wu — BNLMS, SKLSCUSS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Terminal alkynes as novel on-surface reactions precursors have received widespread attention due to their potential in building up diverse nanostructures through different reaction routes. By tuning either the structure of precursors or the metal substrates, terminal alkynes can undergo different reaction pathways and therefore lead to distinct products. Glaser Coupling, cyclotrimerization, radical cyclization, and cross-coupling have all been reported as typical reaction methods of terminal alkynes. However, besides the reactions resulting in covalent bonded structures as mentioned above, terminal alkynes can also take part in the formation of organometallic metal-acetylides which are barely reported as on-surface reaction products of terminal alkynes. In this work, we present a massive formation of highly oriented silver-acetylide chains through the reaction between terminal alkyne and Ag adatoms. The reaction and products were investigated by both STM and DFT calculations. A highly oriented arrangement of chains as well as a perfect match between period of organometallic chains and substrate lattice were observed, and were considered as a significant factor for the stabilization of metal-acetylide chains.

O 73.3 Wed 18:15 Poster A

**Investigation of nanoporous networks of para-hexaphenyl-dicarbonitrile on Au(111) with ultrahigh spatial resolution** — •Leonid Solianyk[1], Juan Carlos Moreno-Lopez[1], Stefano Gottardi[1], Kathrin Müller[1], Tuan Anh Pham[1], Fei Song[1], Jun Li[1], Leticia Monjas[2], Anna Hirsch[2], and Meike Stöhr[1] — [1]Zernike Institute for Advanced Materials, University of Groningen, The Netherlands — [2]Stratingh Institute for Chemistry, University of Groningen, The Netherlands

The formation and investigation of molecular nanoarchitectures on well-defined inorganic surfaces is thought to be highly relevant for the development of future nanoelectronic devices. One way to obtain insight into the underlying interactions controlling molecular self-assembly is through ultrahigh spatial resolution on the submolecular scale.

In this work, the self-assembly of para-hexaphenyl-dicarbonitrile molecules was investigated on Au(111) with low temperature scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) using functionalized CO tips. Two different nanoporous networks were observed for submonolayer coverages. The rhombic network stabilized by C-N...H bonds was found after molecular deposition at room temperature. Upon thermal annealing at 575K, a hexagonal network stabilized by metal-ligand interactions with native gold atoms formed. Due to the ultrahigh spatial resolution of nc-AFM, information on the intermolecular interactions could be directly obtained.

O 73.4 Wed 18:15 Poster A

**Glancing Angle Deposition of Metal Nanostructures** — •Christoph Grüner[1], Sachin K. Srivastava[2], Ibrahim Abdulhalim[2], and Bernd Rauschenbach[1] — [1]Leibniz-Institut für Oberflächenmodifizierung, Permoserstraße 15, 04318 Leipzig, Germany — [2]Ben Gurion University, Beer Sheva, 84105, Israel

Glancing angle deposition (GLAD) is an ultra high vacuum physical vapor deposition process, which utilizes the self-shadowing between growing crystallites, that appears if the substrate is highly tilted with respect to the incoming particle beam. In this configuration separated nanostructures grow, leading to a thin film with very high porosity. GLAD of different metals (Cr, Ti, Al, Ag) is investigated and the resulting nanostructures are compared between each other and with the well investigated growth of silicon nanostructures. The influence of growth temperature, surface diffusion and substrate rotation is discussed. Based on the GLAD technology, a biosensor chip for detection of a protein biomarker of endocrine disrupting compounds in aquatic environment is developed.

O 73.5 Wed 18:15 Poster A

**Tb induced surface structures on Si(001)** — •Stephan Appelfeller[1], Stefan Kuls[1], Paul Reiss[2], Tore Niermann[2], Michael Lehmann[2], and Mario Dähne[1] — [1]Institut für Festkörperphysik, TU Berlin, 10623 Berlin — [2]Institut für Optik und Atomare Physik, TU Berlin, 10623 Berlin

Tb, a rare earth metal, induces a large variety of surface structures on Si(001) ranging from small surface clusters containing only few atoms over wire-like structures and metallic nanowires to large islands. Such structures are interesting for applications, e.g. the clusters might be used in catalysis, but the most promising ones are the metallic nanowires with widths of only few a nm and length exceeding 1$\mu$m, which may lead to a further miniaturization of semiconductor devices by using them as interconnects.

The surface structures were grown by Tb deposition and simultaneous or subsequent annealing. *In-situ* studies using scanning tunneling microscopy and low energy electron diffraction analysing the atomic structure in detail allowed the development of structure models for all observed surface structures.

Furthermore, the metallic nanowires were overgrown with amorphous Si and their cross sections were studied by high resolution transmission electron microscopy. The nanowires stayed intact upon overgrowth, and, using moderate annealing temperatures, they could even be embedded in crystalline Si. Possible structural modifications upon overgrowth will be discussed.

This work was supported by the DFG, FOR 1700, project E2.

O 73.6 Wed 18:15 Poster A

**Structural and electronic properties of the triangular lattice of Sn on SiC(0001)** — •Florian Adler[1], Stefan Glass[1], Gang Li[2], Julian Aulbach[1], Philipp Höpfner[1], Werner Hanke[2], Jörg Schäfer[1], and Ralph Claessen[1] — [1]Physikalisches Institut and Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, Germany — [2]Institut für Theoretische Physik und Astrophysik, Universität Würzburg, Germany

Here we report on a novel two-dimensional electron system on a triangular lattice, namely the $\sqrt{3}\times\sqrt{3}$ reconstruction of Sn on SiC(0001). Using a newly developed recipe of gas phase hydrogen etching, well ordered SiC surfaces could be prepared. By evaporation of Sn and subsequent annealing, a triangular lattice of Sn on SiC(0001) with a coverage of 1/3 monolayer was realized. Both the substrate preparation and the evaporation process were monitored by low-energy electron diffraction and high-resolution scanning tunneling microscopy. While simple electron counting results in a half-filled valence band and therefore metallic behavior, first angle-resolved photoemission data shows a broad, weakly dispersing band with no spectral weight at the Fermi level, indicating Mott-Hubbard physics. The system is isostructural to the well explored Mott-insulator $\sqrt{3}\times\sqrt{3}$ Sn on Si(111), but with a 20% smaller lattice constant. Due to the increased hopping one might expect to be closer to the insulator-metal boundary of the Hubbard model. However, the large bandgap of the substrate may also change the effective Hubbard-$U$ due to a different substrate-related screening. Similarities and differences between both systems will be discussed.

O 73.7 Wed 18:15 Poster A

**Structural and Transport Properties of Etched Silicon Nanowires** — •Stefan Weidemann[1], Maximilian Kockert[1], Anna Mogilatenko[2], Klaus Rademann[3], and Saskia F. Fischer[1] — [1]Neue Materialien, Institut für Physik, Humboldt-Universität zu Berlin, D-12489 Berlin — [2]Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik, D-12489, Berlin — [3]Nanostructured Materials, Institut für Chemie, Humboldt-Universität zu Berlin

Understanding thermal transport on the nanoscale is essential for the miniaturisation of electronic devices and for nanopatterned materials. Rough silicon nanowires (SiNWs) show decreased thermal conductivity [1]. Structural and thermo-electric characterization of an individual nanowire still remains a challenge.

In our study we prepare SiNWs by two-step metal-assisted chemical etching, which allows fabrication on wafer scale [2]. Doping levels range from undoped Si, resistivity $\rho > 1000$ Ωcm, to highly boron-doped Si, $\rho = 0.01$ Ωcm, and the axial crystal orientation is (100). By controlling the etching conditions and the substrate selection the NW lengths $(30-100\mu m)$ and surface morphology (solid, rough and porous) can be adjusted [3]. Single SiNW in the diameter range from 200 - 400 nm are investigated. Electrical conductivities and the thermovoltage are measured on a platform designed in four-point geometry with heaters.

[1] A. I. Hochbaum *et al.*, Nature 451, 163 (2008).
[2] S. Weidemann *et al.*, arxiv:1410.3763 (2014) submitted.
[3] G. Yuan *et al.*, Jour. Phy. Chem C, 116, 13767 (2012).

O 73.8 Wed 18:15 Poster A

**Preparation of undoped and boron-doped silicon nanowires** — •Maximilian Kockert[1], Stefan Weidemann[1], Klaus Rademann[2], and Saskia F. Fischer[1] — [1]Neue Materialien, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — [2]Nanostrukturierte Materialien, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

Silicon nanowires (SiNWs) are potentially efficient thermoelectric materials because of the reduced phonon contribution to the thermal conductivity and they are interesting for biochemical applications due to their big surface-to-volume ratio [1]. In this work we prepare SiNWs of undoped silicon substrates (electrical resistivity $\rho > 1400$ Ωcm) and boron-doped silicon substrates ($\rho = 0.01$ - $0.02$ Ωcm) by metal-assisted chemical etching. We analyse the influence of the concentration of hydrogen peroxide, light and temperature on the wire length [2]. Scanning electron microscope investigations show that an increase of one of these etching parameters lead to longer SiNWs, when the etching time is constant. Further measurements show that after three hours of etching the wire length $l$ of undoped SiNWs reaches $l = 75\ \mu m$ and of boron-doped $l = 43\ \mu m$.

[1] A. Boukai *et al.*, Nature **415**, 168 (2008).
[2] S. Weidemann *et al.*, arXiv:1410.3763 (2014).

O 73.9 Wed 18:15 Poster A

**Effect of electron-phonon coupling on band-structure formation: Chains of Cl-vacancies** — Bruno Schuler[1], Mats Persson[2], Sami Paavilainen[3], •Niko Pavliček[1], Leo Gross[1], Gerhard Meyer[1], and Jascha Repp[4] — [1]IBM Research–Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland — [2]Science Research Centre, University of Liverpool, L69 3BX, United Kingdom — [3]Department of Physics, Tampere University of Technology, 33720 Tampere, Finland — [4]Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany

We have investigated the effects of strong electron-phonon (*e-ph*) coupling on the formation of extended electronic states of Cl divacancies and vacancy chains in a NaCl bilayer on Cu(111) with scanning tunneling spectroscopy, atomic force microscopy and a tight-binding model including linear coupling to phonon modes. Vacancy pairs and chains with different orientation and separation were created by extracting individual Cl anions with atomic precision using vertical manipulation. Symmetric and anti-symmetric vacancy states (VS) and localized interface states are shown to be formed at divacancies, in analogy with the bonding and anti-bonding orbitals of the hydrogen molecule. As expected, the level splitting increases with decreasing inter-vacancy distance. However, splitting of the VSs is significantly enlarged by level repulsion as a result of the strong *e-ph* interaction [1]. Already for chains of a few coupled vacancies we observe an emerging band structure of the defect band.

[1] J. Repp, et al., Phys. Rev. Lett. 95, 225503 (2005).

O 73.10 Wed 18:15 Poster A

**Dynamic Bragg-like scattering in GISAXS from rough gratings** — •Victor Soltwisch[1], Jan Wernecke[1], Anton Haase[1], Michael Krumrey[1], Juergen Probst[2], Max Schoengen[2], and Frank Scholze[1] — [1]Physikalisch-Technische Bundesanstalt — [2]Helmholz-Zentrum Berlin

The decrease in feature size down to several nm is chall enging for the given metrology toolsets. X-ray scattering with grazing incidence angles (GISAXS), close to the critical angle, is a fast and non-destructive method with a high surface sensitivity. We report the observation of dynamic scattering effects from rough structured surfaces which leads to higher ordering of the Yoneda lines.

# O 74: Oxide and Insulator Surfaces

Time: Wednesday 18:15–21:00 Location: Poster A

O 74.1 Wed 18:15 Poster A

**Archimedean snub square tiling in a $BaTiO_3$ derived epitaxial film on Pt(111)** — Martin Trautmann[1], Stefan Förster[1], Florian Schumann[1], Christian Teichert[1,2], •Klaus Meinel[1], and Wolf Widdra[1,3] — [1]Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany — [2]Institute of Physics, Montanuniversität Leoben, A-8700 Leoben, Austria — [3]Max-Planck Institut für Mikrostrukturphysik, D-06120 Halle, Germany

Under specific conditions, ultrathin $BaTiO_3$ films on Pt(111) develop a 2D quasicrystalline structure of twelve-fold rotational symmetry which is composed by an aperiodic arrangement of triangular, quadratic, and rhombic tiling elements [1]. Searching for the basic mechanisms of its formation, a periodic approximant has been identified. It merely consists of the triangular and quadratic elements of the quasicrystal that arrange in a snub square tessellation. In vertex notation, this structure can be described as (3.3.4.3.4) pattern, which has already been considered by Kepler in his general analysis of Archimedean tilings [2]. Applying STM, LEED, and SPA-LEED, the corresponding lattice parameters and the epitaxy matrix with respect to the Pt(111) substrate are determined with high precision. STS indicates that $Ti^{3+}$-O vacancy clusters are constituents of that structure similar to the case which has been deduced for the quasicrystal. The film structure found is an important additional nanoscale observation of the - hitherto rare - five-vertex motives in 2D interface tessellations.

[1] S. Förster, et al., Nature 502, 215 (2013).

[2] J. Kepler, Harmonices Mundi, Johannes Planck, Linz (1619).

O 74.2 Wed 18:15 Poster A

**Initial stages of epitaxy for the growth of ultrathin MgO layers on $Fe_3O_4$/MgO(001)** — •Tabea Nordmann[1], Olga Schuckmann[1], Timo Kuschel[2], Karsten Küpper[1], and Joachim Wollschläger[1] — [1]Physics Department, Osnabrueck University, Germany — [2]CSMD, Physics Department, Bielefeld University, Germany

Magnetite ($Fe_3O_4$) is a promising candidate for electrode material in magnetic tunnel junctions (MTJs) due to its theoretically predicted 100% spin polarisation at the Fermi edge. For high quality MTJs the crystalline structure of the tunneling barrier is as important as the structure of the magnetite. An interesting insulating material for MTJs consisting of magnetite is MgO because of the small lattice mismatch between magnetite and MgO of 0.3% and the symmetry filtering effect of MgO.

In this study the influence of the substrate temperature on the growth of MgO tunneling barriers (thickness 1-3 nm) on $Fe_3O_4$(001) films was investigated. Especially the growth mode and the quality of the crystalline structure of the MgO films were analyzed. The MgO films were deposited in several steps by reactive molecular beam epitaxy (RMBE). After each step x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were performed. The analysis of the XPS measurements reveal island- and layer-plus-island growth at substrate temperatures between 25 °C to 200 °C and layer-by-layer growth at 250 °C. According to the LEED measurements the crystallinity of the MgO increases with the substrate temperature.

O 74.3 Wed 18:15 Poster A

***Ab initio* study of anatase and brookite phases doped with cerium** — •Lukas Sojka[1], Barbora Kacerovska[1], Lenka Matejova[2], and Dominik Legut[3,2] — [1]Nanotechnology Centre — [2]Institute of Environmental Technology — [3]IT4Innovations Centre, VSB-TU Ostrava, Ostrava, Czech Republic

$TiO_2$ is a well known photocatalyst [1], its efficiency in visible-light spectrum could be enhanced further. One way is to create oxygen vacancies or $Ti^{3+}$ defects. Another way is by doping *e.g.* by lanthanides. Here we consider cerium doped $TiO_2$ in the anatase and brookite phases. Our results were obtained using *ab initio* calculations. The electronic structure and thermodynamical properties (enthalphy of formation) of Ce doped $TiO_2$ phases were investigated under pressure as motivated by experimenal studies of processing of Ce-doped titania precursors by pressurized and supercritical fluids. Furthermore, the effect of doped cerium concentration on band gap and optical properties of titania was investigated. Two valences, i.e. $Ce^{3+}/Ce^{4+}$ were considered. The calculations were perforemd using the VASP code [2] and the generalized gradient approximation [3] was used to account for exchange-correlation effects. The financial support of the Grant Agency of the Czech Republic (project reg. No. 14-23274S) is acknowledged. **References:**

1. D. O. Scanlon et al., Nature Mater. **12**, 798 (2013).
2. G. Kresse, J. Furthmueller, J. Comput. Mater. Sci. **6**, 15 (1996).
3. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

O 74.4 Wed 18:15 Poster A

**ZnO growth on c-plane sapphire: Insights from ab initio simulations** — •Marc Landmann, Eva Rauls, and Wolf Gero Schmidt — Universität Paderborn, Germany

The layer quality of heteroepitaxial ZnO films, grown on the most common c-plane sapphire substrate suffers from the large lattice mismatch between both materials. In order to reduce the defect density of ZnO films, the introduction of MgO buffer layers turned out to be beneficial. [1] In addition, the MgO buffer-layer approach facilitates the polarity control of ZnO films grown on c-plane sapphire. Experimentally, a Zn-polar (+c) growth has been observed for MgO layer thickness greater than 3 nm. In contrast, an O-polar (-c) film growth has been observed for layer thickness less than 2 nm. [2] Here, we have studied the ZnO growth process on the sapphire c-plane surface with and without inclusion of MgO buffer layers of varying thicknesses by state-of-the-art density functional theory calculations. Our results provide new insights into the fundamental growth dynamics of ZnO films and the driving forces behind the ZnO surface polarity.

[1] M. W. Cho, A. Setiawan, H. J. Ko, S. K. Hong, and T. Yao, Semicond. Sci. Technol. 20, 13 (2005) [2] H. Kato, K. Miyamoto, M. Sano, and T. Yao, Appl. Phys. Lett. 84, 4562 (2004)

O 74.5 Wed 18:15 Poster A

**Electronic structure of cerium titanates - first-principles calculations** — •Barbora Kacerovska[1], Lukas Sojka[1], Lenka Matejova[2], and Dominik Legut[3,2] — [1]Nanotechnology Centre — [2]Institute of Environmental Technology — [3]IT4Innovations Centre, VSB-TU Ostrava, Ostrava, Czech Republic

Cerium titanates offer broad range of technological applications because of their optical and catalytic properties. Cerium titanate can form various phases, which depend on the oxidation state of cerium. In $CeTiO_4$ and $CeTi_2O_6$ compounds cerium is in the oxidation state $Ce^{4+}$. The latter is a safe analogue to actinide-containing brannerite-like titanate phase (e.g. $UTi_2O_6$) used for nuclear waste storage. We have investigated electronic structure of these compounds as well as $CeO_2$ using *ab initio* calculations. For $CeTiO_4$ we considered both orthorhombic and monoclinic phases. Furthermore, the influence of pressure applied to Ce titanate phases on various properties was revealed. Electronic structure, thermodynamical and optical properties were calculated using the single-electron framework of density functional theory employed in VASP code [1]. For the exchange-correlation term the generalized gradient approximation was considered [2]. The financial support of the Grant Agency of the Czech Republic (project reg. No. 14-23274S) is acknowledged.

**References:**

1. G. Kresse, J. Furthmueller, Phys. Rev. B **54**, 11169 (1996).
2. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

O 74.6 Wed 18:15 Poster A

**Influence of strain on the adsorption site of Au anions on epitaxial NaCl films** — •Wolfram Steurer[1], Bruno Schuler[1], Niko Pavlicek[1], Leo Gross[1], Jascha Repp[2], Ivan Scivetti[3], Mats Persson[3], and Gerhard Meyer[1] — [1]IBM Research-Zurich, Switzerland — [2]University of Regensburg, Germany — [3]University of Liverpool,UK

We present a detailed experimental and theoretical study of Au adatoms adsorbed on 2–10 ML thick NaCl films grown on Cu(111), Cu(100), and Cu(311) surfaces. Atomically-resolved scanning tunneling microscopy and atomic force microscopy images reveal a clear influence of lattice strain: Whereas Au anions adsorb in a site bridging two Cl atoms on unstrained and tensionally strained films, compressive strain shifts the energetically favored adsorption position to a site on top of a chlorine atom. Using a simplified density-functional theory approach to handle charged adsorbates, we show that, apart from the interaction with the metal substrate, the stability of the on-top site strongly depends on the lattice mismatch between the NaCl film and the Cu substrate, indicating the possibility to engineer the adsorption site of adsorbates by means of the film thickness and lattice parameter.

Financial support by the EU project ARTIST (Contract No. 243421), PAMS (Contract. No. 610446), Qtea (Contract. No. 317485) and the ERC Advanced Grant CEMAS is acknowledged.

## O 75: Plasmonics and Nanooptics

Time: Wednesday 18:15–21:00 Location: Poster A

O 75.1 Wed 18:15 Poster A

**Control of light-SPP coupling at step edges by local interference** — •Alwin Klick[1], Sergio de la Cruz[2], Christoph Lemke[1], Malte Grossmann[1], Hauke Beyer[1], Jacek Fiutowski[3], Jakob Kjelstrup-hansen[3], Horst-Günter Rubahn[3], Eugenio R. Méndez[2], and Michael Bauer[1] — [1]Institute for Experimental and Applied Physics, University of Kiel, Leibnizstr. 19, 24118 Kiel, Germany — [2]División de Física Applicada, Centro de Investigación Científica y de Educación Superior de Ensenada, Carretera Ensenada-Tijuana No. 3918, Ensenada 22860, BC, Mexico — [3]Mads Clausen Institute, University of Southern Denmark, NanoSYD Alsion 2, 6400 Sønderborg, Denmark

A combined experimental and theoretical study on the efficiency of laser-induced surface plasmon polariton (SPP) excitation at defined step edges at a gold-vacuum interface as one of the most basic coupling geometries is presented. As a relevant parameter determining the coupling efficiency we identify the ratio between step height $h$ and excitation wavelength $\lambda$ [1]. For specific values of $h/\lambda$ a substantial suppression of laser-SPP coupling is observed arising from destructive interference of the laser field reflected at the two step levels, respectively. Experiment and theory show, furthermore, that the interference affects also the phase of the SPP with respect to the exciting laser field.

[1] De la Cruz, S. et al., 2012. Physica Status Solidi (B), 249(6).

O 75.2 Wed 18:15 Poster A

**Super-resonant infrared near-field microscopy** — •Denny Lang[1,2], Tino Uhlig[1], Susanne C. Kehr[1], Manfred Helm[2], and Lukas M. Eng[1] — [1]Institut für Angewandte Physik, Technische Universität Dresden, 01069 Dresden — [2]Institut für Ionenstrahlphysik und Materialforschung, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden

Scattering-type scanning near-field optical microscopy (s-SNOM) is an AFM-based technique for achieving nanoscale resolution even at infrared wavelengths [1]. s-SNOM thus is of valuable impact when e.g. investigating low-dimensional conductors or semiconductors. In order to enhance the signal strength we face two options, by either tuning the tip or sample into resonance using appropriate or tunable laser light sources.

In this work we use a $CO_2$-laser with a tunable center wavelength from 9.7 $\mu$m to 11.3 $\mu$m as an infrared excitation source in combination with self-prepared AFM particle-tips as probes [2]. The tip particles consist of spherical SiC, $Si_3N_4$ or $SiO_2$ nanoparticles with a diameter of $\sim$60 nm. Those materials show phonon resonances in or around the $CO_2$-laser wavelength range and thus enhance the signal significantly. We explore here the scenario when using both resonant tips and samples, hence resulting in a tip-sample coupled super-resonance. Accordingly, a significantly increased near-field image contrast and resolution is expected in this case.

[1] S.C. Kehr et al., Nat. Commun. 2, 249 (2011).

[2] M.T. Wenzel et al., Opt. Express 16, 12302 (2008).

O 75.3 Wed 18:15 Poster A

**Hybrid quantum dot nanoantenna systems: fabrication and characterization** — •Manuel Peter, Cody Friesen, and Stefan Linden — Physikalisches Institut, Universität Bonn, Nußallee 12, 53115 Bonn, Germany

This poster will provide an overview of the fabrication and characterization methods we use to investigate hybrid quantum dot nanoantenna systems. We present a two-step electron lithography process for the reliable positioning of colloidal quantum dots in the vicinity of plasmonic nanoantennas with sub-50nm spatial accuracy and a first experiments with such structures In the first lithography step, gold nanoantennas are fabricated with spectral features at the emission wavelength of the used quantum dots ($\lambda$=780 nm). Following this, a second layer of PMMA is deposited on the sample. Then a template is written with the electron beam to define the positions for the colloidal quantum dots. After development, the surface of the substrate as well as that of the quantum dots are chemically modified such that a linker molecule can bind the quantum dots to the predefined spots. After removing the PMMA mask, we obtain hybrid nanostructures composed of gold nanoparticles and quantum dots. With our fabrication method, we are able to precisely control all geometrical parameters of the hybrid nanostructures. In this contribution we show an example of a successful coupling of quantum dots and rod nanoantennas. By examining the polarisation of the fluorescence light of the structure, we could confirm that the quantum dots are still functional and interact with the nanoantenna.

O 75.4 Wed 18:15 Poster A

**Tuning the Localized Surface Plasmon Resonance: An Annealing Study for Aluminium, Copper, Gold and Silver Nanostructures Prepared by Nanosphere Lithography** — •Stefan Moras, Jacek Gasiorowski, Ovidiu D. Gordan, and Dietrich R. T. Zahn — Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz

Metallic nanostructures attract great interest due to their unusual characteristics. The optical response of such nanostructures differs markedly from bulk material because of the localized surface plasmon resonance (LSPR) of these structures. Optical properties associated with LSPR are determined by shape, size, structure, and the local dielectric environment of the metal nanostructures. Here we present a detailed characterization of the tunability of the LSPR in aluminium, copper, gold, and silver nanostructures by annealing up to 500 °C in nitrogen atmosphere. All structures were prepared by nanosphere lithography (NSL) where self-assembled monolayer of polystyrene particles served as a mask for metal evaporation. UV-vis spectroscopy was used to determine the LSPR of these structures. Changes in morphology were investigated using scanning electron microscope (SEM). Gold and especially silver show pronounced tunability in the visible region due to their change of shape from triangular towards spherical. Copper shows a difference in LSPR which we attribute to a different type of surface oxide whereas aluminium shows no tunability in the temperature range used due to the capping by an aluminium oxide layer.

O 75.5 Wed 18:15 Poster A

**Plasmonic Nanoparticles prepared by Nanosphere Lithography for local Excitation of Molecular Aggregates** — •Tamam Bohamud[1], Mohammadreza Bahrami[1], Lukas Steffen Rathje[1], J.A.A.W Elemans[2], Ingo Barke[1], and Sylvia Speller[1] — [1]University of Rostock, Institute of Physics, 18051 Rostock, Germany — [2]Institute for Molecules and Materials, RU Nijmegen, NL

Nanosphere lithography (NSL) is an effective technique to fabricate nanoparticles with tailored arrangement and dimensions. We used this method to obtain periodic arrays of silver nanotriangles using beads of polystyrene as a mask on glass and silicon substrates. Periodic hexagonal arrangements of semi-spherical nanoparticles are created by subsequent annealing. Correlation between the morphology of the nanoparticles and their plasmonic signatures indicate different types of resonances depending on size and shape. The utilization of these nanoparticles as an environment to locally excite copper porphyrin aggregates is discussed.

O 75.6 Wed 18:15 Poster A

**Studies on the nonlinear optical properties of lithographically fabricated nanoantennas** — •jiyong wang[1,2], anke horneber[1], pierre michel adam[2], and dai zhang[1] — [1]Institut für Physikalische und Theoretische Chemie, Eberhard Karls Universität Tübingen, 72076 Tübingen, Deuschland — [2]Laboratoire de Nanotechnologie et d'Instrumentation Optique, Universite de Technologie de Troyes, 10004 Troyes, France

Metallic nanostructures exhibit fascinating linear and nonlinear optical properties when they are excited by incident light. Localized surface plasmons (LSPs) generated by a collective oscillation of electrons in conduction band offer the possibility of enhancing and concentrating electrical field in a subwavelength volume, which enable the nanostructures to act similar to antennas in the microwave or radiowave regime.

In order to explore the dependence of nonlinear optical properties on the LSPs for nanoantennas and their potential applications in the field of enhanced spectroscopy, we fabricated nanoantennas with different geometrical parameters (shape, dimension and gap) and materials by electron beam lithography. These nanoantennas were firstly characterized by far field extinction spectroscopy, which reflects footprints of their LSPs resonances. The nonlinear optical signals including second harmonic generation and two photon photoluminescence were investigated using far-field confocal optical microscopy and scanning near-field optical microscopy. . Gap-, material-, and position-dependent nonlinear optical properties of these nanoantennas will be systematically compared.

### O 75.7 Wed 18:15 Poster A

**Positioning colloidal nanocrystals next to plasmonic nanostructures using electron-beam lithography** — •Marvin Berger[1,3,4], Daniela Wolf[1], Thorsten Schumacher[1], Stuart Earl[2,3], Daniel Gomez[3,4], and Markus Lippitz[1] — [1]Experimentalphysik III, Universität Bayreuth, Germany — [2]School of Physics, The University of Melbourne, Parkville, Victoria, 3010, Australia — [3]The Melbourne Centre for Nanofabrication (MCN), Australian National Fabrication Facility, Clayton, Victoria, 3168, Australia — [4]CSIRO, Materials Science and Engineering, Private Bag 33, Clayton, Victoria 3168, Australia

The plasmon resonance of a nobel-metal nanoparticle leads to an increased optical near-field. This can be used to enhance nonlinear optical effects such as third-harmonic generation or transient absorption. However, this requires that the nonlinear object is positioned in the plasmonic near-field.

We use semiconducting colloidal CdSe nanocrystals, localised within the range of some tens of nanometers to a gold or silver nanorod. Our approach to create such well defined structures is two-step Electron Beam Lithography (EBL). We discuss details of this process, especially the placement of the colloidal nanocrystals. Moreover we will use data from AFM, SEM and optical measurements to characterize our structures.

### O 75.8 Wed 18:15 Poster A

**Enhanced near-field coupling of plasmonic antennas with few-nm gap sizes fabricated by helium ion beam milling** — Heiko Kollmann[1], Xianji Piao[2], Martin Esmann[1], Simon F. Becker[1], Dongchao Hou[1], Henning Vieker[3], André Beyer[3], Armin Gölzhäuser[3], Namkyoo Park[2], •Martin Silies[1], and Christoph Lienau[1] — [1]Carl von Ossietzky-Universität Oldenburg — [2]Seoul National University, Korea — [3]Universität Bielefeld

Metallic nanoantennas are able to localize far-field electromagnetic waves on sub-wavelength scales. Standard fabrication tools such as Electron Beam Lithography and Ga-based Focused Ion Beam (FIB) milling lead to sub-20-nm feature sizes. In the recent past, He-ion based lithography (HIL) has proven to push this limit below 10 nm [1,2]. Here, we combine Ga-based FIB and HIL for the fabrication of gold antennas with variable gap sizes down to a few nanometers. Using polarization-sensitive linear and nonlinear third harmonic (TH) spectroscopy, the linear optical resonances of single gold antennas and the TH emission intensities are analyzed for different feed gap distances. Both the spectral red-shift of the linear emission and the increased TH signal for small feed gaps are taken as a signature for the improved coupling of the antennas. Our experimental findings are strongly supported by FEM calculations and demonstrate that He-ion beam lithography is a highly attractive and promising new tool for the fabrication of plasmonic nanoantennas with few-nanometer feature sizes.

[1] M. Melli et al., Nano Letters 13, 2687-2691 (2013) [2] H. Kollmann et al., Nano Letters 14, 4478-4784 (2014)

### O 75.9 Wed 18:15 Poster A

**Sphere-based Aperture SNOM: A tool for ultrafast nano-optics** — •Michael Hartelt, Cristian González, Anna-Katharina Mahro, Daniela Bayer, Elena Ilin, Deirdre Kilbane, Stefan Mathias, Egbert Oesterschulze, and Martin Aeschlimann — Department of Physics and Research Center OPTIMAS, TU Kaiserslautern, Germany

In traditional aperture Scanning Near-field Optical Microscopy (a-SNOM), the sample is illuminated through a sub-wavelength sized aperture at the apex of a tapered fiber or an Al-coated $SiO_2$ pyramid. These constructions have a number of drawbacks, such as the metal-metal interaction between tip and sample and the low transmission which causes problems for achieving the high intensities that are required for time-resolved measurements. We developed a new cantilever design, in which a $SiO_2$-sphere was added at the apex of such a pyramid. Here, we demonstrate the various benefits of this design for the imaging of localized and propagating surface plasmons, as well as ultrafast pump-probe experiments with pulse lengths well below 100 fs. Illuminating with an Optical Parametric Oscillator (OPO) allows us to address a wide spectral range from the UV up to the infrared regime. A setup combining these components provides a versatile tool for the investigation of ultrafast phenomena in nano-optics.

### O 75.10 Wed 18:15 Poster A

**Plasmonic nanostructure fabrication based on FIB milling of high-quality monocrystalline gold flakes and transfer** — •Xiaofei Wu[1,2], Peter Geisler[1], Enno Krauss[1], René Kullock[1], and Bert Hecht[1] — [1]Nano-Optics and Biophotonics Group, Experimentelle Physik 5, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Present address: Experimentalphysik III, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

Good fabrication techniques are vital for successful experiments because they not only make it possible to obtain structures with expected performance, but also significantly boost the working efficiency and success rate. Moreover, a novel fabrication technique also inspires new experimental ideas. Therefore it is always important to keep developing advanced fabrication techniques. Here we present our developments in preparing high-quality chemically synthesized monocrystalline gold flakes on substrates and their use in plasmonic nanostructure fabrication with focused ion beam (FIB) milling. To make the FIB-fabricated nanostructures available for substrates that are not suitable for FIB milling as well, we have developed approaches to transfer the nanostructures with 100% efficiency. A few typical applications based on these techniques are also presented.

### O 75.11 Wed 18:15 Poster A

**Implantation of gold into pure and silver containing glass by means of ArF-excimer laser irradiation** — Maximilian Heinz[1], Manfred Dubiel[1], •Jörg Meinertz[2], and Jürgen Ihlemann[2] — [1]Institute of Physics, Martin Luther University of Halle-Wittenberg, Halle, Germany — [2]Laser-Laboratorium Göttingen e.V., Göttingen, Germany

The generation of plasmonic Au/Ag nanostructures in glass surfaces showing a tunable surface plasmon resonance in a wide range of wavelengths should be realized by laser implantation of gold by means of excimer laser irradiation. These are promising materials for optoelectronics and nanoplasmonics. Thin films of Au were applied to the glass surface and then Au species were incorporated by means of intense UV radiation using fluences below the ablation threshold of the glass. The formation of Au and Au/Ag nanoparticles with surface plasmon resonances between 500 and 620 nm could be verified by optical spectroscopy. These results demonstrate that such procedures enables the space-selected generation of plasmonic Au/Ag structures in glass surfaces by excimer laser irradiation.

### O 75.12 Wed 18:15 Poster A

**Periodic plasmonic nanoparticle arrays with controllable interparticle distances and plasmon resonance coupling** — •Kirsten Volk and Matthias Karg — Physical Chemistry I, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany

Surface plasmons (SPs) are light induced collective oscillations of the electron liquid in respect to the crystal lattice at a metamaterial-dielectric interface with permittivities of different signs. When employing nanoparticles with a size smaller than the sink depth, optical fields can penetrate its entire volume and drive localized surface plasmon oscillations. The plasmon resonance wavelength of metallic nanoparticles is highly dependent on the size, shape and the material of the nanoparticle. Additionally the localized surface plasmon resonance (LSPR) is sensitive to the dielectric environment and the interparticle distance in nanoparticle arrays. Varying these two parameters significant changes of the optical properties of the system due to coupling can be achieved.

In this contribution we show how to make use of the dielectric environment and interparticle distance dependence of LSPRs to create functional materials with tailored optical properties. As particular building blocks we employed silver nanoparticles, which are coated by a polymer shell. The particles are then self-assembled into highly ordered hexagonally packed monolayers by a floatation approach. The interparticle distances can be exactly tuned by the dwell-time of the particles at the liquid-air interface. By placing the monolayers on substrates with high refractive indices the optical properties of the system can be further enhanced.

O 75.13 Wed 18:15 Poster A

**Characterization of Single Gold Nanoparticles Using Confocal Interference Microscopy in Combination with Cylindrical Vector Beams** — •Otto Hauler, Frank Wackenhut, Tina Züchner, and Alfred J. Meixner — 1Eberhard-Karls-Universität Tübingen, Institut für physikalische Chemie, 72076 Tübingen, Germany

By using confocal interference microscpoy in combination with cylindrical vector beams it is possible to directly image the orientation and to detect the shape of single metal nanoparticles, with sizes well beyond the diffraction limit [1,2]. Metal nanoparticles can be imaged by detecting both their luminescence and the elastically scattered light. In the scattering detection mode the visualized pattern strongly depends on the local environment, e.g. the refractive index of the surrounding medium [3]. By shifting the resonance of the particles via coupling e.g. to a flat gold film and simultaneously measuring the luminescence and the elastic scattered signal we can further analyze the scattering properties. [1] A.V. Failla, H. Qian, H. Qian, A. Hartschuh, A. J. Meixner (2006), Nano Lett. 6, 1374. [2] T. Züchner, A. V. Failla, A. J. Meixner (2008), J. Microsc. 229, 337. [3] T. Züchner, A. V. Failla, M. Steiner, A. J. Meixner (2008), Opt. Expr. 16, 14635.

O 75.14 Wed 18:15 Poster A

**Nanodiamonds with singe nitrogen vacancy centres in laser-written microstructures** — •Bernd Sontheimer[1], Qiang Shi[2], Johannes Kaschke[2], Tanja Neumer[1], Joachim Fischer[2], Andreas W. Schell[1], Martin Wegener[2], and Oliver Benson[1] — [1]AG Nanooptik, Humbodt-Universität zu Berlin, Germany — [2]DFG-Center for Functional Nanostructures, Karlsruhe Institute of Technology (KIT), Germany

Hybrid integration of nano-sized quantum emitters in photonic structures can be achived by random methods or by nanomanipulation techniques. We report on our recent progress using another approach. In our method, the nanodiamonds are embedded in a photoresist, which is subsequently structured [1]. This allows for fabrication of a variety of different structures, such as resonators and waveguides coupled to single emitters. By pre-characterizing the emitter's properties and position, such structures can be fabricated in a highly controlled way [2].

[1] Schell et al.. Sci. Rep. 3, 1577 (2013)

[2] Schell et al., Appl. Phys. Lett. (accepted)

O 75.15 Wed 18:15 Poster A

**Sputter deposition of Ag on PDMS thin films for flexible SERS substrates** — •Gonzalo Santoro[1], Isabel M. Ochando[2], Torsten Boese[1], Ralph Döhrmann[1], Peng Zhang[1], and Stephan V. Roth[1] — [1]DESY, Notkestr. 85, D-22607 Hamburg, Germany — [2]Institute of Polymer Science and Technology, ICTP-CSIC, Juan de la Cierva, E-28006 Madrid, Spain

Silver (Ag) nanoclusters present excellent plasmonic properties that can be exploited for Surface Enhanced Raman Scattering (SERS) based sensors. To optimize the sensitivity of SERS substrates, it is crucial to achieve a profound understanding of the Ag nanocluster growth kinetics and to correlate the thin film morphology with its functionality [1].

This work presents in-situ time-resolved Grazing Incidence Small Angle X-ray Scattering (GISAXS) [1-3] results concerning the evolution of the nanostructures developed during the RF-sputtering of Ag on semiconductor (SiOx) and polydimethylsiloxane (PDMS) thin films, a highly flexible and stretchable silicone widely used for microfluidics. The SERS activity of the prepared thin films and the correlation of morphology and sensitivity are also presented.

[1] Santoro et al. Appl. Phys. Lett. 104, 243107 (2014); [2] Yu et al. J. Phys. Chem. Lett. 4, 3170 (2013); [3] Schwartzkopf et al. Nanoscale 5, 5053 (2013).

## O 76: Overview Talk (Michael Horn-von Hoegen)

Time: Thursday 9:30–10:15 Location: HE 101

**Invited Talk** O 76.1 Thu 9:30 HE 101

**1D Metal Wires at Surfaces: Preparation, Phase Transitions, and Ultrafast non-Equilibrium Dynamics** — •Michael Horn-von Hoegen — Fakultät Physik und Center for Nanointegration CENIDE, Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg

The Indium induced (4×1) reconstruction on Si(111) is a famous prototype for 1D metal wires at surfaces. Indium atoms form parallel zigzag chains with anisotropic metallic conductivity. At 130 K a metal-insulator transition to the (8×2) ground state takes place. A Peierls-like distortion causes periodicity doubling and opening of a bandgap. A robust hysteresis of 8.6 K width during temperature cycling proves that this phase transition is first-order. The non-equilibrium structural dynamics of the (8×2) is studied by ultra-fast electron diffraction. We use a pulsed electron gun in a RHEED geometry with a fs laser system in a pump probe setup. A tilted pulse front scheme improves the temporal resolution to 350 fs. Upon photo excitation the (8×2) ground state is driven in less than 400 fs to the (4×1) excited state as observed through the transient RHEED spot intensity. Heating of the In atoms from 30 to 60 K occurs delayed on a time scale of 3 ps. Thus the phase transition is driven electronically and not thermally. The surface then remains for nanoseconds in a super cooled metastable (4×1) state, which is not accessible under equilibrium conditions. The relaxation into the (8×2) groundstate happens through the nucleation of the (8×2) at pre-existing adsorbates which trigger a 1-dim. recrystallization front propagating with 100 m/s as determined from a transient spot profile analysis of the (8×2) spots.

## O 77: Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses

Time: Thursday 10:30–13:15 Location: MA 005

**Topical Talk** O 77.1 Thu 10:30 MA 005

**Photoinduced phase transitions in vanadium dioxide revealed by ultrafast electron diffraction and broadband spectroscopy** — •Bradley Siwick[1], Vance Morrison[1], Robert Chatelain[1], Kunal Tiwari[1], Ali Hendaoui[2], Andrew Bruhacs[1], and Mohamed Chaker[2] — [1]Departments of Physics and Chemistry, Center for the Physics of Materials, McGill University, Montreal, Canada — [2]Institut National de la Recherche Scientifique, Centre Énergie Matériaux et Télécommunications, Varennes, Canada

The complex interplay between strong electron-electron correlations and structural distortions is thought to determine the electronic properties of many oxides, but the respective role of the two contributions is often extremely difficult to determine. Vanadium dioxide is a particularly notorious example. We will report on combined radio-frequency compressed ultrafast electron diffraction (RF-UED) and infrared transmissivity experiments in which we directly watch and separate the lattice and charge density reorganizations that are associated with the optically induced semiconductor-to-metal transition in vanadium dioxide. These studies have uncovered a previously unreported photoinduced transition to a metastable intermediate state with the periodic lattice distortion characteristic of the insulator intact, but differing by a 1D rearrangement of charge density along the octahedrally coordinated vanadium dimer chains and a transition to metal-like mid IR optical properties. The results demonstrate that UED is capable of following details of both lattice and electronic structural dynamics on the ultrafast timescale.

**Topical Talk** O 77.2 Thu 11:00 MA 005

**Spatial and temporal resolution studies on a highly compact ultrafast electron diffractometer and lattice dynamics in few-layer graphene** — Christian Gerbig, Arne Senftleben, Silvio Morgenstern, Marlene Adrian, Cristian Sarpe, and •Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Straße 40, D-34132 Kassel

Time-resolved diffraction with femtosecond electron pulses has become a promising technique to directly provide insights into photo induced primary dynamics at the atomic level in molecules and solids. Ultrashort pulse duration as well as extensive spatial coherence are desired, however, space charge effects complicate the bunching of multiple electrons in a single pulse. We experimentally investigate the interplay between spatial and temporal aspects of resolution limits in ultrafast electron diffraction (UED) on our highly compact transmission electron diffractometer. To that end, the initial source size and charge density of electron bunches are systematically manipulated and the resulting bunch properties at the sample position are fully characterized in terms of lateral coherence, temporal width and diffracted intensity. We obtain electron pulse durations down to 120 fs and transversal coherence lengths up to 20 nm. The performance of our compact UED setup at selected electron pulse conditions is finally demonstrated in a time-resolved study of lattice dynamics in few-layer graphene after optical excitation. During the heating process, we observe shearing modes and acoustic breathing modes.

O 77.3 Thu 11:30 MA 005

**First principles molecular dynamics simulations of nonthermal structural dynamics in nanoscale materials** — Tobias Zier, Bernd Bauerhenne, Benjamin Bartocha, Sergej Krylow, Martin E. Garcia, and •Eeuwe S. Zijlstra — Theoretical Physics, FB10, University of Kassel, Germany

Femtosecond-laser pulses create extreme out-of-hermodynamic-equilibrium conditions in matter with electrons that are orders of magnitude hotter than the ions. We simulated the ensuing nonthermal structural dynamics in Si, Ge, Sb, TiO2, and BN-nanotubes with our ab initio Code for Highly excIted Valence Electron Systems (CHIVES) [1], where the laser-excited potential energy surface is computed on the fly. Our simulations allow us to follow materials through exotic types of motion, for example, fractional diffusion in Si [2]. Computed time-resolved structure factors and structure functions provide a direct link to ultrashort electron diffraction experiments.

[1] E. S. Zijlstra, A. Kalitsov, T. Zier, and M. E. Garcia: "Squeezed thermal phonons precurse nonthermal melting of silicon", Phys. Rev. X 3, 011005 (2013).

[2] E. S. Zijlstra, A. Kalitsov, T. Zier, and M. E. Garcia: "Fractional diffusion in silicon", Adv. Mater. 25, 5605 (2013).

**Coffee Break 15min.**

O 77.4 Thu 12:00 MA 005

**Ultrafast metamorphosis of a complex charge-density wave** — Kerstin Haupt[1], Maximilian Eichberger[2], Nicolas Erasmus[1], Andrea Berenike Rohwer[1], Jure Demsar[3], Kai Rossnagel[4], and •Heinrich Schwoerer[1] — [1]Stellenbosch University, Stellenbosch 7600, South Afrika — [2]University of Konstanz, 78457 Konstanz, Germany — [3]University of Mainz, 55128 Mainz, Germany — [4]University of Kiel, 24098 Kiel, Germany

The transitions between commensurately and incommensurately modulated crystalline phases generally involve the formation and rearrangement of domain walls (discommensurations) and is thus thought to be extremely slow. Here, using ultrafast electron diffraction, we directly observe the structural dynamics of a photo-induced transition between a nearly commensurate and an incommensurate charge-density-wave phase in the strongly correlated layer compound 1T-$TaS_2$. The formation of the incommensurate phase is found to proceed in two steps, an ultrafast (≈1 ps) nucleation and a slower, thermally activated growth of domains. The transition can be fully completed in ≈100 ps, orders of magnitude faster than previously observed for commensurate-to-incommensurate transitions. The mechanism and time scales of this transition may be generic for ultrafast structural transformations between complex phases in which there is no direct path via coherent excitation of specific lattice modes.

O 77.5 Thu 12:15 MA 005

**Structural dynamics in 2D semiconductors probe by ultrafast electron diffraction.** — •Roman Bertoni, Lutz Waldecker, and Ralph Ernstorfer — Structural & Electronic Surface Dynamics, Fritz-Haber-Institut der MPG, Berlin, Germany

Femtosecond electron diffraction is known to be a powerful tool to study the interaction of lattice and electrons in two-dimensional systems during out-of-equilibrium dynamics. Recently, a new class of materials, transition metal dichalcogenide (TMDC), appears promising in order to build nanoscale devices.

We excite a nanometric thin film of WSe2 in resonance with an excitonic band and probe the resulting structural dynamics with ultrafast electron diffraction. We also use complementary technics implying femtosecond optical spectroscopy. By doing so, we address the impact of excitonic excitations onto the lattice and the electron-phonon coupling. Our results reveal an energy transfer from the electronic system to the lattice on picosecond time scale. In parallel, we observe a coherent structural response via the instantaneous activation of coherent phonon.

O 77.6 Thu 12:30 MA 005

**Initial Dynamics of the Photo Induced (8×2)↔(4×1) Peierls-like Phase Transition of the In/Si(111) System** — •T. Frigge, B. Hafke, B. Krenzer, C. Streubühr, P. Zhou, M. Ligges, D. von der Linde, U. Bovensiepen, and M. Horn-von Hoegen — Department of Physics, University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

The wire-type arrangement of Indium atoms on a Silicon(111) surface serves as a famous prototype for the formation of a quasi one-dimensional charge density wave in the groundstate. We used ultrafast time-resolved surface-sensitive electron diffraction to investigate the transient non-equilibrium dynamics of the impulsively driven $(8 \times 2) \rightarrow (4 \times 1)$ phase transition. Excitation of the $(8 \times 2)$ groundstate with fs-laser pulses revealed the formation of a metastable, supercooled $(4 \times 1)$ excited state at 30 K. Utilizing a tilted pulse front scheme together with a new 30 keV electron gun design we improved the temporal resolution to less than less 400 fs. The high transversal coherence length of 40 nm allows to follow both the initial dynamics in the unit-cell and the kinetics of the phase front on the nano-scale. At fluences of 4 mJ/$cm^2$ the CDW groundstate is lifted across the entire surface on timescales of less than 400 fs. A transient temperature rise of the Indium layer was determined through the intensity of the thermal diffuse background intensity utilizing the Debye-Waller effect. The laser induced heating by less than 40 K takes place on timescales 5 times slower than the metal-to-insulator transition which clearly rules out a simple thermal excitation scenario of the phase transition.

O 77.7 Thu 12:45 MA 005

**Fluence-Dependence of the Photo Induced (8×2)↔(4×1) Phase Transition in the In/Si(111) System** — •B. Hafke, T. Frigge, B. Krenzer, C. Streubühr, P. Zhou, M. Ligges, D. von der Linde, U. Bovensiepen, and M. Horn-von Hoegen — Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Deutschland

High-energy electron diffraction at grazing incidence (RHEED) in a pump-probe setup is used to study ultrafast surface phenomena on a femtosecond timescale. We employed this technique to follow the initial dynamics of a driven phase transition of Indium on a Silicon(111) substrate. Optical pumping of the Charge Density Wave (8×2) ground state at a base temperature of 30 K triggers an electronically driven structural phase transition to an undercooled metastable (4×1) phase. For fluences above 1.3 mJ/cm$^2$ the entire surface is excited into the (4 × 1) phase. At lower fluences the surface is excited only partially. We observe fluence-dependent changes of diffraction intensities: For low fluences the transition into the (4 × 1) phase occurs within 11 ps, at higher fluences of 1.8 mJ/cm$^2$ within 5 ps. We explain this by excitation of free electrons upon laser excitation, which accumulate at specific surface areas, e.g. defects, domain walls or steps. These areas act as nucleation seeds for the (8 × 2) → (4 × 1) transition which propagates linear in time. At higher fluences more nucleation seeds contribute, resulting in a shorter conversion time. For fluences below 1.3 mJ/cm$^2$ the excited carrier density is not sufficient to induce the conversion of the entire surface.

O 77.8 Thu 13:00 MA 005

**Femtosecond-laser-excited silicon surfaces** — •Tobias Zier, Eeuwe S. Zijlstra, and Martin E. Garcia — University of Kassel, Germany

A femtosecond-laser irradiation of crystalline silicon leads to interesting ultrafast phenomena, like thermal phonon squeezing [1], fractional diffusion and ultrafast melting [2], because of the highly nonequilibrium conditions created by the excitation. In particular, the energy is deposited mostly in the electronic system, which results in a very high electronic temperature (of the order of 10 000 K), and gives rise to an extreme change in the potential energy surface for the ions and therefore in the bonding character of the crystal. With our inhouse code CHIVES we perform MD-simulations of femtosecond-laser excited solids which allows us to analyse the microscopic atomic motions near the surface. We check the possibility of femtosecond-laser-induced structural phenomena at the surface, the existence of coherent vibrational surface states and the influence on the above mentioned phenomena.

[1] E. S. Zijlstra, A. Kalitsov, T. Zier, M. E. Garcia, Phys. Rev. X 3,011005 (2013)

[2] E. S. Zijlstra, A. Kalitsov, T. Zier, M. E. Garcia, Adv. Mater. 25, 5605 (2013)

## O 78: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale V

Time: Thursday 10:30–13:15 Location: MA 004

**Invited Talk** O 78.1 Thu 10:30 MA 004

**Interaction and Correlation Effects in Quasi Two-dimensional Materials** — •Steven G. Louie — Physics Department, University of California at Berkeley, and Lawrence Berkeley National Lab, Berkeley, CA 94720 USA

Experimental and theoretical studies of atomically thin quasi two-dimensional materials and their nanostructures have revealed that these systems can exhibit highly unusual behaviors. Owing to their reduced dimensionality, these systems present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry and many-body interaction effects often play a critical role in shaping qualitatively and quantitatively their properties. In this talk, we present some theoretical studies on graphene as well as other quasi-2D systems such as monolayer and few-layer transition metal dichalcogenides (e.g., MoS2, MoSe2, WS2, and WSe2) and metal monochalcogenides (such as GaSe and FeSe). Several quantum phenomena are discussed, including novel and dominant exciton effects, tunable magnetism, electron supercollimation by disorder, unusual plasmon behaviors, and possible enhanced superconductivity in some of these systems. We investigate their physical origins and compare theoretical predictions with experimental data.

O 78.2 Thu 11:00 MA 004

**Screening of the Coulomb interaction in two-dimensional semiconductors: The case of transition metal dichalcogenides** — •Ersoy Sasioglu, Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute forAdvanced Simulation, Forschungszentrum Jülich and JARA, 52425Jülich, Germany

Experimentally determined large exciton binding energies and nonhydrogenic Rydberg series in monolayer transition metal (TM) dichalcogenides indicate a long-range behavior of the Coulomb interaction. By means of first-principles calculations in conjunction with the random-phase approximation [1,2] within the FLAPW method [3] we study screening of the Coulomb interaction in two-dimensional semiconducting TM dichalcogenides MX$_2$ (M=Cr, Mo, W; X=S, Se). We show that the screening in these systems deviates substantially from the bulk behavior, i.e., the short-range interaction is strongly screened, while the long-range interaction is anti-screened. This unconventional screening reduces the gradient of the Coulomb interaction giving rise to weak correlation effects, which explains the experimentally observed large exciton binding energies as well as the success of the one-particle density functional theory in the description of the electronic structure of these systems. This work has been supported in part by DFG-FOR-1346.

[1] C. Friedrich *et al.*, Phys. Rev. B. **81**, 125102 (2010).
[2] E. Şaşıoğlu *et al.*, Phys. Rev. B **83**, 121101(R) (2011).
[3] www.flapw.de

O 78.3 Thu 11:15 MA 004

**Ultra-fast transient absorption spectra of monolayer MoS2 by first principle** — •Margherita Marsili[1], Deborah Prezzi[1], Davide Sangalli[2], and Andrea Marini[2] — [1]CNR Istituto di Nanoscienze S3, Modena, Italy — [2]CNR ISM, Montelibretti, Italy

We compute ultrafast transient absorption spectra of MoS2 monolayers by employing a novel approach which combines density-functional and non-equilibrium Green's function theories. This approach allows the description of pump-probe optical experiments where the system is excited by an ultrashort laser pulse, and the variation of the optical response is probed at different time delays, thus providing a wealth of information on the fundamental physics of the relaxation processes. The case of monolayer MoS2 is extremely challenging due to the interplay of excitonic, electron-phonon and spin-orbit coupling effects. We describe the excitation of the MoS2 electronic system and follow the subsequent dynamics using a fully non-collinear spin formulation of the theory, including excitonic effects. The results are compared with experimental pump-probe data.

O 78.4 Thu 11:30 MA 004

**Plasmon and exciton dispersion in two dimensions** — •Pier Luigi Cudazzo — LSI Ecole Polytechnique and ETSF, Palaiseau, France

Understanding the electronic properties of 2D materials requires the investigation of their elementary excitations that dictate their optical and transport properties. Using state-of-the-art Green's function many body approach we present a first principle study of the collective excitations (namely excitons and plasmons) in 2D materials. In particular from the evaluation of the dielectric function we investigated the exciton dispersion in graphane and hBN and the plasmon dispersion in metallic TMDs[1-3]. From our results we provide an exact analytic form of the two-dimensional screened potential. In contrast to 3D systems where the macroscopic screening can be described by a static dielectric constant in 2D systems the macroscopic screening is non local (q-dependent) showing a logarithmic divergence for small distances and reaching the unscreened Coulomb potential for large distances[4].

[1] P. Cudazzo, et. al. New J. Phys. 15 125005 (2013). [2] P. Cudazzo, et. al. (in preparation) [3] P. Cudazzo, et. al. Phys. Rev. Lett. 104 226804 (2010). [4] P. Cudazzo, et. al. Phys. Rev. B 84 085406 (2011).

O 78.5 Thu 11:45 MA 004

**Origin of metallic edge states in transition-metal-dichalcogenide nanostructures** — •Marco Gibertini and Nicola Marzari — Theory and Simulation of Materials (THEOS) and National Center for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, Switzerland

The existence of metallic edge states in transition-metal-dichalcogenide nanostructures has been reported both in the experimental and theoretical literature. Such nanostructures include for instance triangular islands and zigzag nanoribbons. Nonetheless, a thorough understanding of the mechanism giving rise to metallic states at the edge of such bulk insulating materials is still missing. Here we suggest a possible origin of such states and support our findings with first-principles density-functional-theory simulations. The key observation is that transition metal dichalcogenides like $MoS_2$ display a finite *formal* polarization that induces a charge reconstruction with the appearance of free carriers at the edges. We also suggest possible innovative applications in nanoelectronics and solar-energy devices.

O 78.6 Thu 12:00 MA 004

**Starting-point dependence in the Bethe-Salpeter equation: example of rutile $TiO_2$** — •Olga Turkina, Ute Werner, Dmitrii Nabok, and Claudia Draxl — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, D-12489 Berlin, Germany

Many-body perturbation theory, combining the GW approach and the Bethe-Salpeter equation (BSE), is a powerful tool for the description of one- and two-particle excitations. However, employing density functional theory as a starting point for these methods may lead to results that depend on the choice of the exchange-correlation (xc) functional. This starting-point dependence is well known for the $G_0W_0$ approximation. Such dependence is expected to occur also for BSE calculations, however, has not yet been investigated. With the example of rutile $TiO_2$, we show that this is, indeed, the case. We employ two different xc functionals: the generalized gradient approximation (PBE) and a hybrid functional (PBE0'), combining a fraction of 25% exact exchange with PBE. The electronic structure is calculated using the $G_0W_0$ approximation. The BSE is solved to obtain the optical absorption spectra. These are analyzed with regard to the influence of eigenvalues, wave functions, and screening as originating from different xc functionals.

O 78.7 Thu 12:15 MA 004

**Efficient exchange-correlation kernels for the description of excitonic effects in solids** — •Santiago Rigamonti[1,4], Silvana Botti[2,4], Valérie Veniard[3,4], Claudia Draxl[1,4], Lucia Reining[3,4], and Francesco Sottile[3,4] — [1]Physics Department, Humboldt-Universität zu Berlin, Germany — [2]Friedrich-Schiller Universität Jena, Institut für Festkörpertheorie und -optik — [3]Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France — [4]European Theoretical Spectroscopy Facility (ETSF)

One of the major challenges for time-dependent density-functional theory is the accurate and efficient description of excitonic effects in solids, captured by the exchange-correlation (xc) kernel. In a recent empirical approach, the so-called "bootstrap" kernel has been proposed. Due to its high efficiency and some promising results [1] it appeared indeed interesting. In this work, we find a physically motivated derivation for it, opening the way to understand its weaknesses and to propose a new xc kernel. Our kernel is both simpler and more reliable, as confirmed by our numerical results [2]. We also propose a simple method to estimate exciton binding energies from the dielectric functions computed in the random-phase approximation alone. This method makes the approach accessible to a wide range of scientists.

[1] S. Sharma, J. K. Dewhurst, A. Sanna, and E. K. U. Gross, *Phys. Rev. Lett.* **107**, 186401 (2011).
[2] S. Rigamonti, S. Botti, V. Veniard, C. Draxl, L. Reining, and F. Sottile, *submitted.*

O 78.8 Thu 12:30 MA 004

**Excitonic effects in many-body calculations** — •Matteo Gatti[1,2], Igor Reshetnyak[1], Giorgia Fugallo[1], Pierluigi Cudazzo[1], Francesco Sottile[1], and Lucia Reining[1] — [1]LSI, CNRS-Ecole Polytechnique and ETSF, Palaiseau, France — [2]Synchrotron Soleil, Gif-sur-Yvette, France

The Bethe-Salpeter equation (BSE) is the state-of-art approach to calculate the absorption spectra of a large variety of materials [1]. Here we show that that the BSE is a powerful and accurate method also for the calculation of the exciton dispersion [2-4] (i.e. the exciton energy as a function of the momentum $q$ carried by the electron-hole pair), and of the off-diagonal elements of the dielectric function in reciprocal space $\epsilon_{G,G'}(q,\omega)$ [5]. On the one hand, this allows the ab initio simulation of spectra measured by Electron Energy-Loss Spectroscopy (EELS) and Inelastic X-ray Scattering (IXS), including its Coherent version (CIXS), well beyond the optical limit $q\to 0$. On the other hand, this opens the door to the calculation of spectral functions [6-8] using the cumulant expansion for the Green's function $G$ with a screened Coulomb interaction $W$ that includes excitonic effects beyond the random-phase approximation employed in the GW approximation.

[1] G. Onida, *et al.*, Rev. Mod. Phys. **74**, 601 (2002). [2] M. Gatti and F. Sottile, Phys. Rev. B **88**, 155113 (2013). [3] P. Cudazzo, *et al.*, Phys. Rev. B **88**, 195152 (2013). [4] G. Fugallo, *et al.*, unpublished. [5] I. Reshetnyak, *et al.*, unpublished. [6] M. Guzzo, *et al.*, Phys. Rev. Lett. **107**, 166401 (2011). [7] M. Gatti and M. Guzzo, Phys. Rev. B **87**, 155147 (2013). [8] M. Guzzo, *et al.*, Phys. Rev. B **89**, 085425 (2014).

O 78.9 Thu 12:45 MA 004

**Efficient parameter-free calculation of absorption spectra for insulators, semiconductors and metals from time-dependent current DFT** — •Arjan Berger — LCPQ - IRSAMC, Université de Toulouse III - Paul Sabatier, CNRS, Toulouse, France and European Theoretical Spectroscopy Facility

In this work we show that with a simple dynamical kernel we can obtain good absorption spectra from time-dependent current-density functional theory (TDCDFT) for insulators, semiconductors and metals. Our approach is fully parameter free since no artificial broadening parameter is used to match calculated and measured spectra. The cost of a calculation is equal to an RPA calculation. Moreover, our TDCDFT approach scales better with system size than standard TDDFT implementations.

O 78.10 Thu 13:00 MA 004

**Optical excitations in $MoS_2$ within ab-initio many-body perturbation theory** — •Matthias Drüppel, Peter Krüger, and Michael Rohlfing — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany

The transition metal dichalcogenides (TMDC), and $MoS_2$ as its most prominent member, open the door to a field of two dimensional atomically thin semiconductors which offer rich physics.

The state of the art theoretical description of electronic excitations in these materials starts with density-functional calculations (DFT), followed by the $GW$ method in combination with a solution of the Bethe-Salpeter equation. The *converged* calculation (especially with respect to the size of the basis, i.e. number of plane waves, and k-meshs) of the last two steps has shown to be numerically extremely challenging.

We apply the efficient LDA+$GdW$ [1] approach to the excited states which enables us to describe electronic excitations in $MoS_2$ at substantially lower numerical cost. In the LDA+$GdW$ approximation the quasiparticle self-energy corrections to the LDA-DFT energies result from the difference between the correct screening (semiconducting) and hypothetical metallic screening.

This approach sets us in a position where more atoms per unit cells can be treated, e.g., for defects and for $MoS_2$ on substrates.

[1] M. Rohlfing, Phys. Rev. B. **82**, 205127 (2010)

# O 79: Scanning Probe Techniques: STM

Time: Thursday 10:30–13:00 Location: HE 101

O 79.1 Thu 10:30 HE 101

**Landau quantization in graphite studied by STM in a 30 Tesla magnet** — •Bas Hendriksen[1], Suruchi Singh[1,2], Wei Tao[2], Jan Gerritsen[1], Uli Zeitler[2], Peter Christianen[2], and Jan Kees Maan[2] — [1]Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands — [2]High Field Magnet Laboratory and Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Experiments in high field magnet laboratories play an important role in the discovery of new electronic phenomena in solid state materials. Superconducting laboratory magnets are typically limited to fields up to 20 Tesla and it requires resistive Bitter magnets at dedicated large-scale facilities to go to fields as high as 37 Tesla. In this talk I will present our pioneering experiments with a scanning tunneling microscope, which operates in the 30 Tesla Bitter magnets of the High Field Magnet Laboratory (HFML) user facility in Nijmegen. This STM provides access to atomic- and nanoscale physics in the high magnetic field regime, where the magnetic length is of the order of a few nanometers and energy level splitting is significant.

I will demonstrate the STM's performance in the noisy environment of the magnets (140l/s cooling water, 40kA magnet current). I will show our first results of Landau level spectroscopy in a graphite sample at 4.2K, which exhibits the characteristics of Landau levels in graphene. I will discuss how this is a first step towards solving the mystery of the quantum Hall effect in graphene at room temperature (K.S. Novoselov et al. Science 315 (2007) 1379).

O 79.2 Thu 10:45 HE 101

**Determining absolute values of the critical Josephson current from Josephson STM experiments** — •Berthold Jäck[1], Matthias Eltschka[1], Markus Etzkorn[1], Christian R. Ast[1], and Klaus Kern[1,2] — [1]Max-Planck Institute for Solid State Research, D-70569 Stuttgart — [2]École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

In Josephson junctions the critical Josephson current $i_0$ directly relates to the superconducting order parameter. Hence, Josephson Scanning Tunneling Microscopy (JSTM) has high potential as a local probe of superconductor physics, addressing questions such as the pairing symmetry of non-conventional superconductors [1]. However, extracting absolute values for $i_0$ from experiments renders difficult since both the surrounding environment and temperature strongly change the junction characteristics. Here, we present results on the Josephson effect in vanadium tunnel junctions using an STM that operates at a temperature of 15 mK [2]. Employing $P(E)$-theory as given in Reference [3], which considers the coupling to the environment and temperature effects, we can fit our experimental data. From this fit we find values of $i_0$ being in good agreement to values calculated from theory [4], which represents a fundamental step towards the realization of JSTM.

[1] J.Smakov *et al.*, Phys. Rev. B **64**, 212506 (2001)

[2] M.Assig *et al.*, Rev. Sci. Instrum. **84**, 033903 (2013)

[3] G.-L.Ingold and H.Grabert, Europhys. Lett. **14**, 371 (1991)

[4] V.Ambegaokar and A.Baratoff, Phys. Rev. Lett. **10**, 11 (1963)

O 79.3 Thu 11:00 HE 101

**Laser induced charge dynamics at the GaAs(110) surface investigated with Scanning Tunneling Microscopy** — •Philipp Kloth, Katharina Kaiser, Ole Bunjes, Terence Thias, and Martin Wenderoth — IV. physikalisches Instut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

Using optical pump probe excitation and Scanning Tunneling Microscopy we have studied the carrier dynamics at the GaAs(110) surface. We have developed a compact and convenient laser setup that provides any Tunnel Microscope with time resolution in a range from nanoseconds to microseconds. Detailed spectroscopic analysis shows that photo-excited charge carriers, trapped in a very local region beneath the STM tip, contribute to the tunneling current. By changing the bias voltage or the set point current we are able to actively select whether this optically induced tunnel channel or the common tunneling channel, present under dark conditions, dominates the overall tunneling process. This allows us to distinguish between the dynamics of inter-band recombination of the electron and hole pairs and the dynamics of the charge annihilation of the photo-excited carriers via the tunnel current.

O 79.4 Thu 11:15 HE 101

**A Self-Tracking Spectroscopic Method for Surface Photovoltage Measurements on Semiconducting Surfaces** — •Kevin Oldenburg, Stefan Polei, Sylvia Speller, and Ingo Barke — University of Rostock, Institute of Physics, 18051 Rostock, Germany

Spatially resolved surface photovoltage (SPV) measurements by means of scanning tunneling microscopy enable access to the local band topology at semiconductor surfaces. In the presence of metallic surface states the SPV can be easily obtained from I(V) curves under continuous wave (cw) illumination [1]. For semiconducting surfaces, however, the weak Fermi level pinning leads to tip induced band bending [2] that is difficult distinguish from the effect of the SPV under cw conditions. We present a new experimental approach that automatically keeps the electric field between tip and sample constant with respect to the light intensity by tracking the SPV simultaneously with its measurement. The method is benchmarked for the case of Si(100)-c(4x2) at different bulk doping levels. The role of tip-induced band bending is discussed in comparison to alternative techniques.

[1] K. Sell et al., Phys. Stat. Sol. B 247, 1087 (2010).

[2] M. McEllistrem, G. Haase, D. Chen, and R. J. Hamers, Phys. Rev. Lett. 70, 2471 (1993).

**Invited Talk** O 79.5 Thu 11:30 HE 101

**Spin Excitations and Correlations in Individual Molecules on Surfaces** — •Markus Ternes — Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Scanning probe microscopes and, in particular, the scanning tunneling microscope have been shown to be very powerful tools for the investigation of magnetism at the atomic and molecular scale.

In my talk I will discuss recent results on an all organic radical molecule with $S = 1/2$ and on cobalt-hydrogen complexes adsorbed on a strongly anisotropic surface. In these systems we detect the quantum magnetism by inelastic spin-flip excitations and the emergence of correlation effects which are due to the interactions between the localized spin and the substrate electrons. I will show that the results can be well understood by employing third-order scattering theory using a Kondo Hamiltonian which also enables a deeper insight into spectroscopic features measured on single atoms. Expanding this model by coupling the spin to a dissipative quantum bath, enables to understand the experimentally observed interplay between magnetic anisotropy and the exchange interactions with the substrate. Furthermore, I will show that by changing the coupling between individual spins the emerging spectroscopic features enables to determine the spin-spin correlation quantitatively.

O 79.6 Thu 12:00 HE 101

**Scanning Tunneling Potentiometry: Magnetotransport on the Atomic Scale** — Philip Willke, •Thomas Kotzott, Anna Sinterhauf, and Martin Wenderoth — IV. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

The method of scanning tunneling potentiometry (STP) has been introduced by Muralt and Pohl [1] as a technique for mapping the electrochemical potential locally and has been developed continuously [2]. Here we present a new STP setup with a home-built low-temperature STM operating at 6K and applicable magnetic field of up to 6T. We study high-resolution STP of scattering centers on a sub-nanometer scale, especially the spatial evolution of the electrochemical potential for the graphene monolayer/bilayer junction. We perform magnetotransport STP measurements mapping the local electrochemical potential as a function of the applied magnetic field. This allows us to identify localized and delocalized contributions to the magnetoresistance in epitaxial-grown graphene. This work was supported by DFG priority program 1459 ”Graphene”.

[1] P. Muralt, D. W. Pohl, Appl. Phys. Lett. 48, 514 (1986)

[2] T. Druga, M. Wenderoth, J. Homoth, M. A. Schneider and R. G. Ulbrich, Rev. Sci. Instrum. 81, 083704 (2010)

O 79.7 Thu 12:15 HE 101

**Inelastic tunneling through a hydrogen molecule** — •Matthias

Stocker, Simon Röger, and Berndt Koslowski — Universität Ulm, Ulm, Deutschland

Recent studies showed strong characteristic features in Inelastic Electron Tunneling Spectroscopy if molecular hydrogen was physisorbed on a metallic substrate surface [1,2]. In the low energy regime not only huge inelastic signals were measured but also a step-like change of the tunneling current corresponding to a strong negative differential conductivity appeared. This characteristic behavior was explained by a two-level system exhibiting two distinct conductivities, and the occupation of the two levels being controlled by the applied bias. However, details of the two-level system are a matter of speculation, yet. On the basis of detailed spectroscopic measurements, we will propose a new formalism to analyze the behavior of such I-V characteristics. We will try to explain the observed features by dynamic properties of a hydrogen molecule in the tunneling junction.

[1] F. Natterer, F. Patthey, H. Brune, PRL 111, 175303 (2013). [2] S. Li, A. Yu, F. Toledo, Z. Han, H. Wang, H.Y. He,R. Wu, W. Ho, PRL 111, 146102 (2013).

O 79.8 Thu 12:30 HE 101

**Role of the microscopic tip apex in STM-IETS measurements** — Norio Okabayashi[1,2], Alexander Gustafsson[3], •Angelo Peronio[1], Magnus Paulsson[3], Toyoko Arai[2], and Franz J. Giessibl[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, D-93053 Regensburg, Germany — [2]Graduate School of Natural Science and Technology, Kanazawa University, Ishikawa, Japan — [3]School of Computer Science, Physics and Mathematics, Linnaeus University, 391 82 Kalmar, Sweden

The tunnelling process at the heart of Scanning Tunnelling Microscopy (STM) involves both the electronic states of the sample under study and of the tip of the microscope. Hence, STM imaging and spectroscopy are heavily affected by the microscopic structure of the tip apex, which is difficult to characterize. This uncertainty can be in addressed by combined STM/AFM experiments, using an adsorbed CO molecule to image the tip apex itself, the so-called COFI technique [1].

With this technique, we addressed the role of tip apex termination in IETS vibrational spectroscopy, by investigating single CO molecules adsorbed on a copper surface.

References:

[1] Hofmann T, Pielmeier F, and Giessibl FJ. Chemical and Crystallographic Characterization of the Tip Apex in Scanning Probe Microscopy. Physical Review Letters 112 066101 (2014). http://dx.doi.org/10.1103/PhysRevLett.112.066101

O 79.9 Thu 12:45 HE 101

**Tip radius quantification using feature size mapping of field ion microscopy images** — •Sören Zint[1], Daniel Ebeling[1], Dirk Dietzel[1], Jens Falter[1,2], and André Schirmeisen[1] — [1]Institute of Applied Physics (IAP), Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany — [2]TransMIT-Center of Adaptive Cryotechnology and Sensors, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

We are presenting a novel and rapid approach to determine the tip radius of sharp tungsten tips characterized by field ion microscopy. Utilizing certain features with well known dimensions on the surface of these tips around the crystallographic [111] direction allows us to increase the accuracy of the radius measurement by almost one order of magnitude in comparison to standard methods. Employing a few reasonable approximations it is possible to derive an analytical expression for the tip radius as a function of the observed feature size on the microchannel plate and some geometric parameters of the setup. Finally, we show that field ion microscopy images can be reconstructed on the atomic level by using a perfect hemisphere with the determined radius as a starting value and a low number of modifications in the topmost surface layers. In particular, this is useful for quantifying tip-sample interactions and characterizing material properties in atomic force microscopy.

## O 80: Graphene: Structure

Time: Thursday 10:30–13:00 Location: MA 041

O 80.1 Thu 10:30 MA 041

**Manganese Intercalation in Graphene/Ir(111): a structural study** — •Stefan Böttcher[1], Hendrik Vita[1], Yuriy S. Dedkov[2], and Karsten Horn[1] — [1]Fritz-Haber Institute, Faradayweg 4-6, 14195 Berlin — [2]SPECS Surface Nano Analysis GmbH, Voltastrasse 5, 13355 Berlin

The graphene/substrate interaction is of interest for a many applications, and to understand and classify the interaction mechanism as such. For example, the 3d transition metals Fe, Co and Ni on the one hand, and Cu on the other suggest that a classification into strongly and weakly interacting systems may be possible, as judged by criteria such as the survival of the Dirac cone or the crystallographic structure of the graphene layer. Here we present a structural study, through LEED and STM, of manganese intercalation on graphene/Ir(111), a system that has so far not been studied. We follow the stages of the intercalation process, from the deposition of Mn on top through the formation of the intercalated phase. Manganese is found to be arranged pseudomorphically to the Ir(111) substrate underneath graphene. While several criteria for a weak interaction are fulfilled, the graphene/Mn/Ir(111) system also shows structural evidence for a strong interaction between the graphene and the Mn layer, e.g. a lower separation between graphene and the intercalated layer, a conclusion that is further supported by ARPES. Manganese intercalation may therefore be special because it fills the gap between the strongly and weakly interacting transition metals. In addition, at higher intercalation temperatures a new, possibly surface alloyed phase is observed.

O 80.2 Thu 10:45 MA 041

**Manganese Intercalation in Graphene/Ir(111): electronic structure** — •Hendrik Vita[1], Stefan Böttcher[1], Yuriy Dedkov[2], and Karsten Horn[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]SPECS Surface Nano Analysis GmbH, Berlin, Germany

Transition metal surfaces are ideal templates for the growth of high quality graphene films. The system graphene/Ir(111) shows rather weak interaction between substrate and the graphene layer. It is well known that transition metals such as Ni and Co, intercalated under graphene/Ir(111), show a rather strong interaction with graphene, yielding massive modifications of the graphene $\pi$-band. The intercalation of Mn thin films underneath graphene seems interesting in this context, since Mn has a half filled 3d shell, and the graphene sheet may act as an inert, passivating cover. Here we investigate graphene/Mn/Ir(111) by deposition on top of graphene/Ir(111), and follow the intercalation process by annealing at moderate temperatures using XPS. Investigating the band structure by high resolution ARPES, the Dirac cone is preserved, and we observe a trigonal suppression of the replica Dirac cones, probably due to an enhanced corrugation of the graphene film. A totally different situation occurs if the intercalation process is performed at much higher temperatures. Drastic changes in the band structure emerge, with a shifted $\pi$-band to higher binding energies, and a chemical shift of the C1s core level. Additionally, a restructuring of the intercalated Mn thin film is observed by LEED.

O 80.3 Thu 11:00 MA 041

**Atomically Resolved Graphitic Surfaces in Air by Atomic Force Microscopy** — •Daniel S. Wastl, Alfred J. Weymouth, and Franz J. Giessibl — University of Regensburg, Universitätsstrasse 31, 93053 Regensburg, Germany

Imaging at the atomic scale with atomic force microscopy in biocompatible environments is an ongoing challenge. We demonstrate here atomic resolution of graphite and hydrogen-intercalated graphene on SiC in air1. The main challenges arise from the overall surface cleanliness and the water layers which form on almost all surfaces2. To further investigate the influence of the water layers, we compare data taken with a hydrophilic bulk-silicon tip to a hydrophobic sapphire tip. While atomic resolution can be achieved with both tip materials at moderate interaction forces, the strong differences in force versus distance spectra can be related to the water layers on the tips and samples. Imaging at very low tip-sample interaction forces results in the observation of large terraces of a naturally-occurring stripe structure on the hydrogen intercalated graphene[1]. This structure has been previously reported on graphitic surfaces that are not covered with disordered adsorbates in ambient conditions (i.e. on graphite and bilayer graphene on SiC[3], but not on monolayer graphene on SiC). Both these observations indicate that hydrogen-intercalated graphene is close to an ideal graphene sample in ambient environments.

[1] Wastl, Weymouth, Giessibl, ACS Nano 8, 5233 (2014).
[2] Wastl Weymouth, Giessibl, Phys. Rev. B 87, 245415 (2013).
[3] Wastl et al., ACS Nano 7, 10032 (2013).

O 80.4 Thu 11:15 MA 041

**A route to free-standing graphene by removal of the Ni substrate by a gas phase reaction** — •Ann-Kathrin Henss[1], Patrick Zeller[1], Michael Weinl[2], Matthias Schreck[2], and Joost Wintterlin[1] — [1]Ludwig-Maximilians-Universität, Munich, Germany — [2]Universität Augsburg, Augsburg, Germany

An essential step for the use of graphene in electronic devices is the removal of the underlying metal substrate after graphene growth. We have tested a new route to free-standing graphene grown on thin single crystalline Ni(111) films. The 150 nm thick metal films were epitaxially grown on a Si(111) wafer separated by a 120 to 150 nm thick yttria-stabilized zirconia (YSZ) buffer layer. Aligned monolayer graphene was grown by chemical vapor deposition using ethylene as precursor gas under ultra high vacuum conditions. The graphene quality was monitored by scanning tunneling microscopy and low energy electron diffraction. The subsequent removal of the nickel substrate was performed in a pure gas phase reaction. In the so called Mond process, a chemical transport reaction, nickel reacts with carbon monoxide to gaseous nickel tetracarbonyl at 350 K. By applying a temperature gradient in the reaction furnace the formed carbonyl complex is transported to areas with higher temperature leaving graphene on the isolating YSZ buffer layer of the substrate. X-ray photoelectron spectroscopy, scanning electron microscopy and Raman spectroscopy were used to study the samples after this process.

O 80.5 Thu 11:30 MA 041

**Freestanding lateral nanostructures of two-dimensional carbon materials** — •Andreas Winter[1], Yasin Ekinci[2], Rainer Stosch[3], Thomas Weimann[3], Johannes Biskupek[4], Ute Kaiser[4], and Andrey Turchanin[1] — [1]Faculty of Physics, Bielefeld University, 33615 Bielefeld, Germany — [2]Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen, Switzerland — [3]Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany — [4]Electron Microscopy Group of Materials Science, Ulm University, 89081 Ulm, Germany

Two-dimensional (2D) carbon materials like graphene, hexagonal boron nitride or carbon nanomembranes (CNMs) have recently attracted enormous interest due to their potential use in electronics, chemical and biological sensors, nanofilters, hybrid materials etc. Most applications require a lithographic patterning of these 2D materials. Here we present various micro- and nanostructures of graphene and CNMs as well as their in-plane heterostructures fabricated via optical, e-beam and EUV interference lithography. The preparation of these structures on supporting substrates as well as large area freestanding nanomembranes with patterns varying from ca. 100 $\mu$m to 50 nm will be shown. Via electron irradiation, graphene and dielectric CNMs can be stitched together, forming electrically heterogeneous ultrathin 2D carbon sheets. We characterize their properties employing X-ray photoelectron and Raman spectroscopy, helium ion microscopy and high-resolution TEM.

O 80.6 Thu 11:45 MA 041

**Graphene Membranes as Electron Transparent Windows for Photoelectron Spectroscopy** — •Jürgen Kraus[1], Robert Reichelt[1], Sebastian Günther[1], Luca Gregoratti[2], Matteo Amati[2], Maya Kiskinova[2], Alexander Yulaev[4], Ivan Vlassiouk[3], and Andrei Kolmakov[4] — [1]TU München Chemie Department, Lichtenbergstr. 4, D-85748 Garching — [2]Sincrotrone Trieste, Area Science Park, 34149 Trieste, Italy — [3]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA — [4]Center for Nanoscale Science and Technology, NIST, Gaithersburg, MD 20899, USA

The high mechanical stability of graphene (g) allows the construction of ultrathin gas tight membranes. Transferred few layer thick g covering the orifice of an environmental cell could be used to seal a water droplet inside the cell from the surrounding vacuum of the ultra-high vacuum chamber into which the cell was introduced. The used membranes were transparent even for slow photoelectrons (PEs), so that the sealed water could be characterized by x-ray photoelectron spectroscopy (XPS). We also measured the electron attenuation length of monolayer g on Cu for PEs of 200-1000 eV kinetic energy. We were able to produce free standing monolayer g by locally electrochemically etching the Cu-substrate underneath the as-grown g. After deposition of gold on the membrane backside and acquiring Au 4f PEs from the opposite site, we proved that $< 1\%$ of a monolayer Au can be detected through the suspended g membrane. This pushes the applicability of our membrane based XPS technique towards surface characterization under ambient conditions.

O 80.7 Thu 12:00 MA 041

**Irradiation of Graphene-FETs with highly charged Ions** — •Philipp Ernst[1], Roland Kozubek[1], Oliver Ochedowski[1], Jens Sonntag[2], Axel Lorke[2], and Marika Schleberger[1] — [1]Universität Duisburg-Essen, AG Schleberger, Duisburg, Germany — [2]Universität Duisburg-Essen, AG Lorke, Duisburg, Germany

We have studied the influence of ion bombardment on the properties of graphene field-effect transistor (FET) structures. We used highly charged ions (HCI) with different potential energies at roughly the same kinetic energy (charge state $\mathrm{Xe}^{32+}$ and $\mathrm{Xe}^{25+}$ with $E_{\mathrm{kin}} = 220$ keV and $E_{\mathrm{kin}} = 195$ keV). Electrical transport measurements, Raman spectroscopy, and atomic force microscopy were used to investigate the electrical and structural modifications of the graphene-FETs induced by the ion irradiation. The electrical analysis was performed *in-situ* in the ultra-high vacuum set up used for the irradiation. For all investigated fluences, the experiments show a reduction of the mobility, which scales with the potential energy of the ions. Remarkably, the influence of the impact of highly charged ions is already measurable at extremly low fluences $< 15$ ions/$\mu$m$^2$. As a consequence of the irradiation, a p-doping effect could be observed. Further experiments at lower kinetic energies ($< 50$ keV) are planned to clarify how the potential energy of the impinging HCIs will affect the observed irradiation effects in graphene.

O 80.8 Thu 12:15 MA 041

**Increasing the mobility of holes in graphene FETs by irradiation with swift heavy ions** — •Tobias Foller, Philipp Ernst, Oliver Ochedowski, Roland Kozubek, Lukas Madauss, and Marika Schleberger — Fakultät für Physik and CeNIDE, Universität Duisburg-Essen, 47048 Duisburg, Germany

In this work graphene field-effect transistors (FETs) are modified by irradiation with swift heavy ions (SHI, $\mathrm{Xe}^{23+}$ with $E_{\mathrm{kin}} = 91$ MeV). Graphene FETs are prepared by exfoliation of a HOPG crystal followed by deposition of metal contacts via Photolithography. They allow to investigate the mobility of charge carriers in graphene. Current measurements, Raman spectroscopy and atomic force microscopy have been used to investigate the electrical and structural modifications of graphene due to the ion irradiation. By irradiation with swift heavy ions under perpendicular incidence with small fluences ($\approx 2500$ ions/$\mu m^2$), we have succeeded in almost doubling the mobility of holes compared to the unirradiated sample.On the other hand irradiation under glancing incidence ($\leq 2°$) with fluences of 10 ions/$\mu m^2$ have revealed that, despite the rather small changes in the ($I_{\mathrm{D}}/I_{\mathrm{G}}$)-ratio in the Raman spectrum, the charge carrier mobility is significantly reduced.

O 80.9 Thu 12:30 MA 041

**Structure, strain distribution and energetics of basal-plane dislocations in bilayer graphene** — •Konstantin Weber and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

A recent TEM study [1] demonstrated that substrate-grown graphene bilayers are typically not perfect in registry, but contain a high concentration of basal-plane dislocations. Using atomistic simulations based on the registry-dependent potential of Kolmogorov and Crespi [2] and the classical AIREBO potential we investigated the atomic structure and the properties of the 4 different types of dislocations with shortest possible Burgers vector in bilayer graphene, the thinnest imaginable crystal that can host such 1D defects. We find that each of the 4 different dislocations splits into two partial dislocations. The partials are equally spaced due to the absence of a stacking fault energy, a peculiar property of bilayer graphene. Furthermore, partials with a step component give rise to a pronounced buckling of the graphene bilayer. An analysis of the atomic structure, local strain distribution, disregistry and dislocation energy of the dislocations will be given and we will highlight how their properties differ from textbook examples of dislocations in 3D crystals.

[1] B.Butz, C. Dolle, F. Niekiel, K. Weber, D. Waldmann, H.B. Weber, B. Meyer, E. Spieker, *Nature* **505**, 533 (2014).

[2] A. Kolmogorov, V. Crespi, *Phys. Rev. B* **71**, 235415 (2005).

O 80.10 Thu 12:45 MA 041

**Plasma-enhanced chemical vapor deposition of graphene on metallic substrates** — •Nicolas Wöhrl[1], Oliver Ochedowski[2], Steven Gottlieb[2], Stephan Schulz[1], and Volker Buck[2] — [1]Faculty of Chemistry and CENIDE, University Duisburg-Essen, 47057 Duisburg, Germany — [2]Faculty of Physics and CENIDE, University Duisburg Essen, 47057 Duisburg, Germany

In this work we present the synthesis of graphene on copper and nickel substrates by microwave Plasma-enhanced Chemical Vapor Deposition (PE-CVD) process. The special construction of the plasma source allows the deposition at a wide range of different process parameters giving a fast and inexpensive method to synthesize graphene. Additional advantages of the plasma deposition of graphene are lower substrate temperatures compared with thermal CVD processes. In contrast to the thermal CVD the gaseous precursors are already decomposed in the plasma and the plasma parameters are varied to investigate the influence on the nucleation and growth of graphene and on the defect density in the graphene layers. Optical emission spectroscopy is used to characterize the plasma properties while Raman spectroscopy and AFM measurements are used as nondestructive tools for the characterization of the synthesized graphene films. Especially Raman spectroscopy is used as a suitable tool to determine the number of graphene layers, the disorder and the defect density. We present a possible way to produce large area of monolayer graphene on metallic substrates with the prospect to make graphene available for industrial applications.

## O 81: Gerhard Ertl Young Investigator Award

Time: Thursday 10:30–13:00 Location: MA 042

O 81.1 Thu 10:30 MA 042

**Caught in the act! Live observations of catalysts using high-pressure scanning probe microscopy** — •Irene M.N. Groot[1] and Joost W.M. Frenken[2] — [1]Huygens-Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9502, 2300 RA Leiden, the Netherlands — [2]Advanced Research Center for Nanolithography, P.O. Box 41883, 1009 DB Amsterdam, the Netherlands

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum (UHV) conditions of traditional laboratory experiments. These observations made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts were designed to operate under UHV conditions.

This talk focuses on the development of scanning probe microscopy for operando observations of active model catalysts. We have developed set-ups that combine a UHV environment with a high-pressure flow reactor cell, integrated with scanning probe microscopy and mass spectrometry. In this way, we can correlate structural changes of the catalyst with its catalytic performance.

This talk highlights a short overview of the instruments we developed. Some results for CO oxidation will be shown. But additionally, results for a more complex reaction, production of chlorine, will be discussed.

O 81.2 Thu 11:00 MA 042

**High Spatial Resolution Operando IR and X-ray Microspectroscopy Measurements of Multistep Catalytic Reactions in Flow Reactor** — •Elad Gross — Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Molecular-level analysis of catalytic reactions in flow reactors and detection of short lived intermediates are essential for optimization of complex reactions. In this study, multistep catalytic reaction in flow reactor was analyzed by spectral mapping of the catalyst and the organic phase with a spatial resolution of 15 $\mu$m, employing micrometer-sized synchrotron-sourced IR and X-ray beams. The catalyst in this reaction was two nanometer sized Au nanoclusters that were encapsulated within a dendrimer matrix and loaded on mesoporous SiO2 support. The catalyst was packed within a flow microreactor and its reactivity was tested toward the cascade reaction of dihydropyran formation. In-situ synchrotron-sourced IR microspectroscopy detected the reactant-into-product transformation along the flow reactor. By tuning the residence time of the reactants, full kinetic analysis of the catalytic reaction was achieved. X-ray absorption microspectroscopy scan along the flow reactor correlated locally-enhanced catalytic conversion, as detected by IR microspectroscopy, to areas with high concentration of Au(III), the catalytically active species. This study demonstrates the fundamental understanding of mechanism of catalytic reactions that can be gained by detailed in-situ mapping of multistep reactions in flow reactors.

O 81.3 Thu 11:30 MA 042

**Atto-to-Nanosecond Electron Dynamics at Surfaces probed by Time-Resolved Core-Level Photoelectron Spectroscopy** — •Stefan Neppl — Lawrence Berkeley National Laboratory, Berkeley, CA, USA

In the first part of my talk, I will discuss recent experiments that address the ultrafast dynamics inherent to all photoemission processes in condensed phase matter. In these measurements, an XUV attosecond light pulse launches photoelectron wave packets inside a solid. The emission dynamics of the photoelectrons are probed with a few-cycle VIS/NIR laser pulse [1,2]. We demonstrate that this streaking approach is capable of resolving subtle emission delays between electron wave packets that are released from different energy levels of the solid with a precision of only a few attoseconds (1 as = 10-18 s). For the simple metal magnesium we show that these time shifts can be interpreted as the real-time observation of photoelectrons propagating through the crystal lattice prior to their escape into vacuum [3]. In the second part, I will describe the implementation of femto- and picosecond time-resolved photoelectron spectroscopy at the Linac Coherent Light Source and at the Advanced Light Source with the goal to follow light-driven electron dynamics at dye-semiconductor interfaces on femto- to nanosecond timescales [4,5].

[1] Cavalieri et al. Nature 449, 1029 (2007); [2] Neppl et al. Phys. Rev. Lett. 109, 087401 (2012); [3] Neppl et al. Nature (2014) accepted; [4] Siefermann et al. J. Phys. Chem. Lett 5, 2753 (2014); [5] Neppl et al. Faraday Discuss. 171, 219 (2014).

O 81.4 Thu 12:00 MA 042

**A surface science route towards fully controlled single molecule manipulation** — •Christian Wagner — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — JARA-Fundamentals of Future Information Technology

Exploring the potential of molecular nanotechnology requires accurate manipulation of large functional molecules. For this purpose, the surface science approach of using a low-temperature scanning probe microscope is currently without alternatives. Still, reliable control requires knowledge of the potential energy surface (PES) experienced by the molecule. In my talk I will outline how the controlled manipulation of organic molecules, in combination with sensitive force-detection, yields new insights into the energetics of adsorption. The freedom to position the tip-attached molecule in any feasible geometry, even far above the surface, allows to reconstruct the entire adsorption potential, from equilibrium height [1] to the asymptotic regime of weak van der Waals interaction [2]. The controlled extraction of a molecule from a monolayer yields complementary information about the intermolecular potential. By comparing differently sized molecules we study the transferability and scalability of experimentally determined molecule-surface potentials. Iteratively improving our knowledge of the PES through more and more precise manipulation, atomic level control over complex molecules might soon become reality.

[1] Wagner, Fournier, Tautz, Temirov, *PRL* **109**, 076102 (2012).

[2] Wagner, Fournier, Ruiz, Li, Müllen, Rohlfing, Tkatchenko, Temirov, Tautz, *Nat. Commun.* **5**, 5568 (2014).

O 81.5 Thu 12:30 MA 042

**A phantom force and lateral force microscopy** — •Alfred J. Weymouth and Franz J. Giessibl — University of Regensburg, 93040 Regensburg, Germany

Atomic force microscopy (AFM) allows us to investigate mechanical properties of surfaces and adsorbates at the atomic scale. With a conducting tip, scanning tunnelling microscopy (STM) can be simultaneously performed.

When we measured simultaneous STM and AFM on Si, the unsaturated Si atoms surprisingly appeared repulsive. Our theory is that this is due to a decrease of the electrostatic force [1]. The attractive chemical interaction is still present, but the electrostatic force can be detected at further tip-sample distances. We called this the phantom force, and explained it by an additional resistance within the sample [2]. This resistance can also affect STM measurements, and this effect has recently been observed on Cu surfaces with sub-monolayer oxide layers [3].

Although most AFM measurements are sensitive to vertical forces, we can rotate the AFM sensor and measure lateral forces, a technique we call Lateral Force Microscopy (LFM). We applied LFM to quantify the bending of a CO molecule at the apex of an AFM tip [4]. In this talk, I will compare these findings to new data with a bare metal tip.

[1] Weymouth et al, Phys. Rev. Lett. 106, 226801
[2] Weymouth and Giessibl, Appl. Phys. Lett. 101, 213105
[3] Matencio et al, submitted
[4] Weymouth, Hofmann and Giessibl, Science, 343, 1120

## O 82: Nanostructure at Surfaces: Dots and Clusters

Time: Thursday 10:30–13:30 Location: MA 043

O 82.1 Thu 10:30 MA 043

**CO2 Activation on ultra-small Au particles on MgO Thin Films** — •Christian Stiehler[1], Florencia Calaza[1], Martin Sterrer[1], Niklas Nilius[2], and Hans-Joachim Freund[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26111 Oldenburg, Germany

Metal particles exhibit favorable catalytic properties that are unknown for the respective bulk metals [1]. Although several reasons are discussed in the literature, the true origin for their enhanced activity remains unknown. Electron quantization and the associated bandgap opening at the Fermi level are certainly involved in the unusual catalytic response of the nano-islands. In this talk, we discuss the electronic structure of Au clusters that contain 50-200 atoms and are of monolayer height [2,3]. Simultaneously, we have probed the ability of the particles to bind and activate carbon dioxide (CO2), by using STM, XPS, TPD and IRAS measurements. The molecules preferentially bind along the cluster edge, at which a charge transfer from the electron-rich perimeter into the adsorbates takes place. Our talk addresses possible interrelations between the CO2 adsorption behavior and the quantized electronic structure of the gold islands.

[1] M. Valden et al., Sci 281, 1647 (1998)
[2] X. Lin et al., PLR 102, 2068011 (2009)
[3] C. Stiehler et al., PRB 88, 115415 (2014)

O 82.2 Thu 10:45 MA 043

**Ripening mechanisms of supported size-selected clusters** — •Fabian Knoller, Michael König, Yves Fukamori, Friedrich Esch, and Ueli Heiz — Technische Universität München, Chair of Physical Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany

Truly monodisperse clusters give an unprecedented access to the investigation of ripening in the non-scalable size regime. Here, the ripening dynamics of individual Pd19 clusters have been studied on a strongly interacting Rh(111) surface and on a weakly interacting supported, periodically wettable Moiré-graphene film [1]. Whereas on the former substrate Ostwald ripening is observed in series of STM images at room temperature, the latter shows Smoluchowski ripening at slightly elevated temperatures of about 323 K. In both cases, the lateral resolution is sufficient to detect isomerization processes that influence the ripening kinetics: shape-dependent atom detachment linked to atom diffusion, respectively height fluctuations linked to cluster diffusion. These movements act intermittently, on much faster time scales than the mean ripening process. We try to tackle this experimental problem by two additional STM measurement techniques, implemented by one electronic device: With FastSTM, time series with a temporal resolution of up to now 10 frames/s have been gained, while Atom Tracking allows for lateral and vertical determination of the cluster maxima with a time resolution down to 5 ms and a lateral resolution below atomic dimensions.

[1] Y. Fukamori, M. König, B. Yoon, B. Wang, F. Esch, U. Heiz and U. Landman, ChemCatChem 5 (2013) 3330-3341

O 82.3 Thu 11:00 MA 043

**STM and STS study of Tb induced magic clusters on Si(111)7x7** — •Jan Grosse, Martin Franz, and Mario Dähne — Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

Surface clusters constitute a promising new research field in solid state physics due to their interesting quantum properties and possible future applications in nanodevices and catalysis. In this work, scanning tunneling microscopy (STM) and spectroscopy (STS) was used to study Tb induced clusters on the Si(111)7x7 surface. The samples were prepared by molecular beam epitaxy using submonolayer Tb coverages and annealing at moderate temperatures. It was found that the self-organized growth of clusters occurred in the center of the 7x7 half unit cells. These clusters have a triangular shape, but do not show the mirror symmetry of the half unit cell, thus they form one of the two equivalent rotated configurations. Furthermore, the ability of tip-induced switching between these two configurations was demonstrated. From atomically resolved STM images a structure model explaining nicely our observations could be developed. Additionally, STS measurements were performed in order to compare the electronic structure of the centered clusters with the surrounding Si(111)7x7 surface.

This work was supported by the DFG, FOR 1282, project D.

O 82.4 Thu 11:15 MA 043

**Simulation of AFM-images for Fe-clusters on Cu(111)** — •Svitlana Polesya[1], Sergiy Mankovsky[1], Diemo Ködderitzsch[1], Jan Minár[1], Hubert Ebert[1], and Franz Giessibl[2] — [1]LMU München, Dept. Physikalische Chemie, München, Germany — [2]Institut für Experimentelle Physik, Univ. Regensburg, Germany

The present work is motivated by a study on small Fe$_n$-clusters ($n = 1, 2,$ and 3) on Cu(111) surface using Atomic Force Microscopy (AFM) at subatomic level. The first part of the work is devoted to the investigation of the ground state properties of deposited Fe clusters by means of DFT calculations. The crucial role of the relaxation of the Cu surface for the equilibrium position of Fe atoms is demonstrated. The effect of electronic correlations on the equilibrium positions have been investigated within the LSDA+U calculations using different U values. In the second part of the work the forces on the tip approaching the Fe/Cu(111) surface are studied. The tip was modeled by a single atom of inert gas as well as by an H atom. The dependence of the AFM image on the tip-cluster distance is shown that is in agreement with the experimental findings.

O 82.5 Thu 11:30 MA 043

**Structure of graphene/Ir(111) supported Pt/Rh clusters** — •Dirk Franz[1,2], Nils Blanc[3,4,5], Johann Coraux[3,4], Heshmat Noei[2], Roman Shayduk[2], and Andreas Stierle[1,2] — [1]Universität Hamburg, D-20355 Hamburg, Germany — [2]DESY NanoLab, D-22607 Hamburg, Germany — [3]Université Grenoble Alpes, Inst NEEL, F-38042 Grenoble, France — [4]CNRS, Inst NEEL, F-38042 Grenoble, France — [5]CEA-UJF, INAC, F-38054 Grenoble, France

Ultrasmall metallic nanoparticles exhibit altered structural, chemical and magnetic properties as compared to their bulk counterparts making them attractive for applications as highly active heterogeneous catalysts or high storage density magnetic media. To pinpoint structure-functionality relationships for systems containing nanoparticles with diameters smaller than 2 nm an atomic scale understanding of their structure is mandatory.

It was previously shown that different 2D metal cluster arrays can be grown using the moiré of graphene/Ir(111) as a template [1]. We have employed several surface sensitive techniques (SXRD, XRR, GISAXS, XPS) to investigate the structure and composition of Pt/Rh particles (shape, epitaxy, strain) with less than 50 atoms grown on a graphene/Ir(111) support. SXRD and GISAXS essentially benefit from the ordered arrangement of the clusters and are able to reveal the average atomic structure of these small clusters [2].

[1] A. T. N'Diaye, et al., New J. Phys. 11, 103045 (2009).
[2] D. Franz, et al., Phys. Rev. Lett. 110, 065503 (2013).

O 82.6 Thu 11:45 MA 043

**Activation Energies for Chemical Reactions of size-selected Cobalt Oxide Clusters determined by Electron Diffraction** — •Stephan Bartling, Ingo Barke, and Karl-Heinz Meiwes-Broer — University of Rostock, Institute of Physics, 18051 Rostock, Germany

Size-selected cobalt oxide clusters deposited on different substrates can act as selective and efficient nanocatalysts [1]. In this contribution we present a new setup for determination of kinetic reaction parameters (i.e. apparent activation energy) of metal clusters using reflection high energy electron diffraction (RHEED) under reactive conditions. Soft-landed Co clusters of sizes in the range of 6 to 17 nm are exposed to oxygen or hydrogen and heated during the experiment. The evolution of RHEED patterns reveals significant changes of the particle structure during the treatment (cf. [2]). Analysis of the temperature dependence yields the effective activation energy $E_a$ for CoO oxidation and $Co_3O_4$ reduction. The results for different cluster diameters are discussed in view of size dependence and the role of cluster morphology.

[1] E.C. Tyo et al., ACS Catalysis **2 (11)**, 2409 (2012)
[2] A. Kleibert, Phys. Status Solidi B **247**, 1048 (2010)

O 82.7 Thu 12:00 MA 043

**Photoelectron spectroscopy of nearly free $C_{60}$ fullerenes on noble gas layers (Ar/Kr/Xe): Dependence of the HOMO peak position on the noble gas electron affinity** — •Dominik Wolter, Christoph Schröder, and Heinz Hövel — Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany

We have investigated $C_{60}$ deposited on argon (Ar), krypton (Kr) and xenon (Xe) layers, with ultraviolet photoelectron spectroscopy (UPS). The noble gas layers are intended to decouple the $C_{60}$ fullerenes from the underlying substrate. As substrates we used copper(111), silver(111) and gold(111) single crystals covered with 60 monolayers (ML) of Xe and optional additional 10 ML of Kr or Ar on top of the Xe films. The first ML of each gas was adsorbed at slightly higher temperatures than the following ones to get a well ordered surface. To extract the signal of nearly free fullerenes we measured the spectra for the noble gas covered substrate before $C_{60}$ deposition and subtracted them from measurements after the $C_{60}$ deposition. Compared to the expected position we were able to observe a shift of the $C_{60}$ signal, which is identical to the electron affinity of the noble gas layers. This is of importance for the interpretation of UPS on mass selected metal clusters on similar surfaces.

O 82.8 Thu 12:15 MA 043

**XANES measurements and corresponding FEFF simulations on Ag clusters deposited in PDMS and silica aerogel** — •Stefanie Roese, David Engemann, and Heinz Hövel — Fakultät Physik / DELTA, Technische Universität Dortmund

The knowledge of the geometric structure, size and electronic properties is essential for many applications of clusters.

Ag clusters produced in a supersonic expansion can be deposited without coalescence into matrix materials like silica aerogel or PDMS.

In addition to optical measurements X-ray absorption near edge structure spectroscopy (XANES) has developed as a powerful tool to determine geometric and electronic information about the sample. The measurements were carried out at the synchrotron radiation sources ESRF and DELTA.

The experimental data are compared to ab initio multiple scattering calculations (FEFF) [1] for different cluster sizes and structures like icosahedra and cuboctahedra. The comparison between the measured data and the simulations yields information about the geometric and electronic structure of the deposited clusters as well as about the influence of chemical environments. With the aid of the FEFF simulations the cluster aggregation process due to high deposition amounts can be visualized. Further, the reaction of the clusters with oxygen in the x-ray bam can be modeled.

[1] J. J. Rehr et al., Phys. Chem. Chem.Phys., 12, 5503-5513 (2010)

O 82.9 Thu 12:30 MA 043

**Deposition of Ti nanoclusters by Gas Aggregation Source and HiPIMS** — •Oleksandr Polonskyi, Waqas Saddique, Alexander Hinz, Thomas Strunskus, and Franz Faupel — Institute for Materials Science, Chair for Multicomponent Materials, Christian-Albrechts University at Kiel, Kaiserstr. 2, 24143 Kiel, Germany

Metal nanoparticles have been of high scientific interest in the last decades as they are intermediate objects between single atoms or molecules and solid matter and have unique chemical, physical, electrical, magnetic and optical properties. Nanocluster and nanoparticle production in the gas phase and their deposition have been extensively investigated within the last three decades using various cluster sources. In our work we focus on deposition of Ti (TiOx) nanoparticles using magnetron based Gas Aggregation cluster Source (GAS) in combination with High Power Impulse Magnetron Sputtering (HiPIMS) discharge. First, Ti sputtering at relatively high working pressure (100-200Pa) using HiPIMS was studied in details. With regard to nanoparticles deposition, it was observed that the utilization of HiPIMS discharge allows, at certain window parameters, generation of pure Ti nanoparticles without oxygen admixture, what was not possible with conventional DC magnetron sputtering. The purity of prepared films was studied by XPS immediately after deposition. In case of reactive HiPIMS, high deposition rate of TiOx nanoparticles was achieved. The effect of HiPIMS parameters on nanoparticles deposition rate, their size and chemical composition was investigated. It was shown that size can be controlled in range 5-25 nm.

O 82.10 Thu 12:45 MA 043

**Patterned deposition of nanoparticles on arbitrary substrates using hydrogel nanomembranes** — Nikolaus Meyerbröker and •Michael Zharnikov — Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

Patterns of nanoparticles (NPs) on solid supports are usually restricted to a particular substrate or a class of substrates. Here we present a procedure which decouples the patterning step from the target substrate, enabling the fabrication of custom designed NP assemblies on nearly any solid support, including non-flat ones. The procedure relies on a hydrogel template prepared on the primary, conductive substrate and transferred to the target support as a sacrificial nanomembrane. The template is structured by electron beam lithography (EBL) which seals predefined areas of poly(ethylene glycol) based hydrogel film, making them inert to NP deposition in contrast to pristine areas that adsorb NPs in high densities. The deposition of NPs, occurring from an aqueous solution into the transferred membrane, follows EBL generated structure, delivering the desired NP pattern on the target support after removal of the organic matrix. Efficiency and flexibility of the procedure is illustrated by creating a variety of representative submicrometer patterns of densely packed gold and silver NPs on glass, including a useful pattern of a miniaturized quick-response code. The arrangement of NPs in these patterns corresponds to the negative image of EBL generated template, which is especially useful for designs where large areas covered with NPs are separated by thin, NP-free stripes.

O 82.11 Thu 13:00 MA 043

**Single-island formation on prepatterned surfaces: a simulation approach** — •Oleg Buller[1], Wenchong Wang[2], Lifeng Chi[2], and Andreas Heuer[1] — [1]Institut für Physikalische Chemie, WWU, Münster — [2]Physikalisches Institut, WWU, Münster

Interesting structures are observed in vapor deposition experiments with organic semiconducting molecules on surfaces which are prepatterned with gold on a silicon oxide substrate. The gold is forming a regular grid. The interaction of the deposited molecules is much higher with the gold rather than with the substrate. In dependence on the experimental parameters flux, substrate temperature, and lattice size different structures are observed, reaching from the absence of molecular clusters to the limit of multi-island formation per square.

We use a simple discrete stochastic model to reproduce the observed structures and the scaling of the formations with substrate temperature, flux and lattice size. Among others we check to which degree the experimentally relevant scenario of just a single cluster per square can be understood from a theoretical perspective.

O 82.12 Thu 13:15 MA 043

**Optical Printing of Hybrid Plasmonic Nanostructures** — •Alexej Klushyn[1,2], Andreas Graw[1,2], Anastasia Babynina[1,2], Paul Kühler[1,2], Spas Nedev[1,2], Theobald Lohmüller[1,2], and

Jochen Feldmann[1,2] — [1]Photonics and Optoelectronics Group, Ludwig Maximilian University of Munich, Munich, Germany — [2]Nanosystems Initiative Munich (NIM), Munich, Germany

Hybrid assemblies of nanoparticles made from different materials are intriguing systems for the reason that the combined properties of a hybrid structure can often outperform the properties of its individual components. However, the exact positioning of the individual particles in a dimer configuration right next to each other is challenging and usually requires high-end nanofabrication methods such as scanning probe or eBeam lithography.

Here, we introduce an all-optical approach for the precise patterning of dimer structures of both plasmonic and non-metallic nanoparticles. First, we will demonstrate how individual gold particles can be optically printed on glass by optical force [1] and illustrate strategies to apply this method for the fabrication of plasmonic nanoantennas. Second, we will show how both, metallic and non-metallic nanoparticles, can be patterned in a dimer configuration with a precision of a few nanometers by taking advantage of plasmonic heating and near-field effects.

[1]A.S. Urban, A.A. Lutich, F.D. Stefani, and J. Feldmann; Nano Lett. 2010, 10(12), 4794-4798

## O 83: Surface Chemistry and Growth

Time: Thursday 10:30–13:30 Location: MA 144

O 83.1 Thu 10:30 MA 144

**Temperature-dependent Reactions of Phthalic Acid on Ag(100)** — •Matthias Franke[1], Florencia Marchini[2], Quratulain Tariq[1], Michael Röckert[1], Federico José Williams[2], and Hans-Peter Steinrück[1] — [1]Universität Erlangen-Nürnberg — [2]Universidad de Buenos Aires

Small aromatic molecules on single crystal surfaces are particularly interesting, since they may be used not only as model systems, but also as precursors for the formation of larger organic molecules, e.g. polymers.

We applied high resolution X-ray photoelectron spectroscopy (XPS) using synchrotron radiation and temperature programmed desorption (TPD) to study the temperature-dependent reactions of phthalic acid on Ag(100). After deposition at 110 K, the species adsorbed on the surface can be identified as phthalic acid. Upon heating, both monomeric and polymeric anhydride species are formed. This is accompanied by a change in molecular orientation, as observed by near edge X-ray absorption fine structure (NEXAFS) measurements. The monomer, phthalic anhydride, desorbs at 300 K, whereas the polymeric species remains on the surface until it decomposes above 400 K into phthalic anhydride, water, CO2 and benzene.

The project is supported by the DFG through FOR 1878 (funCOS).

O 83.2 Thu 10:45 MA 144

**Effect of hydrogen bonds on the adsorption and reactivity of alcohols on noble metal surfaces** — •Rodrigo García–Muelas and Núria López — Institute of Chemical Research of Catalonia, Tarragona, Spain.

The adsorption and decomposition of alcohols on noble metals has been subject of theoretical studies as a potential renewable source of chemicals. These studies usually omitted the lateral interactions between vicinal alcohol molecules or functional groups, and the effect of the ubiquitous hydrogen bonds on the reactivity in the liquid–metal interface is still a matter of debate. We show that lateral interactions between OH groups can selectively stabilize the OH over CH dehydrogenation, thus altering the preferred reaction path for methanol decomposition on Pt(111). The presence of these lateral interactions can explain the apparent divergence between previous theoretical and experimental studies.

O 83.3 Thu 11:00 MA 144

**Metalation of deuterated tetraphenylporphyrin on Cu(111): Insights into the reaction pathway** — •Ole Lytken, Michael Röckert, Matthias Franke, Quratulain Tariq, Stefanie Ditze, Michael Stark, Andre Kaftan, Dominik Lungerich, Norbert Jux, Mathias Laurin, Jörg Libuda, Hubertus Marbach, and Hans-Peter Steinrück — Universität Erlangen-Nürnberg

Temperature-Programmed Desorption (TPD) of the metalation of deuterated 5,10,15,20-tetraphenyl-21,23D-porphyrin on Cu(111) reveals that the metalation reaction proceeds through the transfer of the central aminic deuterium atoms to the Cu(111) surface and not, as might be expected from gas phase calculations, through the combination of the hydrogen atoms to molecular hydrogen above the partial inserted metal center. Experimentally, desorption of mostly hydrogen and very little deuterium is observed as the deuterated porphyrin molecule metalates. Despite the absence of deuterium in the periphery of the molecule before metalation, desorption of deuterium is not observed until the periphery dehydrogenates at higher temperatures. This is caused by hydrogenation and dehydrogenation of the periphery of the molecule exchanging deuterium produced during metalation with hydrogen from the periphery. The reactions have been modeled with a simple micro kinetic model able to describe the main features of the TPD spectra.

O 83.4 Thu 11:15 MA 144

**Effect of metal substrates on immobilised catalyst performance** — •David A. Duncan[1], Peter S. Deimel[1], Anthoula Weingarten[1], Runyuan Han[1], Kevin C. Prince[2], Robert G. Acres[2], Albano Cossaro[2], Alberto Verdini[2], Luca Floreano[2], Wilhelm Auwärter[1], Peter Feulner[1], Anthoula C. Papageorgiou[1], Francesco Allegreti[1], and Johannes V. Barth[1] — [1]TU München, Germany — [2]Elettra, Trieste, Italy

A key motivation for surface science is to merge the selectivity of homogenous catalysts with the ease of recovery in heterogenous catalysis. Recent studies[1] in this field have focussed on immobilising metal-organic species at solid surfaces for improved control of catalytic conversions. However, with metal supports the reactivity of surface-anchored species has been lacklustre, frequently requiring either low temperatures or large exposures for axial ligation at complexed metal centres[2] suggesting that the interaction with the substrate has a notable effect. We have studied, in UHV, the reactivity of ruthenium tetraphenyl porphyrin (Ru-TPP) and its Ti analogue towards molecular oxygen when confined to the Ag(111) surface. For surface-confined Ru-TPP, after a dosage of 20,000 L, no oxo-ruthenium species evolved, whereas exposing Ti-TPP to $\sim$100 L induces nearly complete oxidiation. This might suggest a shift in the so called “Volcano plot” of the Sabatier Principle towards metal complexes that are traditionally thought of as being too reactive for certain catalytic reactions.

1) B. Hulsken et al Nat Nano, 2007, 2 285; 2) BE Murphy et al. ACS Nano, 2014, 8, 5190; K Seufert et al., Nat Chem, 2011, 3, 114

O 83.5 Thu 11:30 MA 144

**A chrysene derivative as a promising candidate for an on-surface chemical reaction studied by LT-STM/STS** — •Frank Eisenhut[1,2], Justus Krüger[1,2], Jörg Meyer[1,2], Robin Ohmann[1,2], Gianaurelio Cuniberti[1,2], and Francesca Moresco[1,2] — [1]Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — [2]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

On-surface chemistry of $\pi$-conjugated carbon-systems become more and more relevant as these systems are interesting for the use in molecular electronic devices. In this study the promising molecule tetramethyldibenzochrysene has been investigated. The desired reaction for this molecule is a dehydrogenation of the methyl groups and subsequently a closing of carbon rings, to form dimethylphenantroperylene. This study deals with the characterization of the initial molecule via scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) at low temperatures on Ag(100). After the adsorption of the chrysene to the surface, the molecule forms supramolecular assemblies consisting 3 or 4 molecules. Detailed topographic and spectroscopic analysis of the assemblies have been fulfilled. Further the influence of applying voltage pulses to the assemblies and the heating of the system at different temperatures has been investigated.

O 83.6 Thu 11:45 MA 144

**The hydrated electron at the ice surface: insight into the**

**dissociative electron attachment to adsorbates** — •Philipp Auburger[1] and Michel Bockstedte[1,2] — [1]Lst. Theor. Festkörperphysik, Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — [2]FB Materialwissenschaften & Physik, Universität Salzburg, 5020 Salzburg, Austria

On ice, the solvated electron facilitates electron-induced reactions of adsorbates via dissociative electron attachment (DEA) that for instance take place in atmospheric chemistry. The simultaneous interaction of the electron with the molecule and the ice surface enhances the cross section as compared with the gas phase. The current understanding of the physical mechanisms at work is rather incomplete, in particular a picture on the molecular scale is missing. In this work we address this probleme within the framework of density functional theory, hybrid DFT, and many body perturbation theory. Prototypical surface electron traps, such as orientational disorder, surface vacancies and vacancy clusters are used as a model system. Halogenated hydrocarbons favor adsorption sites that are strong electron traps. Their antibonding molecular orbitals are scattering states with negative electron affinity. By the interaction with the trap states the binding energy is considerably increased. Our results show clear trends across the series F, Cl, and Br.

O 83.7 Thu 12:00 MA 144

**Extension of energy-resolved XPS towards a quantitative depth-profiling method and its application to ion-surface interactions** — •Martin Köppen[1], Martin Oberkofler[2], Johann Riesch[2], Klaus Schmid[2], Antje Vollmer[3], and Christian Linsmeier[1] — [1]Forschungszentrum Jülich, Institut fur Energie- und Klimaforschung - Plasmaphysik, Jülich — [2]Max-Planck-Institut für Plasmaphysik, Boltzmannstr. 2, Garching — [3]Helmholtz-Zentrum Berlin für Materialien und Energie, BESSY II, Albert-Einstein-Str. 15, Berlin

XPS as a work horses of surface science is capable of chemical analysis, but quantitative depth-profiles have always been an issue. Since solid state reactions are usually governed by diffusion, the latter is crucial to understand processes at surfaces.

This work extends energy-resolved XPS using variable photon energies towards a chemically resolved, quantitative depth-profile analysis. A model is derived which calculates the depth-resolved composition and the composition-dependent electron inelastic mean free path in a self-consistent way. Input is the normalised XPS data.

In fusion research, reactions of first wall materials like Be and W as well as reactions with ions leaving the plasma must be understood for a dynamic description of the surface composition. Formation of compounds is induced by temperature and implantation of particles. The model is applied to describe the interaction of O-ions with $Be_2W$. Using this approach it was possible to elucidate the interaction of ions with this surface quantitatively on a nanometre scale.

O 83.8 Thu 12:15 MA 144

**In silico prediction of dissolution rates of molecular crystals** — •Berna Dogan[1], Julian Schneider[1,2], and Karsten Reuter[1] — [1]Technische Universität München, Germany — [2]QuantumWise A/S, Copenhagen, Denmark

Dissolution testing is not only helpful for quality control of drug formulations, but also provides important information for drug development e.g. to optimize the dissolution kinetics by admixture of pharmaceutically inactive excipients. At present, a rational optimization process is hereby limited by a lack of understanding of the underlying molecular processes during crystal dissolution. We contribute to this context with detailed kinetic modeling based on atomistic moleular dynamics (MD) simulations. Within a spiral dissolution model valid for low undersaturation the velocity of a retracting screw dislocation can be determined from the free energy of kink sites and the rate constant for the molecular detachment process of kink site molecules. We present molecular simulation protocols for both quantities [1,2] and use them to determine a macroscopic dissolution rate of the wide-spread excipient alpha lactose-monohydrate that is fully consistent with experimental rates obtained from single crystals. [1] J. Schneider, C. Zheng, and K. Reuter, J. Chem. Phys. **141**, 124702 (2014); [2] J. Schneider and K. Reuter, J. Phys. Chem. Lett. **5**, 3859 (2014).

O 83.9 Thu 12:30 MA 144

**Is a surface reconstruction really necessary for an epitaxial Fe growth on a GaAs(001) surface?** — •Dominique Handschak, Frank Schönbohm, Tobias Lühr, Christoph Keutner, Ulf Berges, and Carsten Wetsphal — TU Dortmund, Exp. Physik 1, Otto-Hahn-Str.4, 44221 Dortmund, Germany

Multilayer consisting of the ferromagnet Iron (Fe) and the semiconductor Gallium-Arsenide (GaAs) are in the focus of the research in spintronics. The GMR effect arises at the interface, where the electrons are scattered differently depending on their spin and mutual orientation of the magnetization within the Fe-film. Therefore, the knowledge of the chemical composition and structure of the interface are important in order to improve the efficiency of the effect. We report on the interface structure of two similar system, Fe/GaAs(clean) and Fe/GaAs(4x2) using x-ray photoelectron diffraction (XPD) patterns in order to examine the necessity of a reconstruction for an epitaxial Fe growth. It can be shown that the inter-diffusion between the substrate and the adsorbate is prevented if Fe is prepared on a GaAs(4x2)-sample. Furthermore, the predicted stronger out-diffusion of the Arsenic can be confirmed by the XPD patterns of the Fe/GaAs(clean) system.

O 83.10 Thu 12:45 MA 144

**Theoretical evidence for unexpected O-rich phases at corners of MgO surfaces** — Saswata Bhattacharya[1], Daniel Berger[2], Karsten Reuter[2], •Sergey V. Levchenko[1], Luca M. Ghiringhelli[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]Technische Universität München, Garching, DE

Introducing charge carriers into MgO via *p* doping greatly reduces formation energy of an O-vacancy in the bulk and at the (100) surface [1]. In this work, we use hybrid density functional theory to explore O-vacancy and $O/O_2$-ad-species defects at corners of MgO surfaces. The defects are modelled using MgO clusters embedded into a field of norm-conserving pseudopotentials and point charges. The long-range response of the oxide to the charge carriers trapped at the defects is taken into account using a polarizable force field. The low-energy defect atomic structures are found using an *ab initio* genetic algorithm [2]. Concentrations of O-vacancies and O-ad-species at realistic temperatures and pressures are obtained with *ab initio* atomistic thermodynamics. Unexpectedly, we find that O-ad-species rather than O-vacancies are dominating defects at realistic conditions. The stability of the O-ad-species over O-vacancies and pristine corners is explained by an interplay between bond-breaking, bond-making, and charge-carrier trapping. – [1] N. Richter *et al.*, Phys. Rev. Lett. **111**, 045502 (2013); [2] S. Bhattacharya *et al.*, New J. Phys., in press (2014).

O 83.11 Thu 13:00 MA 144

**Monitoring the formation of quasicrystalline barium titanate on Pt(111) using XPS and NEXAFS** — •Alireza Bayat[1], Stefan Förster[1], Rene Hammer[1], Eva-Maria Zollner[1], Wolf Widdra[1,4], Reinhard Denecke[2], Silvano Lizzit[3], Paolo Lacovig[3], and Karl-Michael Schindler[1] — [1]Institut für Physik, Martin-Luther-Universität, Halle-Wittenberg, D-06120 Halle, Germany — [2]Wilhelm-Ostwald-Institut, Universität Leipzig, D-04103 Leipzig, Germany — [3]Elettra-Sincrotrone Trieste S.C.p.A. I-34149 Basovizza, Trieste, Italy — [4]Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle, Germany

The discovery of a 2D quasicrystalline $BaTiO_3$-derived (BTO) layer on Pt(111) opened a new field in fundamental physics as well as applications [1]. Using high-resolution XPS and NEXAFS, we have determined chemical states and coordination environments of all elements in the layer. In addition, the reversible transformation between BTO(111) islands and the quasicrystalline layer has been monitored using fast-XPS. The XPS spectra show that the islands contain titanium only as $Ti^{4+}$ and are fully oxidized. The quasicrystalline layer contains $Ti^{3+}$ and $Ti^{4+}$ in approximately equal amounts and their formations from Ti in the islands happen simultaneously. The chemical shifts indicate that the coordinations of both Ti species in the quasicrystalline layer are different from bulk. NEXAFS spectra at Ti L- and O K-edges in normal and grazing incidences confirm an anisotropy in the quasicrystalline layer, presumably arising from a planar or near planar coordination of Ti. [1] S. Förster et al., Nature, 502 (2013) 215-218

O 83.12 Thu 13:15 MA 144

**nc-AFM study of $C_{60}$ islands on organic compound crystals** — •Sara Freund[1], Antoine Hinaut[1], Rémy Pawlak[1], Shi-Xia Liu[2], Silvio Decurtins[2], Ernst Meyer[1], and Thilo Glatzel[1] — [1]Department of Physics, University of Basel, Switzerland — [2]Department of Chemistry and Biochemistry, University of Bern, Switzerland

Organic layered compound crystals have rarely been investigated by the means of room temperature noncontact atomic force microscopy (nc-AFM). This kind of material offers the possibility to design surfaces with different chemical compounds and molecular orientations [1]. The study of adsorbed molecules on such surfaces under ultra-high vacuum (UHV) conditions might be of great interest in the field of optoelectronics. In this study the behaviour of fullerene ($C_{60}$) molecules on the salt bis(benzylammonium)bis(oxalate)cupurate(II) (BNL) was investigated. BNL is a transition-metal oxalate complex which exhibits layer-type crystal structures [2]. The $C_{60}$ molecules were deposited on the substrate by thermal deposition and formed small islands. High resolution images of the substrate and the $C_{60}$ islands were obtained. Manipulations of the molecular islands have been induced by controlled tip interactions. It was observed that they can be split up and redistributed by these interactions to form larger islands. Tip-induced shape modifications of these $C_{60}$ islands was also observed and analysed.
[1] G. Fessler et al., Appl. Phys. Lett., 98(8), 083119, 2011.
[2] S. Decurtins et al., Mol. Cryst. Liq. Sci. Technol., Sec A 305, 227, 1997.

# O 84: Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses

Time: Thursday 15:00–18:15 Location: MA 005

**Topical Talk** O 84.1 Thu 15:00 MA 005
**Femtosecond electron probes for the investigation of structural dynamics and ultrafast currents in nanomaterials** — •Ralph Ernstorfer, Melanie Müller, Lutz Waldecker, Roman Bertoni, Thomas Vasileiadis, and Alexander Paarmann — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

We investigate ultrafast structural as well as electronic dynamics in low-dimensional systems such as two-dimensional materials, one-dimensional nanowires, and nanoparticles. Such studies require femtosecond probes strongly interacting with small-volume samples. Electrons with energies ranging from 50 to 1000 eV exhibit extremely large scattering cross sections and high sensitivity to electric fields. Employing a laser-triggered point-like source of either divergent or collimated electron wave packets, we developed a hybrid approach for femtosecond point projection microscopy (fsPPM) and femtosecond low-energy electron diffraction (fsLEED) [1]. We investigate ultrafast electric currents in nanowires with sub-100 femtosecond temporal and few 10 nm spatial resolutions. This new low-energy electron technique is complemented by femtosecond transmission electron diffraction performed with 100 keV electrons. A highly compact diffractometer design allows for delivering 100 fs long pulses containing up to 5000 electrons to the sample [2]. We will discuss structural dynamics and electron-lattice interaction in confined materials such as quasi-2D materials and nanoparticles. References: [1] M. Müller et al., Nature Communications 5, 5292 (2014). [2] L. Waldecker, arXiv:1412.1942 (2014).

O 84.2 Thu 15:30 MA 005
**Ultrafast transmission electron microscopy with nanoscopic electron sources** — Armin Feist, Reiner Bormann, Katharina Echternkamp, Jakob Schauss, Nara Rubiano, •Sascha Schäfer, and Claus Ropers — 4th Physical Institute, University of Göttingen, Göttingen, Germany

Ultrafast transmission electron microscopy (UTEM) is a laser-pump/electron-probe technique, which promises to combine the ultrafast temporal resolution of pump-probe approaches with the spatial resolution of electron microscopy [1]. However, to harness the full capabilities of UTEM, novel laser-triggered electron sources are required, which deliver high-brightness sub-picosecond electron pulses.

Here, we present the development and application of an advanced UTEM instrument based on the custom modification of a commercial electron microscope. Specifically, we employ electron sources based on the localized photoemission [2] from a nanoscale needle photocathode. The enhanced optical field at the tip apex confines nonlinear photoemission to small emitter areas, enabling electron focal spot sizes on the sample of about 10 nm with electron pulse durations of less than 700 fs. First applications are presented, including time-resolved Lorentz microscopy and the nanoscale probing of quantum coherent interactions between free electrons and optical near-fields [3].

[1] A. H. Zewail, Science 328, 187-93 (2010). [2] M. Gulde, S. Schweda, G. Storeck, M. Maiti, H. K. Yu, A. M. Wodtke, S. Schäfer, C. Ropers, Science 345, 200-204 (2014). [3] A. Feist, K. Echternkamp, J. Schauss, S. V. Yalunin, S. Schäfer, C. Ropers, submitted.

O 84.3 Thu 15:45 MA 005
**Simultaneous observation of quantization and interference of a surface plasmon polariton by PINEM** — •Yoshie Murooka[1], Tom Lummen[1], Luca Piazza[1], Erik Quiñonez[2], Bryan Reed[3], Brett Barwick[2], and Fabrizio Carbone[1] — [1]École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland — [2]Trinity College, Hartford, CT 06106, USA — [3]Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

For applications in photonics and optical data storage, surface plasmon polariton (SPP) is intensively studied because of its high spatial confinement and precise optical control with, for example, its quantum properties. SPP can be photo-generated on a metal surface as a propagating electromagnetic wave, while the vertical confinement is in the sub-wavelength regime. Lately, such SPP fields have been studied in terms of their wave-particle duality. Here, using recently developed Photo-induced near field electron microscopy (PINEM), we have imaged both the quantization and the interference of the confined fields simultaneously on an isolated metal nanowire. PINEM was realized on femtosecond-TEM equipped with an electron energy analyzer. The SPP field was induced by pulsed laser, and probed by electron pulses that were spatio-temporally overlapped with the light. The exchange of energy between the field and the electrons was found to be quantized, and the spatial distribution of the field was synchronously revealed as its interference pattern. This methodology enables to visualize and control SPP fields at nanoscale, and provides a novel tool to understand the fundamental properties of confined electromagnetic fields.

O 84.4 Thu 16:00 MA 005
**Coherence Properties of Laser-Triggered Field Emitters** — •Dominik Ehberger[1,2], Jakob Hammer[1,2], Max Eisele[2], Michael Krüger[1,2], Jonathan Noe[3], Alexander Högele[3], and Peter Hommelhoff[1,2,4] — [1]Friedrich Alexander University Erlangen-Nuremberg, Department of Physics, D-91508 Erlangen — [2]Max Planck Institute of Quantum Optics, D-85748 Garching — [3]Fakultät für Physik and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, D-80539 München — [4]Max Planck Institute for the Science of Light, D-91508 Erlangen

Sharp metal nanotips provide bright and spatially coherent electron beams in DC-field emission. They serve as workhorse in electron imaging and holography. However, the spatial coherence properties, commonly quantified by the effective source radius $r_\mathrm{eff}$, are expected to depend strongly on the emission process and have so far not been measured for laser-triggered metal tips.

Here, we present a comparison of $r_\mathrm{eff}$ for a tungsten tip triggered with near-UV pulses and in DC-field emission. From electron interference patterns obtained by means of a freestanding carbon nanotube biprism an upper bound for $r_\mathrm{eff}$ is deduced. We find $r_\mathrm{eff} \leq (0.80 \pm 0.05)$ nm in laser induced and $r_\mathrm{eff} \leq (0.55 \pm 0.02)$ nm in DC-field emission, revealing that the spatial coherence is almost fully preserved in a one-photon emission process.

We expect this finding to have far-reaching ramifications for ultrafast electron imaging applications.

O 84.5 Thu 16:15 MA 005
**Deflection of Electron Pulses by THz Fields** — •Waldemar Schneider[1,2], Andrey Ryabov[1,2], Daniel Kreier[1,2], Ferenc Krausz[1,2], and Peter Baum[1,2] — [1]Max-Planck-Institute of Quantum Optics — [2]Ludwig-Maximilians-University Munich

Pump-probe electron diffraction and microscopy, based on laser excitation and probing with electrons, can provide a four-dimensional visualization of atomic motion in space and time. The time resolution is determined by the temporal and spatial structure of the electron pulse. Here, the temporal information of a single-electron pulse is mapped with THz fields into the transverse position on a screen, realising a THz-driven streaking camera. By spatially sectioning the electron pulse, spatial information was obtained. The deflection trace also revealed the shape of the THz-field at the sample.

The described approach represents a readily improvable method for temporal and spatial characterization of single-electron pulses for ultrafast diffraction applications.

**Topical Talk** O 84.6 Thu 16:30 MA 005

**Exploring the Spatial and Temporal Resolution Limits of Ultrafast Electron Microscopy** — •David J. Flannigan, Dayne A. Plemmons, Daniel R. Cremons, and David T. Valley — University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN, 55455, USA

In ultrafast electron microscopy (UEM), the capabilities of transmission electron microscopy are extended into the femtosecond temporal domain. The operating principle of UEM requires spatiotemporal overlap of the photon pulse and electron packet at the specimen; at time zero, significant photon absorption by the freely-propagating electrons can occur. Overlap at the specimen suggests this phenomenon can be used to measure the response function and the electron packet properties. In this talk, I will discuss considerations for isolating the inherent artifacts of the highly non-linear near-field interactions from the actual packet characteristics. Further, I will discuss how temporal cross-sections of peaks in the electron-energy spectra corresponding to high-order transitions are expected to exhibit the true temporal behavior of the electron packets. In general, the exceedingly small portion of the pump laser pulse capable of initiating such transitions results in temporal widths converging to the electron packet duration. Additionally, population of quantized virtual states occurring for an electron beam focused on a nanostructure suggests that the resulting energy distribution may produce discrete chromatic aberrations arising from the velocity dependence of the Lorentz force. I will discuss the prospect for detecting such phenomena in bright-field images.

O 84.7 Thu 17:00 MA 005

**Developments in ultrafast electron microscopy and diffraction** — Alexander Bainbridge and •William Bryan — Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP, UK

A progress report on recent ultrafast electron microscopy and diffraction studies at Swansea University (UK) will be presented. Facilities to time-resolve charge migration on nanometre to micron scales are to be discussed, and are currently propagating sub-100fs electron pulses from a nanoscale metal tip (NSMT) to thin solid state samples mounted on a TEM substrate. This work employs the 20fs 2uJ output from a Light Conversion Orpheus-N OPA, which is split into a pump pulse illuminating the target and probe driving electron emission from the NSMT. Laser delivery includes an external compressor, FROG and pointing stabilisation. Field emission from this system indicates imaging to sub-hundred nm is currently possible.

Recent simulations investigating the ultimate time resolution of our PPM instrument will also be presented, and we will discuss balancing the requirements for field of view over time resolution. Modelling of electron pulse collimation with an electrostatic microlens will be presented, which will facilitate coherent diffractive imaging with time resolution, opening the door to tracking charge motions on the atomic scale. Clearly instrument design and implementation is just the start, and to illustrate our broad interests in this field, research directions involving graphene liquid cells, coupling nanorods to 2D crystalline materials and tracking charge flow through plasmonic nanoparticle strings will be discussed.

**Topical Talk** O 84.8 Thu 17:15 MA 005

**Ultrafast single-electron diffraction and its perspectives** — •Peter Baum — Ludwig-Maximilians-Universität München — Max-Planck-Institut für Quantenoptik

Matter transformations are basically defined by atomic and electronic motions from initial to final conformations. Ultrafast electron diffraction and microscopy are good at seeing the atoms, but purely electronic motion is still mostly hidden. Here we report our recent progress with single-electron wave packets without space charge [1-2] for advancing 4D diffractive imaging into novel resolution and application regimes. Specifically, we report our shortest pulses so far (28 fs) and first diffraction applications on graphite and carbon nanotubes [3].

[1] Peter Baum, J. Phys. B 47, 124005 (2014).
[2] Gliserin, Apolonski, Krausz, Baum, NJP 14, 073055 (2012).
[3] Lahme, Kealhofer, Krausz, Baum, Struct. Dyn. 1, 034303 (2014).

O 84.9 Thu 17:45 MA 005

**Radiation-induced transitions in solids** — Nikita Medvedev, Zheng Li, and •Beata Ziaja — CFEL DESY, Notkestrasse 85, 22607 Hamburg

Femtosecond intense light pulses from free-electron lasers can trigger structural transitions in solids. Their theoretical description is a challenge, as it has also to include contributing non-equilibrium processes. In order to account both for thermally and nonthermally triggered transitions, we extended our recently developed hybrid model by including non-adiabatic electron-phonon coupling. In this way the heating of a material due to the electron-phonon coupling could also be treated. We show model application for laser-induced transitions in carbon and silicon. The developed scheme is general and can be used in any molecular dynamics model, also with an implementation to describe structural transitions induced by electron pulses.

O 84.10 Thu 18:00 MA 005

**Ultrafast Electron Diffraction on nano-crystalline Graphene** — •Silvio Morgenstern, Christian Gerbig, Marlene Adrian, Cristian Sarpe, Arne Senftleben, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D - 34132 Kassel, Germany

In carbon layered materials the electronic subsystem, stimulated by high currents or optical excitations, is strongly coupled to a small set of optical phonons which limits the ballistic conductance. A detailed understanding of phonon decay mechanism is thus essential in improving the performance of carbon based future devices [1,2]. Time-resolved diffracton experiments using x-rays or electrons probes, has become a promising technique to directly provide insights into fundamental dynamics in solids at the microscopic level and on the pico- to subpicosecond timescale [3,4]. In this contribution we present results on photo-induced structural dynamics in single layer nano-crystalline graphene [5] obtained whit our compact and well characterized Ultrafast Electron Diffractometer [6] and discuss the influence of the main strutural properties for our results[7].

[1]T.Kampfrath et.al.,Phys.Rev.Lett.95,187403(2005)
[2]S.Schäfer et.al.,New J.Phys.13,063030(2011)
[3]A.H.Zewail,J.Phys.Chem.98,2782-2796(1994)
[4]B.Siwick et.al.,Science Vol.302,No.5649,1382-1385(2003)
[5]A.Turchanin,ACS Nano Vol.5,No.5,3896(2001)
[6]C.Gerbig et.al.,in submission
[7]S.Morgenstern et.al.,in preparation

**Coffee Break, 15min.**

# O 85: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale VI

Time: Thursday 15:00–18:30 Location: MA 004

**Invited Talk** O 85.1 Thu 15:00 MA 004

**Natural orbital functional theory with higher-order occupation probabilities** — •Ralph Gebauer[1], Roberto Car[2], and Morrel Cohen[2,3] — [1]International Centre for Theoretical Physics (ICTP), Trieste, Italy — [2]Department of Chemistry, Princeton University, Princeton, USA — [3]Department of Physics and Astronomy, Rutgers University, USA

We introduce a novel energy functional for ground-state electronic-structure calculations. Its fundamental variables are the natural spin-orbitals of the implied singlet many-body wave function and their joint occupation probabilities. The functional derives from a sequence of controlled approximations to the two-particle density matrix. Algebraic scaling of computational cost with electron number is obtainable in general, and Hartree-Fock scaling in the seniority-zero version of the theory. Results obtained with the latter version for saturated small molecular systems are compared with those of highly-accurate quantum-chemical computations. The numerical results are variational, capturing most of the correlation energy from equilibrium to dissociation. Their accuracy is considerably greater than that obtainable with current density-functional theory approximations and with current functionals of the one-particle density matrix only.

O 85.2 Thu 15:30 MA 004

**Electronic Properties of Surfaces and Interfaces with Self-Consistent Interatomic van der Waals Density Functional** — •Nicola Ferri[1], Robert A. Distasio Jr.[2], Alberto Ambrosetti[1], Roberto Car[2], Matthias Scheffler[1], and Alexandre Tkatchenko[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Princeton University, USA

Ubiquitous long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems. Within the DFT framework, the vdW energy represents a crucial, but tiny part (0.001%) of the total energy, hence its influence on the electronic density, $n(\mathbf{r})$, and derived electronic properties is typically assumed to be rather small. Here, we address this question via a fully self-consistent (SC) implementation of the interatomic Tkatchenko-Scheffler vdW functional [1] and its extension to surfaces [2]. For several transition metal surfaces, self-consistency increases their dipole moments and induces non-trivial electron density rearrangements. As a consequence, we observed changes of up to 0.3 eV in the surface work-functions, with vdW self-consistency improving the agreement with experiments. Similar behavior is observed for molecules adsorbed on metals, where vdW contributions influence both Pauli push-back and charge transfer, the two phenomena that determine interface work-functions. [1] A. Tkatchenko and M. Scheffler, PRL (2009). [2] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, PRL (2012).

O 85.3 Thu 15:45 MA 004

**Exact functionals for a lattice model** — •Tanja Dimitrov[1], Heiko Appel[1,3], and Angel Rubio[1,2,3] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Nano-bio Spectroscopy Group/ETSF Scientific Development Centre, Universidad del Pais Vasco UPV/EHU, San Sebastian — [3]MPI for the Structure and Dynamics of Matter, Hamburg

Standard local exchange-correlation and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, and barriers of chemical reactions [1,2]. To understand the failures of approximate functionals, to gain insight into the behavior of the exact functional, and to devise new approximations, we investigate the exact solution of the many-body Schrödinger equation in Fock space for a lattice model with a softened Coulomb interaction term. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitely construct the *exact* density-to-potential and density-to-wave-function map. We discuss the behavior of functionals in the low-density limit.

[1] A. J. Cohen et al. Science **321**, 792 (2008).
[2] P. Mori-Sanchez et al., Phys. Rev. Lett. **100**, 146401 (2008).

O 85.4 Thu 16:00 MA 004

**Many-body dispersion meets non-local density functionals: A unified approach for van der Waals correlations** — •Jan Hermann, Matthias Scheffler, and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

It is an ongoing challenge to develop an efficient method for van der Waals (vdW) non-local correlation within DFT which would be both accurate and broadly applicable. Current approaches can be loosely divided into the fragment-based ones, two-point density functionals and methods based on the density-density response function. The fragment-based models utilize parameters not derivable from the electron density. Two-point approaches are explicit density functionals, but difficult to generalize to include many-body correlations.

Here, we show that these seemingly contrasting approaches can be unified within a single framework based on the adiabatic-connection formalism in the random-phase approximation. We use a local response-function model from the VV09 functional [1] together with the many-body dispersion approach to create an atom-based model with no external parameters. We introduce a consistent correlation-functional-based coupling of the short- and long-range correlation energy. We show that this unification provides new insights into the different approaches, naturally deals with the partitioning of ionic and delocalized states and paves path towards self-consistent description of many-body vdW correlations.
[1] O. A. Vydrov, T. Van Voorhis, Phys. Rev. Lett. 103, 063004

O 85.5 Thu 16:15 MA 004

**Reduced Density-Matrix Functional Theory: correlation and spectroscopy** — Stefano Di Sabatino[1], Jan A. Berger[2], Lucia Reining[3], and •Pina Romaniello[1] — [1]Laboratoire de Physique Théorique, CNRS, IRSAMC, Université Toulouse III - Paul Sabatier, Toulouse, France and ETSF — [2]Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Toulouse III - Paul Sabatier, CNRS, Toulouse, France and ETSF — [3]Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, Palaiseau, France and ETSF

We study the performance of approximations to electron correlation in reduced density-matrix functional theory (RDMFT) and of approximations to the observables calculated within this theory [1]. We use the exactly solvable Hubbard molecule as test case. In particular we focus on the atomic limit and we explore how degeneracies and spin-symmetry breaking are treated in RDMFT. We find that, within the used approximations, RDMFT is not able to describe the signature of strong correlation in the spin-singlet ground state, whereas it give the exact result for the spin-symmetry broken case. [1] S. Di Sabatino, J.A. Berger, L. Reining, and P. Romaniello, submitted

O 85.6 Thu 16:30 MA 004

**Does *GW* obey the straight-line condition?** — Matthias Dauth[1,3], Fabio Caruso[2], Stephan Kuemmel[1], and •Patrick Rinke[3] — [1]University of Bayreuth, Germany — [2]University of Oxford, England — [3]Aalto University, Helsinki, Finland

Many-body theory in the $GW$ approach has become the method of choice for calculating charged excitations in solids. Recently, it is also increasingly being applied to molecules, but fundamental questions regarding its accuracy remain. One such fundamental theorem requires that the total energy changes linearly with gradual (i.e. fractional) ionisation of the molecule. In this work we investigate, if $GW$ is piecewise linear or if it exhibits a derivation of the straight line error (DSLE). Since the derivative of the total energy with respect to the electron number gives the ionisation energy, we quantify the DSLE by taking the difference between the energy of the highest occupied state of the neutral and the lowest unoccupied state of the singly ionised molecule (which would be equal in the DSLE-free case). We find for a subset of molecules from the quantum chemical G2 benchmark set, that the DSLE in self-consistent $GW$ amounts to 1.1 eV on average. This DSLE can be mitigated in perturbative $G_0W_0$ by varying the starting point. We use density-functional theory as starting point and vary the amount of exact exchange $\alpha$ in the Perdew-Burke-Ernzerhof hybrid functional (PBEh). $G_0W_0$ becomes DSLE-free for $\alpha \approx 0.4$. The average deviation from the experimental IPs is then very close to that of self-consistent $GW$ and amounts to $\sim$0.25 eV.

O 85.7 Thu 16:45 MA 004

**Green's Function embedding for Advanced Electronic Structure Methods based on Dynamical Mean-Field Theory** — •Wael Chibani[1], Xinguo Ren[2], Matthias Scheffler[1], and

Patrick Rinke[3] — [1]*Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany* — [2]*Key Laboratory of Quantum Information, USTC, Hefei, China* — [3]*Aalto University, Helsinki, Finland*

We introduce an embedding scheme for periodic systems that facilitates a self-consistent treatment of the physically important part of a system with electronic structure methods, that are computationally too expensive for periodic systems. We use dynamical mean-field theory [1] (DMFT) to couple to the rest of the system, which is treated with less demanding approaches such as Kohn-Sham density functional theory. In contrast to the original DMFT formulation for correlated model Hamiltonians, we consider here the unit cell as local embedded cluster in an *ab initio* way, that includes all electronic degrees of freedom. The performance of our scheme is demonstrated by treating the embedded region with hybrid and $GW$ self-energies (sc$GW$) for simple bulk systems. The total energy and the density of states converge rapidly with respect to the computational parameters and approach their bulk limit with increasing cluster size. For non self-consistent $GW$ calculations we observe Plasmon satellites for Si – in good agreement with periodic $G_0W_0$ calculations [2] – that vanish at self-consistency. Our sc$GW$ gap of $\sim$ 0.9 eV for a two atom unit cell agrees well with previous $G_0W_0$ calculations and experiment. [1] A.Georges *et al.*, Rev.Mod.Phys.(2006), [2] M.Guzzo *et al.*, PRL(2011)

O 85.8 Thu 17:00 MA 004

**Improved Ground State Electronic Structure and Optical Dielectric Constants With a Semi-Local Exchange Functional** — •Vojtěch Vlček[1], Gerd Steinle-Neumann[1], Linn Leppert[1], Rickard Armiento[2], and Stephan Kümmel[1] — [1]University of Bayreuth, Germany — [2]Linköping University, Sweden

For a set of solids, we explore a recently developed generalized gradient exchange functional (AK13) that has two characteristic features: its enhancement factor diverges for large reduced density gradients $s$ as $s\ln(s)$ and its potential changes discontinuously at integer electron numbers. We apply the functional to semiconductors, Mott insulators, and ionic crystals and compare results for band structure and dielectric constants with a standard GGA. The AK13 functional provides a better description of the KS orbitals and we observe a qualitative improvement both in the bandgaps and in the optical dielectric constants, especially for the small gap semiconductors we explore (Ge, $\alpha$-Sn, and CdO)

O 85.9 Thu 17:15 MA 004

**Accurate, efficient localized resolution of identity of the Coulomb operator across the periodic table** — •Arvid Ihrig[1], Jürgen Wieferink[1], Igor Ying Zhang[1], Patrick Rinke[1,2], Volker Blum[1,3], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Aalto University, Helsinki, Finland — [3]Duke University, Durham, USA

A key component of advanced electronic structure methods is the explicit evaluation of the Coulomb operator. The corresponding four-center integrals can be solved with a “resolution of identity” (RI) approach for numeric atom-centered orbitals, as they are used in, e.g., FHI-aims [1]. In RI, basis function products are expanded in an auxiliary basis. The complete auxiliary basis is used for “RI-V”, the most accurate and most commonly used RI. We developed a localized RI (“RI-LVL”), which expands the products only in the subset of those auxiliary functions centered on the same atoms as the basis functions. This approach yields a superior scaling with system size, both in terms of computational time and memory requirements. At the same time it also retains the accuracy of the RI-V, as we have shown for HF, MP2, PBE0 and RPA calculations. The systems we investigated include weakly interacting molecular dimers (S22 test set) as well as $TiO_2$, Cu, and Au clusters. In all test cases we found that RI-LVL reproduces RI-V very accurately. Even for RPA-calculations of gold with very large basis sets the deviation to RI-V is only ~1.5 meV per atom. [1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009).

O 85.10 Thu 17:30 MA 004

**Explicitly correlated self consistent field theory** — •Christian Lasar and Thorsten Klüner — Carl von Ossitzky Universität, Oldenburg, Germany

There is a variety of methods available which aim to describe molecules and molecular reactions with chemical accuracy. The two main classes of these methods are density functional theory (DFT) and electron correlation approaches. DFT achieves great accuracy for many molecules and is applicable to quite large molecules. Unfortunately, DFT is not systematically improvable since the exact form of the exchange correlation functional remains unknown. Correlation methods do not suffer from this lack of systematic improvement. Unfortunately, they often require too much computational resources for large molecules. Additionally, they show a very slow convergence with the size of the basis set. Explicitly correlated methods are known to be able to solve this convergence problem. In these methods, the wavefunction is augmented with a function $f_{ij}$ which explicitly depends on two electronic coordinates. Combining the advantages of low computational resources and the ability for systematic improvement, one ends up in the following ansatz for the wavefunction $\Psi = (1 + \sum_{ij} f_{ij})\Phi$, where $\Phi$ is one slater determinant. With this ansatz the long determinant expansion is avoided. Additionally, there will be a fast convergence with the basis set size. We currently investigate the derivation of the working equations and their implementation for different functions $f_{ij}$. Some results for small molecules have already been obtained and will be presented in this contribution.

O 85.11 Thu 17:45 MA 004

**Comparison of two self-consistent $GW$ schemes** — •Peter Koval[1], Dietrich Foerster[2], and Daniel Sanchez-Portal[1,3] — [1]Donostia International Physics Center, San Sebastián, Spain — [2]Laboratoire Ondes et Matiére d'Aquitaine, Bordeaux, France — [3]Material Physics Center, San Sebastián, Spain

$GW$ approximation ($GW$A) as a competitor of DFT provides a better description of electronic structure in several respects. However, a $GW$ calculation is more expensive than similar DFT calculation. This fact contributed to a wide usage of simpler calculations based on $GW$A (SEX, COSEX, plasmon-pole approximations etc.) This manyfold of approximations hampers a non-biased evaluation of merits of $GW$A to describe the electronic correlations. We produced a rigorous $GW$ implementation where the only approximation is the use of localized orbitals [1]. The usage of spectral functions allowed us to realize two self-consistent $GW$ schemes: sc$GW$ [2] and qs$GW$ [3] in one code [4]. Furthermore, we used all-electron Gaussian basis sets that allows for a coherent comparison with quantum chemistry methods. We use coupled-cluster methods CCSD and CCSD(T) as reference and compare ionization potentials of 15 molecules. The calculations show trends in sc$GW$ and qs$GW$ and give hints on possible sources of discrepancies/directions towards improving $GW$A. [1] D. Foerster, P. Koval, D. Sánchez-Portal, *J. Chem. Phys.* **135**, 074105 (2011); [2] L. Hedin, *J. Phys. Cond. Mat.* **11**, R489 (1999); [3] S. V. Faleev, M. van Schilfgaarde, T. Kotani, *Phys. Rev. Lett.* **93**, 126406 (2004); [2] P. Koval, D. Foerster, D. Sánchez-Portal, *Phys. Rev.* B **89**, 155417 (2014).

O 85.12 Thu 18:00 MA 004

**Quasiparticle Self-Consistent $GW$ for Molecules** — •Ferdnand Kaplan[1,2,3], Michiel van Setten[1,2,5], Florian Weigend[1,3], and Ferdinand Evers[1,2,3,4] — [1]Institute of Nanotechnology (INT) — [2]Institute for Theoretical Condensed Matter Physics (TKM) — [3]Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany — [4]Universität Regensburg, D-93040 Regensburg, Germany — [5]Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

One of the most used approaches for the computational study of nanoscale systems and molecules is the density functional theory (DFT). However, DFT calculations of single particle excitation spectra, e.g. ionization potentials, often suffer from method-inherent difficulties. To systematically improve the estimation of quasi-particle energies for molecular system, we have implemented the $GW$ method. The approach represents a perturbative expansion of the many-body Green's function with respect to the screened Coulomb interaction, $W$.

On $G_0W_0$ level the $GW$-self energy is calculated with the Kohn-Sham Green's function of the underlying DFT. Hence, one finds a strong dependence of the excitation energies on the reference system, i.e. DFT functionals. To overcome this problem, we implemented a self-consistent cycle which takes into account the deviations of the quasiparicle(qp)-wavefunctions from their Kohn-Sham parents.

We find that this procedure converges to a fixed point solution which is independent of the reference system. For the testset of molecules anlyzed by us so far, the results for ionization-energy and electron-affinity improve upon $G_0W_0$, when comparing to experimental data.

O 85.13 Thu 18:15 MA 004

**Pure state N-representability conditions: Should they be taken into account in Reduced density matrix functional theory?** — •Iris Theophilou[1], Nektarios Lathiotakis[2,3], and

Nicole Helbig[1] — [1]Peter Grünberg Institut (PGI-1), Forschungszentrum Jülich, Jülich, Gernany — [2]Theoretical and Physical Chemistry Institute (TPCI), National Hellenic Research Foundation , Athens, Greece — [3]Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

In Reduced Density Matrix Functional Theory (RDMFT) the natural occupation numbers are minimized under the ensemble N-representability conditions, i.e they are restricted to be between zero and one and sum to the number of electrons. Recently, the pure state N-representability problem for the one-body reduced density matrix has been solved [M. Altunbulak and A. Klyachko, Commun. Math. Phys. 282, 287 (2008)]. In this talk we discuss to which extend these pure state conditions are satisfied without being enforced in 3 electron systems using some standard RDMFT functionals. Our aim is to impose those pure state conditions that are not automatically satisfied and check whether this improves RDMFT results.

## O 86: Nanostructure at Surfaces: Molecular Assembly

Time: Thursday 15:00–17:45 Location: HE 101

**Invited Talk** O 86.1 Thu 15:00 HE 101

**On-surface synthesis of molecular and polymeric nanostructures** — •J. Michael Gottfried — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

The on-surface synthesis of organic molecules, organometallic compounds, and two-dimensional polymeric networks is an increasingly popular field of study in surface science and holds promise as an approach for surface modification and functionalization. Surface reactions in ultrahigh vacuum can produce novel molecular compounds which are not accessible by conventional synthesis in solution or which are too large or too reactive for vapor deposition. Catalytic and template effects exerted by the surface can help driving the reaction into the desired direction. In this contribution, recent advances in the on-surface synthesis of large molecular species and two-dimensional polymeric structures will be reviewed. Prominent examples include conjugated hydrocarbon macrocycles such as hyperbenzene and its homologues, which are synthesized by the surface-assisted Ullmann reaction. This reaction also provides access to cyclic and linear organometallic structures. Related topics that will be covered include strategies for the synthesis of low-defect covalent networks through the on-surface synthesis of suitable molecular building blocks and the role of side products for structure formation.

O 86.2 Thu 15:30 HE 101

**Tuning on-surface coordination polymers to form chains and networks forming quantum boxes to investigate Xe condensation in an atom-by-atom manner.** — •O. Popova, S. Nowakowska, A. Wäckerlin, S. Kawai, T. Ivas, J. Nowakowski, S. Fatayer, C. Wäckerlin, T. Nijs, J. Girovsky, S. Martens, A. Kleibert, N. Ballav, E. Mayer, J. Björk, M. Stöhr, L. Gade, and T. Jung — Basel, Switzerland

Coordination between organic molecular ligands and metal adatoms has been established to form stable, well-ordered and here chemically tunable endo or exo-ligands and corresponding polymers. By combining STM, XPS, NEXAFS and DFT, we demonstrate that the amino-functionalized perylene derivative,DPDI, undergoes specific levels of dehydrogenation depending on the nature of the present adatoms. Moreover, the Cu-coordinated 3deh-DPDI network which is created after the deposition of DPDI on Cu(111) and subsequent annealing confines the Shockley surface state into well-defined quantum boxes.These boxes provide an ideal template for studying Xe condensation process atom-by-atom under the interplay of different well known interactions. Our direct, real-space analysis reveals the subtle interplay of competing directional and non-directional interactions which determine the condensate structure. This approach is applicable significantly beyond the presented Xe case. Also such adsorbate containing *quantum boxes* provide unprecedented systems for the in-depth comparison of simulations using different quantum mechanical models.

O 86.3 Thu 15:45 HE 101

**Self-assembly of NC-Ph3-CN molecules on Cu(111): an unusual alignment with respect to the substrate** — •Giulia E. Pacchioni, Marina Pivetta, and Harald Brune — Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

The self-assembly of dicarbonitrile polyphenyl molecules (NC-Phn-CN) on metal surfaces is a widely studied subject. These molecules on Ag(111) are in most cases aligned along the first or second nearest neighbors directions of the substrate. For NC-Ph5-CN molecules on Cu(111) the alignment along the second nearest neighbors is the only one observed. On Cu(111) the alignment along this direction is particularly favorable, since it allows an almost perfect epitaxial fit of the molecules with respect to the substrate. The behavior of NC-Ph3-CN molecules on Cu(111) is in this respect rather bizarre: while for purely organic assemblies the alignment is, as expected, along the high symmetry directions, when the network is metal coordinated the molecules align along a bunch of directions deviating from the second nearest neighbors ones by 4, 11 and 18 degrees. The resulting networks have a strongly reduced degree of order compared to NC-Ph5-CN on Cu(111) assemblies. We explain this peculiar behavior through the interplay between the gain in energy obtained by forming a straight CN-Cu bond at the molecule ends, and the one given by having the hydrogen and nitrogen atoms placed on favorable adsorption sites on the surface. We show that these two preferences cannot be satisfied at once, so depending on the length of the molecule one or the other will prevail, giving rise to different dispositions on the substrate.

O 86.4 Thu 16:00 HE 101

**Surface mediated synthesis of metal-organic architectures based on thiolate-gold coordination bonds** — •Atena Rastgoo Lahrood[1,2], Matthias Lischka[1,2], Johanna Eichhorn[1,2], Thomas Strunskus[4], Wolfgang M. Heckl[1,2,3], and Markus Lackinger[1,2,3] — [1]Department of Physics, Technische Universität München, Germany — [2]Center for NanoScience (CeNS), Munich, Germany — [3]Deutsches Museum, Munich, Germany — [4]Institute for Materials Science - Multicomponent Materials, CAU, Kiel, Germany

In our previous work we studied self-assembly of 1,3,5-tris(4-mercaptophenyl)benzene on Cu(111) and Ag(111). Upon room temperature deposition, densely packed structures were found that could subsequently be converted into more complex and open structures by mild annealing. On Cu(111) two different metal coordinated structures could be identified. To shine more light on the substrate influence further studies were carried out on Au(111). Contrary to copper and silver surfaces the initial densely packed structure was never observed. In contrast, already after room temperature deposition we observed a variety of less well-ordered structures that could be identified as metal-coordinated based on bond geometry and XPS data. Post annealing of the surface in successive steps led to the emergence of better ordered likewise metal-organic aggregates and networks with a dominance of distinct motifs at specific temperatures. Even higher annealing temperatures eventually result in sulphur cleavage and disordered molecular structures. All the samples were prepaid and analyzed (STM, XPS and NEXAFS) in an UHV chamber.

O 86.5 Thu 16:15 HE 101

**A predictive model for the self-assembly of organic molecules on weakly interacting surfaces** — •Joost van der Lit[1], Jolien Marsman[2], Nadine J. van der Heijden[1], Stephan den Hartog[1], Peter H. Jacobse[1], Robertus J.M. Klein Gebbink[3], Laura C. Filion[2], and Ingmar Swart[1] — [1]Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands — [2]Soft Condensed Matter, Debye Institute, Utrecht University, The Netherlands — [3]Organic Chemisty and Catalysis, Debye Institute, Utrecht University, The Netherlands

Two-dimensional crystals of organic molecules on surfaces are highly attractive for applications ranging from molecular electronics to gas sensors to protective coatings[1]. The geometry of these crystals is an important parameter in determining their functionality. However, currently there is no model available that can be used to a-priori predict what crystal structures will form.

We developed a model, based on electrostatic and van der Waals interactions, that is capable of predicting the ordering of molecules on weakly interacting metal surfaces. Using scanning tunneling microscopy and atomically resolved atomic force microscopy, we studied the self-assembly of two different molecules on Au(111). These bisacethylene molecules form different crystal structures. Our model correctly reproduces the two different crystal structures that we see experimentally. Additionally, we accurately reproduce the crystal structure of molecules whose self-assembly has been reported in literature.

1. L. Bartels, Nat. Chem., 2, 87-95, (2010)

O 86.6 Thu 16:30 HE 101

**Ethene to graphene: surface catalyzed chemical pathways, intermediates, precursors, and assembly** — Bo Wang[1], Michael König[1], Catherine J. Bromley[2], Bokwon Yoon[3], •Friedrich Esch[1], Ulrich Heiz[1], Uzi Landman[3], and Renald Schaub[2] — [1]Chemistry Dept., Technische Universität München, Catalysis Research Center, 85748 Garching, Germany — [2]EaStCHEM and School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, United Kingdom — [3]School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA

Diverse technologies, from catalyst coking to graphene synthesis, entail hydrocarbon dehydrogenation and condensation reactions on transition metal surfaces and assembly into carbon overlayers. Scanning-tunneling microscopy (STM), thermal-desorption spectroscopy (TDS), and density-functional theory (DFT) simulations were used to uncover the hierarchy of atomic-scale pathways and reaction intermediates underlying the catalyzed thermal evolution of ethene adsorbed on Rh(111) to form 2D graphene overlayers:

Upon heating, adsorbed ethene molecules evolve at first via coupling reactions to form segmented 1D polyaromatic hydrocarbon chains. Further heating leads to dimensionality-crossover (1D to 2D) and dynamical restructuring processes at the PAH chain-ends, with subsequent activated detachment of 24-carbon-atom dehydrogenated-coronene-like clusters. Rate-limiting diffusional coalescence of these dynamically self-evolved precursors culminates at even higher temperatures (1000 K) in condensation into a graphene adlayer of high structural perfection.

O 86.7 Thu 16:45 HE 101

**A strategy for surface grafting of covalent networks: a combined STM, NEXAFS, and XPS study of Ullmann coupling of a fluorinated precursor** — •Matthias Lischka[1,2], Johanna Eichhorn[1,2], Atena Rastgoo-Lahrood[1,2], Thomas Strunskus[3], Rochus Breuer[4], Michael Schmittel[4], Wolfgang M. Heckl[1,2,5], and Markus Lackinger[1,2,5] — [1]Department of Physics, Technische Universität München, James-Franck-Str. 1, 85748 Garching — [2]Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — [3]Institute for Materials Science - Multicomponent Materials, Christian-Albrechts- Universität zu Kiel, Kaiserstr. 2, 24143 Kiel — [4]Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, 57068 Siegen — [5]Deutsches Museum, Museumsinsel 1, 80538 Munich

Thermally activated surface chemistry of tetrabromohexafluorobiphenyl on Ag(111) is studied under ultrahigh vacuum conditions by a range of surface sensitive techniques. X-ray photoelectron spectroscopy of C 1s, Br 3d, and F 1s was used to identify chemical changes that indicated the occurrence of three distinct phases. Upon progressive heating, an initial partly organometallic phase becomes fully organometallic, and is eventually converted into a covalent network. The structural characterization of each phase is carried out by a combination of high resolution scanning tunneling microscopy and C 1s near edge x-ray absorption fine structure. The latter offers detailed insights into the orientation of the phenyl rings with respect to the surface.

O 86.8 Thu 17:00 HE 101

**Structure formation of lipophilic molecules on surfaces in a non-equilibrium setting: A computational study** — •Pritam Kumar Jana and Andreas Heuer — Institute for physical chemistry, University of Muenster, Germnay

Recently, the group of Prof. Chi (Muenster) has observed that N9-substituted adenine derivative in solution form two different type of structures (intercalation vs. stripes patterns) on the surface[1]. Extending that study to deposition experiments, information about the impact of deposition rate and substrate temperature on structure formation has been obtained [2]. It has been observed that higher deposition rates and lower substrate temperatures prefer to stabilize the intercalated structure. We present kinetic Monte Carlo simulations where the molecules are represented as model chains with one head-type and a few tail-type monomers. The key interaction properties, i.e., the formation of hydrogen bonds (intercalated structure) and pi-pi interactions (stripe interaction) among the adenine molecules, respectively, and the van der Waals chain-chain interactions, are reflected in this model, based on DFT-based parameters. The quality of structure formation in dependence on deposition rate and substrate temperature as well as the relative fraction of both phases is analysed and compared with experimental data. Good qualitative agreement is achieved.

[1] Mu et al. Langmuir, 29, 10737, 2013

[2] Wang et al. Chem. Comm., 50, 9192, 2014

O 86.9 Thu 17:15 HE 101

**Reversible photoisomerization within monolayers of a $\pi$-expanded oligothiophene 8-mer: A photosensitive molecular cargo nanoarchitecture** — •Jose D. Cojal[1], Masahiko Iyoda[2], and Jürgen P. Rabe[1] — [1]Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany — [2]Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan

A $\pi$-expanded oligoethynylene-thiophene macrocycle has been optically switched between its *E,E*- and *Z,Z*-conformers in different solutions. Here, we report a self-assembled monolayer of *Z,Z*-8mer (*E,E*-8mer) between its octanoic acid solution and HOPG, which upon illumination at 365nm (550nm) with an intensity of $\sim$ 1mW/cm$^2$, photoisomerizes to the of *E,E*-8mer (*Z,Z*-8mer). The switching process was followed using STM imaging while irradiating with the corresponding wavelength. The 2D-hexagonal network of the *Z,Z*-8mer displayed an average unit cell of $a$=(2.76± 0.01)nm, $b$=(2.86± 0.03)nm, $\theta$=(60.8± 0.8)°, while the *E,E*-8mer exhibited a different average unit cell $a$=(2.89± 0.02)nm, $b$=(2.95± 0.03)nm, $\theta$=(60.3± 0.8)° with a 95% of confidence level. To validate the reversible switching, emission spectra were recorded starting with a monolayer of *Z,Z*-8mer, which isomerizes to the *E,E* form after 15 minutes of illumination at 365nm with an intensity of 700mW/cm$^2$, and returns to the original spectrum after 15 additional minutes of illumination at 550nm with an intensity of 500mW/cm$^2$. Combining the photoswitchable properties of the monolayers of the macrocycle with its host-guest capabilities we envisage a photosensitive molecular cargo system.

O 86.10 Thu 17:30 HE 101

**Selfassembly of organic semiconductor monolayer via solid-solid wetting: physico-chemical basics, controllability, process capability** — •Alexander Eberle[1,2,3] and Frank Trixler[1,2,3] — [1]Earth and Environmental Sciences, Ludwig-Maximilians-Universität München (LMU) — [2]Center for NanoSciences (CeNS) — [3]Deutsches Museum, München, Germany

Organic Solid-Solid Wetting Deposition (OSWD) (Trixler et al.: Chem.Eur.J. 13 (2007), 7785) enables to deposit insoluble molecules such as organic pigments and semiconductors on substrate surfaces such as graphite and graphene under ambient conditions. Important for enabling a broader application of OSWD is the exploration of its potential to easily grow and manipulate monolayers. In the presented study we use Quinacridone as a model system, an organic semiconductor and pigment, which finds extensive use in industrial applications. Results of investigations via Scanning Tunneling Microscopy (STM), particle size distribution and zeta potential analysis are presented which give a deeper insight into the physico-chemical basics, the controllability and the process capability of the OSWD technique. The results explain existing and open up new advantages (cheap and fast process, chemical and mechanical resistance, directed domain growth in micro- and nanoscale, nanomanipulation, co-adsorption), explain restrictions (domain-structure, coverage) and point towards prospective applications (band-gap engineering of graphene, Van der waals heterostructures) of OSWD for surface physics, supramolecular chemistry and carbon-based electronics.

# O 87: Graphene: Electronic Structure

Time: Thursday 15:00–18:15 Location: MA 041

O 87.1 Thu 15:00 MA 041

**Tuning the electronic structure of artificial graphene with potential modulation** — •Pilkwang Kim and Cheol-Hwan Park — Department of Physics, Seoul National University, Seoul 151-747, Korea

Among the many different directions of research for tuning the electronic properties of massless Dirac fermions residing in materials like graphene, one of the promising candidates is the artificial graphene system where a conventional two-dimensional electron gas is modulated by external periodic potential, as first predicted theoretically [1,2]. Recently, experimentalists have confirmed the existence of massless Dirac fermions originating from metallic surface states [3,4]. In this presentation, we discuss our theoretical study on the possibility of tuning the electronic properties of massless Dirac fermions residing in 2DEG by exploiting the external potential degree of freedom. This work was supported by Korean NRF funded by MSIP (Grant No. NRF-2013R1A1A1076141).

[1] C.-H. Park and S. G. Louie, Nano Lett. 9, 1793 (2009).

[2] M. Gibertini, A. Singha, V. Pellegrini, M. Polini, G. Vignale, A. Pinczuk, L. Pfeiffer, and K. West, Phys. Rev. B 79, 241406 (2009).

[3] K. K. Gomes, W. Mar, W. Ko, F. Guinea, and H. C. Manoharan, Nature 483, 306 (2013).

[4] S. Wang, L. Z. Tan, W. Wang, S. G. Louie, and N. Lin, Phys. Rev. Lett. 113, 196803 (2014).

O 87.2 Thu 15:15 MA 041

**Using collective electrostatic effects to tune the electronic structure of graphene** — •Gernot J. Kraberger[1], David A. Egger[1,2], and Egbert Zojer[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

Graphene has unique structural and electronic properties, which have attracted huge research interest since its isolation. As a prerequisite of using this material in devices, it is necessary to modify its properties in a controlled way that it fits the needs of the application. This work uses density functional theory calculations to investigate a new approach to change the electronic structure of graphene: using the collective field of a highly ordered arrangement of dipoles to shift the potential in specific regions of graphene (i.e., exploiting so-called collective electrostatic effects). First we discuss a "proof-of-concept" model system: Along a line in graphene, pairs of neighboring carbon atoms are replaced by a boron and a nitrogen atom. Each of the resulting BN-pairs exhibits a dipole moment, which means that a one-dimensional chain of dipoles is formed. This chain impacts the electrostatic potential in its surroundings such that the electronic states in graphene are locally shifted relative to the Fermi level. With two oppositely oriented lines of dipoles it is then even possible to localize states in well-defined stripes. Finally, we explore to what extent similar effects can be generated by assembling rows of quadrupolar molecules on top of the graphene sheet instead of modifying the graphene layer itself.

O 87.3 Thu 15:30 MA 041

**Graphene on weakly interacting metals: Dirac states vs. surface states** — •Wouter Jolie, Fabian Craes, and Carsten Busse — II. Physikalisches Institut, Universität zu Köln, Germany

The epitaxial growth of graphene and other two-dimensional materials on metal surfaces has become a well-established procedure and is extensively used for studies of the electronic properties of two-dimensional materials using surface science methods. However, the substrate itself can have a significant contribution to these properties. We demonstrate this on three different systems: graphene on a thick silver film on Ir(111), graphene on one monolayer of silver on Ir(111), and graphene on Ir(111). We explore the interplay between the states of the substrate (in form of nearly free surface states) and the states of the two-dimensional material on top (in form of graphenes' Dirac fermions) with scanning tunneling spectroscopy, a technique sensitive to the local density of states of the surface. We show that, when present, the surface state represents the dominant contribution in form of Friedel oscillations and confined states on graphene quantum dots. We compare these findings with a system with suppressed surface states where a clear feature of graphene is found in the density of states.

O 87.4 Thu 15:45 MA 041

**Size quantization effects in quasiparticle interference on epitaxial graphene nanoflakes** — •Julia Tesch[1], Philipp Leicht[1], Felix Blumenschein[1], Anders Bergvall[2], Tomas Löfwander[2], Luca Gragnaniello[1], and Mikhail Fonin[1] — [1]Universität Konstanz, Konstanz, Germany — [2]Chalmers University of Technology, Göteborg, Sweden

Graphene nanostructures represent an exciting topic for research, as a strong spatial confinement together with the edge structure impose new electronic properties, making them promising candidates for future nanoscale electronic units. Here, we investigate by means of low-temperature scanning tunnelling microscopy and spectroscopy oblong quasi-freestanding epitaxial graphene nanoflakes prepared on Ag(111) and Au(111) by intercalation with virtually no edge bonding [1]. We implement quasiparticle interference (QPI) mapping to analyze standing wave patterns arising from elastic scattering processes within a single nanoflake. The Fourier analysis of the obtained QPI maps shows that in addition to ringlike structures due to the *intervalley* and *intravalley* scattering observed for large graphene sheets, additional scattering features are visible, which can be related to the transverse modes in a nanoflake [2]. Our experimental results are supported by tight-binding calculations of realistic flakes, which very well reproduce the experimentally observed fingerprints of confinement in the Fourier transform of the standing wave patterns.

[1] P. Leicht *et al.*, ACS Nano **8**, 3735 (2014); [2] A. Bergvall *et al.*, Phys. Rev. B **87**, 205431 (2013).

O 87.5 Thu 16:00 MA 041

**Graphene-supported metal clusters: A two photon photoemission study** — Kira Jochmann and •Thorsten Bernhardt — Institut für Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm

During the last decade considerable attention was drawn to the growth of graphene on metal single crystal surfaces, where it provides an ideal template for the ordered growth of regular metal cluster arrays. Building on various investigations about the detailed growth of these cluster super-lattices, we make use of the possibility to easily grow nanostructures with equally spaced and mono-disperse clusters for fundamental research in laser selective photochemistry. Our new experimental setup enables time-resolved measurements due to a femtosecond laser system on the one hand and surface analysis via scanning tunnelling microscopy on the other hand. In first light interaction measurements time-resolved two-photon photoemission spectroscopy (2PPES) was applied to gain an insight into the unoccupied electronic structure of the Ir(111)/graphene/Ir cluster system at different graphene and cluster coverages. In subsequent experiments the combination of femtosecond laser pump-probe mass spectrometry with resonance enhanced multi-photon ionization and STM will be employed to reveal photo-dissociation dynamics of different adsorbate molecules with spatio-temporal resolution.

O 87.6 Thu 16:15 MA 041

**From ribbons to constrictions: STM lithography on ballistic sidewall graphene nanoribbons** — •Jens Baringhaus[1], Mikkel Settnes[2], and Christoph Tegenkamp[1] — [1]Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany — [2]Technical University of Denmark, DTU Nanotech, Center for Nanostructured Graphene (CNG), 2800 Kgs. Lyngby, Denmark

The selective graphene growth on the sidewalls of SiC mesa structures produces well-ordered graphene nanoribbons (GNR) with exceptional transport properties. Using a 4-tip STM, a probe spacing and temperature independent conductance of $e^2/h$ is found, indicating single channel ballistic transport even at room temperature [1]. The robustness of the ballistic channel makes these GNR ideal templates for morphological alterations. For this purpose, one of the STM tips is used for local lithography. Careful control over the feedback parameters and the bias voltage allows to either fully cut the ribbon or to create narrow, a few nm wide constrictions. Every STM lithography step is monitored directly by local transport. After a full cut, the transport characteristics of the sidewall GNR are completely destroyed. In contrast, in narrow constrictions the ballistic channel is preserved, but only present at bias voltages exceeding 10 mV. Additionally, localized

currents manifest as resonances in the IV curves at bias voltages of about 8 mV. Using a standard tight binding and recursive Green's function approach, the resonances are found to be robust against temperature as well as different types of disorder, e.g. Anderson or edge disorder.
[1] Baringhaus et al., Nature **506**, 349 (2014)

O 87.7 Thu 16:30 MA 041

**Chiral Enhanced Phonon Spectroscopy of Graphene** — •Fabian D. Natterer[1], Yue Zhao[1,2], Jonathan Wyrick[1], Wen-Ying Ruan[3], Yang-Hao Chan[4], Mei-Yin Chou[3,4], Nikolai B. Zhitenev[1], and Joseph A. Stroscio[1] — [1]Center for Nanoscale Science and Technology, NIST, Gaithersburg, USA — [2]University of Maryland, College Park, USA — [3]Georgia Institute of Technology, Atlanta, USA — [4]Academia Sinica, Taipei, Taiwan

In graphene, many phenomena are driven by the interaction with phonons, such as the relaxation of hot carriers or the mediation of many-body interactions. The proper characterization of phonons can therefore shed important insights into graphene based devices. Such devices were characterized by inelastic electron tunneling spectroscopy (IETS) but weak signals and other spectral features obscured a clear distinction between phonons and miscellaneous excitations. In this talk, I show that we are able to map large parts of the graphene phonon density of states by using a back gated graphene device, where the charge carrier density can be varied in magnitude and sign. Our averaging technique combines individual IETS data, obtained over the entire charge carrier range, with the benefit of improving the signal for inelastic excitations. Surprisingly, we observe that the graphene phonon intensity is enhanced when the charge carrier type is switched, indicating that this amplification occurs whenever the inelastic transition allows a change in the graphene chirality. The chiral enhancement follows a linear trend with energy and reaches almost an order of magnitude for the highest mode.

O 87.8 Thu 16:45 MA 041

**Luminescence of Graphene in the Visible Spectral Range after Short-Pulse Excitation in the Near Infrared** — •Martin Rothe, Günter Kewes, Nikolai Severin, Jürgen P. Rabe, and Oliver Benson — Department of Physics and IRIS Adlershof, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany

Graphene is well known for its unique electronic and optical properties. The study and manipulation of its nonlinear optical response at energies in the range of visible light is of interest for the understanding of its charge carrier dynamics in this energy regime [1]. We find a broad luminescence of graphene and graphene multilayers in the entire visible spectral range after excitation with fs laser pulses in the near infrared. The spectrum that starts even above twice the excitation energy indicates multi-photon absorption or efficient electron scattering processes. This method of luminescence excitation is not only well suited for imaging with high contrast but can also gain insight into fundamental electron relaxation and collective excitation processes [2].

[1] Liu, et al., Phys Rev B: 82, 081408 (2010)

[2] Lange, et al., arXiv:1404.6518 (2014)

O 87.9 Thu 17:00 MA 041

**Electroluminescence from carbon-based nanostructures** — •Ji Hoon Ryoo and Cheol-Hwan Park — Department of Physics, Seoul National University, Seoul 151-747, Korea

Light emission from carbon nanostructures upon current flowing reflects their novel electronic structures and is important for applications purposes. Peculiar emission versus photon energy profiles in the electroluminescence from carbon nanostructures have been attributed to inter-band electronic transitions [1], electron-phonon interactions [2] and interference effects [3]. In this presentation, we discuss the origin of multi-peak intensity versus energy feature in the electroluminescence from graphene based on recent experimental results, and look into how the electronic structure of graphene affects its electroluminescence. This work was supported by Korean NRF funded by MSIP (Grant No. NRF-2013R1A1A1076141). Computational resources have been provided by Aspiring Researcher Program through Seoul National University (SNU) in 2014.

[1] D. Mann, Y. K. Kato, A. Kinkhabwala, E. Pop, J. Cao, X. Wang, L. Zhang, Q. Wang, J. Guo, H. Dai, Nature Nanotech. 2, 33-38 (2007).

[2] S. Essig, C. W. Marquardt, A. Vijayaraghavan, M. Ganzhorn, S. Dehm, . Henrich, F. Ou, A. A. Green, C. Sciascia, F. Bonaccorso, K.-P. Bohnen, H. v. Löhneysen, M. M. Kappes, P. M. Ajayan, M. C. Hersam, A. C. Ferrari, R. Krupke, Nano Lett. 10, 1589-1594 (2010).

[3] M. Engel, M. Steiner, A. Lombardo, A. C. Ferrari, H. v. Löhneysen, P. Avouris, R. Krupke, Nature Comm. 3, 906 (2012).

O 87.10 Thu 17:15 MA 041

**Structure and electronic states of the zig-zag graphene/h-BN interface** — •Robert Drost[1], Andreas Uppstu[2], Kezilebieke Shawulienu[1], Fabian Schulz[1], Sampsa K. Hämäläinen[1], Mikko Ervasti[2], Ari Harju[2], and Peter Liljeroth[1] — [1]Department of Applied Physics, Aalto University School of Science, Finland — [2]COMP Centre of Excellence and Helsinki Institute of Physics, Department of Applied Physics, Aalto University School of Science, Finland

Some of the most exciting properties of graphene (G) are only realised in atomically precise nanostructures. The zig-zag (ZZ) edges of this two-dimensional crystal host localised states that have been proposed to be used in spin- and valleytronic applications: Using the spin degree of freedom of the electron or the valley degree of freedom of the honeycomb crystal structure to transmit and process information. While well studied theoretically, experimental realisations remain challenging. We passivate the ZZ edge of epitaxial G with hexagonal boron-nitride (BN), a 2D insulator isostructural to G, to preserve the edge state in the band gap of the insulator. We investigate the growth of atomically perfect G/BN heterostructures on Ir(111) and Ni(111) substrates and discuss the effect of varying substrate interaction. The intrinsic properties of the G/BN interface may be revealed by intercalation with gold. Using low-temperature STM, we demonstrate the existence of a localised electronic state on the ZZ oriented G/BN interfaces. Tight binding and DFT calculations show that the interface retains many important properties of the graphene edge state.

O 87.11 Thu 17:30 MA 041

**Embedding graphene quantum dots into hexagonal boron nitride** — Ferdinand Farwick zum Hagen[1], Caio Silva[1], Christoph Schlueter[2], Nicolae Atodiresei[3], Wouter Jolie[1], Daniela Dombrowski[1], Antonio J. Martinez-Galera[1], Domenik Zimmermann[1], Ulrike Schröder[1], Vasile Caciuc[3], Thomas Michely[1], Stefan Blügel[3], Tien-Lin Lee[2], and •Carsten Busse[1] — [1]II. Physikalisches Institut, Universität zu Köln, Germany — [2]Diamond Light Source, Didcot, UK — [3]Peter Grünberg Institute, Forschungszentrum Jülich, Germany

Graphene (gr) nanostructures can be stabilized by embedding them into an insulating matrix. Hexagonal boron nitride (hBN) is especially suited as it is isostructural to graphene, and dangling C bonds can be satisfied by B and N. In this study, we used sequential epitaxial growth of gr and hBN on Ir(111) to embed graphene quantum dots (GQDs).

First, we investigate pristine hBN/Ir(111) with special attention to the hBN-substrate interaction which is characterized by the local varying layer height as determined with x-ray standing waves (XSW), complemented by density functional theory (DFT) calculations. Distinct differences with respect to gr/Ir(111) are found: A stronger corrugation within the moiré and an enhanced chemical interaction in the strongly bound parts of the supercell. Second, the edge atoms of GQDs on Ir(111) are investigated and an enhanced C-substrate interaction is found. Third, the chemical and structural changes at these edges upon embedding in hBN are probed. The in-plane structure is analyzed using scanning tunneling microscopy (STM).

O 87.12 Thu 17:45 MA 041

**Single 3*d* transition metal atoms on multi-layer graphene systems: electronic configurations, bonding mechanism and role of the substrate** — Violetta Sessi[6], Sebastian Stepanow[1,2], Alexander N. Rudenko[3], Sören Krotzky[1], Klaus Kern[1], Fanny Hiebel[4], Pierre Mallet[4], Jean-Yves Veuillen[4], Ondřej Šipr[5], •Jan Honolka[1,5], and Nick B. Brookes[6] — [1]Max-Planck Institut für Festkörperforschung, Stuttgart, Germany — [2]Department of Materials, ETH Zürich, Switzerland — [3]Radboud University Nijmegen, Inst. for Molecules and Materials, Netherlands — [4]Institut Néel, CNRS-UJF, Grenoble, France — [5]Inst. of Physics, ASCR, Prague, Czech Republic — [6]ESRF, Grenoble, France

We present our recent study on electronic configurations of Fe, Co, Ni and Cu adatoms on graphene and graphite by x-ray magnetic circular dichroism and charge transfer multiplet theory [1]. A delicate interplay between long-range interactions and local chemical bonding is found to influence the adatom equilibrium distance and magnetic moment. The results for Fe and Co are consistent with purely physisorbed species having, however, different 3*d*-shell occupations on graphene and graphite ($d^{n+1}$ and $d^n$, respectively). On the other hand, for the late 3$d$ metals Ni and Cu a trend towards chemisorption is found, which strongly quenches the magnetic moment on both substrates.

[1] V. Sessi et al., New J. of Physics 16, 062001 (2014) [Fast Track Communication]

O 87.13 Thu 18:00 MA 041

***Ab initio* calculation of XNLD in reflection of graphene** — •Dominik Legut[1], Peter M. Oppeneer[2], Christine Jansing[3], Marc F. Tesch[3,4], Markus Gilbert[3], Andreas Gaupp[3], Hans-Christoph Mertins[3], Andrey Sokolov[4], Suk-Ho Choi[5], Hud Wahab[6], Heiko Timmers[6], and R.G. Elliman[7] — [1]IT4Innovations Centre, VSB-TU Ostrava, Ostrava, Czech Republic — [2]Department of Physics and Astronomy, Uppsala, Sweden — [3]FH Münster, Steinfurt, Germany — [4]HZB, Berlin, Germany — [5]Department of Applied Physics, Kyung Hee University, Korea — [6]University of New South Wales Canberra, Canberra BC, Australia — [7]Department of Elect. Mat. Eng., Australian National University, Canberra, Australia

The reflection spectroscopy and in particular angular dependence of the x-ray natural linear dichroism (XNLD) were calculated on free standing monolayered graphene. The anisotropic XNLD was computed in the single electron picture within the framework of the DFT. The excitations stemming from carbon K-edge are considered. The spectral shape of the XNLD is compared with recorded data. The dependence of the reflection spectroscopy, here XNLD, based on the change of the electronic structure of bi-layer and tri-layered graphene is predicted.

## O 88: Electronic Structure: Surface Magnetism and Spin Phenomena

Time: Thursday 15:00–18:15 Location: MA 042

O 88.1 Thu 15:00 MA 042

**Tuning the zero field splitting of single porphyrin molecules on Pb(111)** — •Benjamin W. Heinrich[1], Lukas Braun[1], José I. Pascual[2], and Katharina J. Franke[1] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Germany — [2]CIC nanoGUNE, San Sebastián, and Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

Magnetism in reduced dimensions is governed by the local chemical structure and the interaction with the surrounding on an atomic scale. Here we employ the tip of a low-temperature scanning tunneling microscope to modify reversibly the ligand field of a transition metal atom. Two metal-organic complexes – one high-spin and one intermediate-spin complex – adsorbed on the type I superconductor Pb(111) are studied at 1.2 K. Inelastic electron tunneling spectra reveal changes of the zero field splitting of the spin eigenstates in the order of 10% for both molecules due to the changed potential landscape experienced by the paramagnetic atom.

We explain our results by variations of the ligand field, which modify the $d$-level splitting and thereby the zero field splitting. These experiments highlight the importance of subtle differences in the geometry and surrounding potential, which influence the strength of magnetocrystalline anisotropy in transition metal complexes.

O 88.2 Thu 15:15 MA 042

**High out-of-plane spin polarization induced by non-centrosymmetric crystal structure of BiTeI** — •Christian Langenkämper[1], Koji Miyamoto[1], Oleg E Tereshchenko[2], Konstantin A Kokh[2], Peter Krüger[3], and Markus Donath[1] — [1]Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Germany — [2]Novosibirsk State University, Russia — [3]Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Germany

So far, Rashba spin splittings have been discussed mostly for surface states on the basis of the Rashba-Bychkov model. Recently, a new class of Rashba materials has attracted attention: In non-centrosymmetric materials like $MoS_2$ [1] and BiTeI [2] the bulk Rashba effect is responsible for lifting the spin degeneracy. So far, almost all photoemission studies of BiTeI are focused on Rashba effects in the occupied states around the $\overline{\Gamma}$ point. For future applications, e.g. in opto-spintronics, a substantiated knowledge about the spin-split states above the Fermi level is also needed.

We examined the unoccupied band structure of BiTeI along the $\overline{\Gamma \mathrm{K}}$ direction with spin-resolved inverse photoemission. At the $\overline{\mathrm{K}}$ points at the Brillouin zone boundary, we found a high out-of-plane spin polarization caused by the non-centrosymmetric crystal structure. This case will be discussed on the basis of band calculations.

[1] Suzuki *et al.*, Nat. Nanotechnology **9**, 611 (2014)

[2] Ishizaka *et al.*, Nature Mater. **10**, 521 (2011)

O 88.3 Thu 15:30 MA 042

**Barrier free sub-surface incorporation of 3d-transition metals into the Bi(111) surface** — •Claudius Klein[1], Nora J. Vollmers[2], Percy Zahl[3], Uwe Gerstmann[2], Wolf Gero Schmidt[2], Peter Sutter[3], and Michael Horn-von Hoegen[1] — [1]Faculty of Physics and Center for Nanointegration CENIDE, University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany — [2]Department of Physics, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany — [3]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

For the interesting class of materials with spin-polarized two-dimensional surface states, Bi(111) is a perfect and well understood model system. By combining low temperature scanning tunneling microscopy (LT-STM) measurements and density functional theory, we found the Bi(111) surface to have a well-defined incorporation site for 3d-transition metals within the first bilayer. Atoms like Fe, Co, Ni, Cu become immediately barrier-free embedded and are located within the same specific sub-surface site, as they are not present in STM topography. They only become apparent in STS at tunneling conditions close to the Fermi-energy, as they are surrounded by a pronounced anisotropic threefold electronic scattering pattern. The influence of sample temperature and high coverage regimes for possible surface delta-doping are investigated. Furthermore, this incorporation effect is also observed for some 4d and 5d transition metals.

O 88.4 Thu 15:45 MA 042

**Shot noise as a probe of spin polarized transport through single atoms** — •Andreas Burtzlaff[1], Alexander Weismann[1], Mads Brandbyge[2], and Richard Berndt[1] — [1]IEAP, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — [2]NanoDTU, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Single Fe and Co adatoms on a Au(111) surface were contacted with a Au coated tip in an STM at 4K. The shot noise of the current through the contacts is strongly suppressed compared to the classical value of 2eI. This is a clear indicator of spin polarization in the electronic transmission. Surprisingly, this effect is observed from single atoms, whose spin moment is expected to fluctuate at 4K. Moreover, Co on Au(111) is a Kondo system and the localized spin is expected to be screened. The results will be discussed on the basis of density functional calculations.

O 88.5 Thu 16:00 MA 042

**Spin Chirality in Momentum Space for Surface States on Tl/Si(111) and Tl/Ge(111)** — •Sebastian D. Stolwijk[1], Philipp Eickholt[1], Kazuyuki Sakamoto[2], Anke B. Schmidt[1], Peter Krüger[3], and Markus Donath[1] — [1]Physikalisches Institut, Westfälische Wilhelms-Universität Münster — [2]Department of Nanomaterials Science, Chiba University, Japan — [3]Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster

The Tl/Si(111)-(1×1) surface is known for its spin-orbit-induced rotating spin pattern in momentum space along $\bar{\Gamma}\bar{\mathrm{K}}$ [1,2]. In this contribution, we focus on the unoccupied surface electronic structure around the $\bar{\mathrm{M}}$ point of Tl/Si(111)-(1×1) and the isoelectronic surface Tl/Ge(111)-(1×1). On both surfaces, our spin- and angle-resolved inverse-photoemission experiments reveal a surface-derived state with giant spin-orbit-induced splitting, in agreement with our theoretical findings. While it lies within a band gap for Tl/Ge(111)-(1×1), it is degenerate with bulk bands on the Si substrate. In both cases, the state is purely in-plane polarized along $\bar{\Gamma}\bar{\mathrm{M}}$, whereas the out-of-plane component is dominant along $\bar{\mathrm{K}}\bar{\mathrm{M}}$. As a consequence, spin chirality is found in momentum space around the $\bar{\mathrm{M}}$ point.

[1] K. Sakamoto et al., Nature Commun. 4, 2073 (2013).

[2] S.D. Stolwijk et al., Phys. Rev. Lett. 111, 176402 (2013).

O 88.6 Thu 16:15 MA 042

**Spin-orbit entanglement in the Bi/Ag(111) surface alloy** — •Thiago Ribeiro Fonseca Peixoto, Henriette Maass, Christoph Seibel, Hendrik Bentmann, and Friedrich Reinert — Physikalisches Institut, Experimentelle Physik VII, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

We investigated the valence band of the Bi/Ag(111) surface alloy by means of spin- and angle-resolved photoelectron spectroscopy (SARPES), with variable photon energy and light polarization. The sample growth and all measurements were performed in ultrahigh vacuum conditions. We obtained ARPES-spectra at room temperature, for photon energies between 20 and 30 eV, with *s*- and *p*-polarized light. The spin-splitted Rashba-type $sp_z$ and $p_xp_y$ surface states [1,2] were observed near Fermi level and exhibit strong intensity variations with the incident light polarization, due to the dipole selection rules. Spin-resolved energy distribution curves were measured at particular points of the surface Brillouin zone, for different photon energies and light polarizations. The surface states are strongly spin-polarized, reaching up to 80% spin-polarization. We show that the spin-polarization has a complex dependence on the parallel momentum, the photon energy and the orbital character of the states. We discuss our results in sight of the peculiar entanglement between the spin and the momentum of the electrons in the Rashba-type surface states [1,2].

[1] H. Bentmann *et al.*, Phys. Rev. Lett. 108, 196801 (2012).
[2] S. N. P. Wissing *et al.*, Phys. Rev. Lett. 113, 116402 (2014)

O 88.7 Thu 16:30 MA 042

**Spin-Dependent Size of an Interband Hybridization Gap in the Unoccupied Band Structure of Pb/Cu(111)** — •Katharina T. Ritter[1], Sune N. P. Wissing[1], Peter Krüger[2], Anke B. Schmidt[1], and Markus Donath[1] — [1]Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Germany — [2]Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Germany

Hybridization gaps between states of similar orbital character may become spin dependent in the presence of strong spin-orbit coupling. Using a monolayer of Pb on Cu(111) as a model system, we show that the size of these gaps itself depends on the spin direction of the states.

We use spin- and angle-resolved inverse photoemission in combination with first-principle calculations to investigate the unoccupied electronic structure of Pb/Cu(111). Above the Fermi level we find a spin-dependent hybridization gap where the splitting yields 200 meV for one and even 500 meV for the other spin direction. To gain a greater insight into the hybridization mechanism, an effective two-band tight binding model is developed. Within this model we show that the interaction of substrate and adlayer is crucial to induce a sizeable spin-orbit coupling and hybridization strength to the system.

O 88.8 Thu 16:45 MA 042

**Orbital-selective spin characterization of Dirac-cone-like surface state at W(110)** — •Koji Miyamoto[1], Henry Wortelen[1], Hossein Mirhosseini[3], Jürgen Henk[4], Taichi Okuda[2], and Markus Donath[1] — [1]WWU Münster, Germany — [2]Hiroshima Univ., Japan — [3]JGU Mainz, Germany — [4]MLU Halle, Germany

Recently, for the topological surface state (TSS) of $\mathrm{Bi_2Se_3}$, several groups have observed an interesting phenomenon by spin- and angle-resolved photoemission (SARPE): the observed spin features of the photoelectrons are strongly dependent on the light polarization [1,2]. This effect is currently highly debated in the field of optospintronics. So far, the observations are limited to surfaces with $\mathrm{C}_{3v}$ symmetry.

The surface of W(110) shows a spin-polarized Dirac-cone-like state within a spin-orbit-induced gap, which is reminiscent of a TSS [3]. Here, in contrast to so far studied topological insulators, the surface structure has $\mathrm{C}_{2v}$ symmetry.

We studied the orbital dependence of the spin feature of the Dirac-cone-like surface state along $\overline{\Gamma H}$ at W(110) by using SARPE with *s*- and *p*-polarized light. The observed spin textures are found to be reversed between even and odd orbital symmetry. This finding opens a new way to manipulate the spin polarization of photoelectrons in systems with $\mathrm{C}_{2v}$ symmetry.

[1] C. Jozwiak *et al.*, Nat., Phys. **9**, 293 (2013).
[2] Z. Xie *et al.*, Nat., Commun. **5**, 3382 (2013).
[3] K. Miyamoto *et al.*, Phys. Rev. Lett. **108**, 066808 (2012).

O 88.9 Thu 17:00 MA 042

**Rashba Splitting of $d_{z^2}$ Surface State on Ta(110)** — •Henry Wortelen[1], Koji Miyamoto[1], Hossein Mirhosseini[2], Taichi Okuda[3], Jürgen Henk[4], and Markus Donath[1] — [1]Physikalisches Institut, Westfälische Wilhelms-Universität Münster — [2]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz — [3]Hiroshima Synchrotron Radiation Center, Hiroshima University, Japan — [4]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg

The influence of spin-orbit effects on the surface electronic structure of Ta(110) was investigated by high-resolution spin- and angle-resolved photoemission. We will present photoemission data obtained by excitation with *s*- and *p*-polarized light to reveal the orbital character of the states.

A surface state with $d_{z^2}$ symmetry [1] was detected at a binding energy of 0.45 eV at $\overline{\Gamma}$. It shows a Rashba-type spin splitting, which is large compared with $d_{z^2}$ surface states of other elements of the same period such as Gd(0001) [2] and Tb(0001) [3]. We will discuss our experimental results in the context of electronic-structure calculations concerning spin-dependent spectral densities, spin-dependent photoelectron intensities, and symmetries of the observed states.

[1] E. Kneedler et al., Phys. Rev. Lett. **64**, 3151 (1990)
[2] O. Krupin et al., Phys. Rev. B **71**, 201403 (2005)
[3] O. Krupin et al., New J. Phys. **11**, 013035 (2009)

O 88.10 Thu 17:15 MA 042

**State identification and tunable Kondo effect of MnPc** — •Andreas Krönlein[1], Jens Kügel[1], Michael Karolak[2], Pin-Jui Hsu[1], Jacob Senkpiel[1], Giorgio Sangiovanni[2], and Matthias Bode[1] — [1]Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Germany — [2]Institut für Theoretische Physik und Astronomie, Theoretische Physik I, Universität Würzburg, Germany

In the past the Kondo effect of transition metal phthalocyanine (Pc) molecules has been intensively studied [1]. Recently, by combined scanning tunneling spectroscopy (STS) and density functional theory we could show that also MnPc/Ag(001) exhibits a Kondo effect [2]. The STS data could, however, not satisfyingly be fit by a single Fano function. Rather they appear to be a superimposition of the Kondo feature and another, yet unknown contribution. In this presentation we will show that the tunneling spectrum can be fitted by either two Fano functions, which would indicate two separate Kondo channels [3], or by a combination of a Fano and a Gauss function, with the latter representing an orbital state. We find that spatially resolved Kondo maps are only consistent with the second scenario. This is corroborated by a systematic investigation that, in addition to MnPc, also includes FePc and CoPc. In either case progressive dehydrogenation leads to a continuous shift of what is identified as the $d_{z^2}$ molecular orbital. The influence on the Kondo temperature of MnPc will be discussed.

[1] A. Mugarza *et al.*, Phys. Rev. B **85**, 155437 (2012).
[2] J. Kügel *et al.*, Nano Lett. **14**, 3895 (2014).
[3] K.J. Franke *et al.*, Science **332**, 6032 (2011).

O 88.11 Thu 17:30 MA 042

**Exploring the spectroscopic contrast in spin-polarized scanning tunneling microscopy of the antiferromagnetic e-fct Mn surface: From sub-micrometer to Ångstrom length scales** — •Jiaming Song, Chii-Bin Wu, Bin Zhang, and Wolfgang Kuch — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany

We have investigated the antiferromagnetic (AFM) spin structure in AFM/ferromagnetic (FM) exchange-coupled systems in the model system expanded face-centered tetragonal (e-fct) Mn/Co(001) by spin-polarized scanning tunneling microscopy with an in-plane-sensitive Fe ring probe at room temperature. A thickness-dependent study on the surface of Mn films demonstrates that in differential conductance maps on the length scale of 100 nm, Mn exhibits a thickness-dependent layer-wise contrast at +0.2 V sample bias that proves to be mainly of electronic origin and not related to the spin structure. Still, a smaller layer-wise magnetic contribution could coexist. Atomic-scale measurements reveal a non-collinear spin texture of Mn with a (12x2) periodicity and a geometric superstructure with the same unit cell. This spin structure comprises two orthogonal domains, which are ordered on a larger length scale on 6 ML Mn compared to 5 ML. The non-collinear spin texture of Mn could be caused by competing AFM exchange interactions in the reconstructed Mn layer, possibly in combination with the Dzyaloshinsky-Moriya interaction.

O 88.12 Thu 17:45 MA 042

**Kondo resonance splitting by a spin current** — Deung-Jang Choi[1], Sébastien Guissart[2], Pascal Simon[2], and •Laurent Limot[1] — [1]IPCMS, Université de Strasbourg, UMR CNRS 7504, 67034 Strasbourg, France — [2]Laboratoire de Physique des Solides, Université Paris-Sud 11, UMR CNRS 8502, 91405 Orsay, France

The downscaling of spintronic devices requires developing new strategies for sensing a spin current at the smallest possible length scale. Progress towards this goal has been achieved by experimental advances in probing individual magnetic impurities coupled to non-magnetic electrodes. The spin-flip scattering of an atom is in fact a powerful spin-sensitive spectroscopic probe and information can be gathered on the magnetic interactions, either direct or indirect, between the atom and its environment. Recently, a spin current tunneling into the atom could also be detected in this way provided that the atom ground state is spin-split by a magnetic field (external or effective).

Here we show that the detection of a spin current can be simplified by using the Kondo effect of a single-atom contact. For this purpose, we mimic a multilayered spintronic device by coating a bulk ferromagnetic tip with copper and form a stable single-atom contact with a cobalt atom adsorbed on a copper surface. We find that the strong coupling between the tip and the atom inherent to our contact measurement produces a spin current sufficiently high to promote alone a spin-split Kondo state, the spin polarization of the junction amounting up to 18%.

O 88.13 Thu 18:00 MA 042

**Forces during the manipulation of magnetic properties of individual molecules** — •Christian Lotze, Olof Peters, Xianwen Chen, Benjamin W. Heinrich, and Katharina J. Franke — Freie Universität Berlin, Inst. f. Experimentalphysik, Arnimallee 14, 14195 Berlin

Molecular magnets are promising candidates for future electronic devices. As such they might be useful, for instance, in memory storage applications. Therefore a requirement is to have control over the molecules magnetic properties. In metal-organic complexes the latter are strongly influenced by the interaction of the metal center with the substrate and with its ligands.

Here, we characterize the effect of an additional Cl ligand approached to the center of an iron octaethylporphyrin (FeOEP) molecule adsorbed on a Au(111) surface, employing combined scanning tunneling and atomic force microscopy (STM & AFM). The proximity of a Cl-functionalized tip to the Fe center allows to tune the molecule's spin state, magnetic anisotropy and interaction with the surface. This becomes apparent from the evolution of the tunneling spectra when the tip is approached to the molecule. At tip-molecule contact, we finally reach a regime of Kondo screening. We use simultaneous AFM measurements to detect a mechanical distortion of the molecule causing the change of magnetic properties.

## O 89: Inorganic/Organic Interfaces: Molecular Switches

Time: Thursday 15:00–18:30 Location: MA 043

O 89.1 Thu 15:00 MA 043

**Electronic and Thermal Fluctuations of Functional Molecules on Metals** — Reinhard Maurer[1,2], Wei Liu[3], Igor Poltavskyi[3], Thomas Stecher[2], •Harald Oberhofer[2], Alexandre Tkatchenko[3], and Karsten Reuter[2] — [1]Yale University, New Haven, USA — [2]Technische Universität München, Germany — [3]Fritz-Haber Institut der Max-Planck-Gesellschaft, Berlin, Germany

The prevailing working hypothesis in vacuum surface science is that finite-temperature effects do not significantly alter the equilibrium properties of molecules adsorbed to surfaces. In this work, we show this not to be the case for the adsorption geometry, energetics, and desorption temperature of the molecular switch Azobenzene on Ag(111). Comparing to X-ray standing wave measurements and temperature programmed desorption experiments, we find strong discrepancies to static Density-Functional Theory calculations. We overcome these through anharmonic corrections and explicit *ab initio* molecular dynamics simulations of the free energy of desorption to account for the thermal fluctuations. Additionally, inclusion of many-body dispersion effects accounts for the electronic fluctuations that govern the interaction strength. With respect to both, our calculations show that more modest, prevalent approaches fail to capture the sizable entropy of desorption and therewith the correct desorption temperature. An accurate description of adsorbate interactions and entropies of adsorption in functional hybrid metallic-organic systems thus necessitates a full account of the inherent anharmonicity of adsorbate and substrate, in addition to an accurate description of dispersion interactions.

O 89.2 Thu 15:15 MA 043

**Excited-State Properties of Azobenzene Self-Assembled Monolayers from Many-Body Perturbation Theory** — •Caterina Cocchi and Claudia Draxl — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Self-assembled monolayers (SAMs) of azobenzene-functionalized alkanethiols on gold exhibit remarkable intermolecular interactions in the excited state [1]. Excitonic coupling plays a crucial role in quenching the trans/cis photo-isomerization in the SAMs, compared to single molecules. We perform an in-depth first-principles study of the excited-state properties of the chromophore SAMs. In the framework of density-functional and many-body perturbation theory, as implemented in the all-electron full-potential code exciting [2], we investigate optical and core-level excitations of azobenzene SAMs, functionalized with different end groups. By analyzing the character of the electron-hole pairs, systematically going from the constituent molecules to SAMs of increasing density, we identify the fingerprints of the backbone structures and those of the functional groups. Our results represent an important step forward to interpret available experiments [1], and to gain insight into the microscopic mechanisms that rule excited-state isomerization in these materials. [1] C. Gahl et al. J. Am. Chem. Soc. 132, 1838 (2010). [2] A. Gulans et al. J. Phys.: Condens. Matter 26, 363202 (2014).

O 89.3 Thu 15:30 MA 043

**Azobenzene based self-assembled monolayers as a means to control the work function** — •Swen Schuster[1], Musammir Khan[1], Piotr Cyganik[2], Andreas Terfort[3], and Michael Zharnikov[1] — [1]Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — [2]Smoluchowski Institute of Physics, Jagiellonian University, 30-059 Krakow, Poland — [3]Institute for Inorganic and Analytical Chemistry, Frankfurt University, 60438 Frankfurt, Germany

Controlled adjustment of the work function of surfaces and interfaces by external stimuli is a challenging task. In this context we designed novel photoresponsive, azobenzene-based self-assembled monolayers (SAMs) bearing dipolar functional groups, even though the first experiments were performed on the non-substituted films. To monitor and partly relax the steric constraints upon the photoisomerization we introduced an aliphatic linker of variable parity between the azobenzene unit and the head group, relying on the odd-even effect in the monomolecular assembly. The variation of the packing density was found to be ca. 10% only, which appeared to be insufficient to avoid the steric constraints to the necessary extent. Consequently, photoinduced variation of the work function did not exceed 50 meV, independent of the parity of the aliphatic linker. To improve the photoresponsive properties, the azobenzene-based moieties were diluted with other, short molecules to create sufficient space for isomerization. A clear improvement of the photoisomerization behavior was found, correlated with both the extent of the dilution and the identity of the short molecules.

O 89.4 Thu 15:45 MA 043

**Probing the Photostationary State of Photochromic SAMs by Two-Photon Photoemission Spectroscopy** — •Wibke Bronsch, Daniel Przyrembel, Cornelius Gahl, and Martin Weinelt — Freie Universität, Berlin, Deutschland

In densely packed monolayers of azobenzene derivatives, trans-cis photoisomerization is strongly suppressed due to electronic and steric interaction among the chromophores [1]. Mixing and thus diluting an azobenzene derivative with an alkanethiol of appropriate chain length allows tuning the free volume around the chromophores in the SAM and thereby controlling their interactions. We investigate optical switching in SAMs of azobenzene-decorated undecane thiol diluted with dodecanethiol on Au(111) by means of two-photon photoemission (2PPE) spectroscopy. Along with changes in the electronic structure, we observe a pronounced isomerization-induced shift of the work function up to 250 meV. In order to tune the photostationary state between predominantly trans and cis we vary the intensity ratio of femtosecond UV pulses and a 450 nm continuous-wave laser.

[1] C. Gahl, R. Schmidt, D. Brete, E. R. McNellis, W. Freyer, R. Carley, K. Reuter, and M. Weinelt, J. Am. Chem. Soc. 132, 1831 (2010).

O 89.5 Thu 16:00 MA 043

**Applications of the non-adiabatic molecular dynamics to diarylethene molecule: based light-induced switches** — •Vladimir Zobac[1], Prokop Hapala[1], Enrique Abad[2], Jose Ortega[2], James Lewis[3], and Pavel Jelinek[1] — [1]Institute of Physic, Academy of Sciences of the Czech Republic — [2]Departamento de Fisica Teorica de la Materia Condensada and Condensed Matter Physics Center Universidad Autonoma de Madrid — [3]Department of Physics, West Virginia University

The light-induced molecular processes are frequently studied in various experiments using. One of the most spread methodology allowing to theoretically describe the dynamics of these photochemical processes is non-adiabatic molecular dynamics (NAMD) [1]. Recently, we have implemented the calculation of the non-adiabatic coupling vector, which is the main quantity in NAMD [2]. The NAMD implementation in DFT Fireball code [3] allows to study large systems with more than 100 atoms. We will present the ring closing and opening mechanism of diarylethene based molecules. Most of the statical or dynamical studies were done for this smaller type of molecules on the different level of the accuracy [4]. All of them were performed for the gas phase of the molecule. Here we extend this simulations on the molecules embedded between the gold electrodes in comparison with gas phase simulations. [1] J. C. Tully, J. Chem. Phys. 93, 1061 (1990) [2] E. Abad, et al, J. Chem. Phys., vol. 138, p. 154106, (2013) [3] J.P. Lewis et al, Phys. Stat. Sol. B, 248, 1989 (2011) [4] B. C. Arruda, R. J. Sension, Phys. Chem. Chem. Phys., 4439-4455 (2014)

O 89.6 Thu 16:15 MA 043

**Reversible long range surface state mediated switching of pentacene derivates** — •Verena Schendel[1], Bogdana Borca[1], Ivan Pentegov[1], Ulrike Kraft[1], Hagen Klauk[1], Peter Wahl[1,2], Uta Schlickum[1], and Klaus Kern[1,3] — [1]Max-Planck Institute for Solid State Research, D-70569 Stuttgart — [2]School of Physics and Astronomy, University of St. Andrews, Scotland, KY 16 9SS, United Kingdom — [3]Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Molecular switches represent an essential building block for molecular electronics exhibiting two or more distinct stable states associated with different chemical/physical properties which are reversibly accessible. Therefore they constitute promising candidates for information storage. We report the use of low temperature scanning tunneling microscope (STM) to image and electronically induce reversible conformational changes of the pentacene derivate antracenodithiophene (ADT). ADT adsorbs as statistically distributed monomers on a Cu(111) surface adopting a cis or trans configuration. The conformational switch of an entire array of single molecules is induced by injecting hot electrons from the tip directly into the bare Cu(111) substrate. The (111) faces of noble metals exhibit surface state electrons that have a free electron-like character. Due to the long inelastic mean free path of hot carriers in the surface state switching is enabled over distances on the order of 100 nm. The remote switching process is found to be isomer-selective. We demonstrate a switching process that is fully reversible, isomer selective as well as remotely controlled.

O 89.7 Thu 16:30 MA 043

**Self-assembly and thermally induced conformational changes of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin on Cu(111) studied by STM** — •Michael Lepper, Michael Stark, Liang Zhang, Stefanie Ditze, Hans-Peter Steinrück, and Hubertus Marbach — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

A detailed scanning tunneling microscopy study of the self-assembly and thermally induced conformational changes of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin (Ni-TTBPBP) on Cu(111) will be presented. The coverage-dependent adsorption behavior at room temperature reveals that Ni-TTBPBP molecules can easily diffuse on the surface and self-assemble into islands with square order and a certain registry to the substrate. The role of molecule-molecule and molecule-substrate interactions for the formation of the well-ordered supramolecular structure will be discussed. Interestingly, upon moderate heating two successive, irreversible intramolecular conformational changes are observed. This is explained comprehensively by a thermally induced dehydrogenative, intramolecular aryl-aryl coupling reaction. In addition this intramolecular structural change is coverage dependent, exhibiting a lower rate at higher initial coverage. This modification and the overall adsorption behavior of Ni-TTBPBP on Cu(111) will be discussed and compared to the very different behavior of the similar Ni(II)-tetraphenylbenzoporphyrin on the same substrate.

O 89.8 Thu 16:45 MA 043

**Measuring forces on a single molecule in an STM junction** — •Lukas Gerhard[1], Kevin Edelmann[1], Jan Homberg[1], Marcin Lindner[1], Michal Valasek[1], Marcel Mayor[1,2], Wulf Wulfhekel[1,3], and Maya Lukas[1] — [1]Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen — [2]Department of Chemistry, University of Basel, CH-4056 Basel — [3]Physikalisches Institut, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe

The possibility to incorporate molecular groups into carrier platforms allows to isolate functional units from a metallic substrate. Here we present a low-temperature STM study of spirobifluorene platforms with a benzonitrile head group deposited on a Au(111) surface [1]. We show by systematic variation of the tunneling parameters that the dipole moment of the benzonitrile allows us to exert forces on the molecule by applying electric fields in the STM junction. In this way we are able to form and brake a well defined contact between tip and molecule depending on the applied bias voltage. This switching between ON and OFF states of the conductance is highly reproducible and deterministic. Tuning the electrically applied force such that ON and OFF state are close in energy we observe thermally induced random switching which allows to deduce the energy difference between the two states. We measure this energy difference as a function of the distance between tip and sample and hence derive the force that is needed to pull apart the molecular junction. [1] M. Valášek et al., JOC 2014 79 (16), 7342-7357

O 89.9 Thu 17:00 MA 043

**Conformational switching of single tetraphenylmethane molecules on Au(111) studied by STM** — •Jan Homberg[1], Kevin Edelmann[1], Marcin Lindner[1], Michal Valasek[1], Lukas Gerhard[1], Marcel Mayor[1,2], and Wulf Wulfhekel[1,3] — [1]Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe — [2]Department of Chemistry, University of Basel, CH-4056 Basel — [3]Physikalisches Institut, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe

One of the main challenges in the field of molecular electronics is still the coupling of the molecules to a metallic electrode or substrate. To decouple functional units from the substrate, we follow the idea of tripodal carrier molecules. As a core structure we used tetraphenylmethane with sulfhydryl groups for anchoring. Various derivatives with varying head groups were deposited onto a Au(111) surface via spraying from solution and investigated by low temperature STM. Certain molecules can be switched by the STM tip between different stable conformations. Furthermore we report on the morphology and electronic properties of single molecules on the surface.

O 89.10 Thu 17:15 MA 043

**Switching Orientation of adsorbed Molecules: Reverse Domino on a Metal Surface** — •Taner Esat[1,2], Carolin R. Braatz[3], Christian Wagner[1,2], Ruslan Temirov[1,2], F. Stefan Tautz[1,2], and Peter Jakob[3] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — [2]JARA-Fundamentals of Future Information Technology — [3]Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, 35032 Marburg, Germany

In a two-pronged approach, using infrared absorption spectroscopy and scanning tunneling microscopy, a thus far unknown monolayer phase of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) on Ag(111), characterized by an all perpendicular orientation of the planar molecules has been identified. This conclusion is based on a quantitative analysis of characteristic vibrational modes with specific polarizations, as well as STM images of the standing NTCDA molecules. Formation of the vertically standing NTCDA phase requires second layer NTCDA to squeeze into empty spaces between relaxed monolayer NTCDA molecules. This process causes initially parallel oriented

NTCDA to likewise adopt the inclined adsorption geometry. The new phase shows a pronounced tendency to form 1D rows or narrow islands. We suggest that extra NTCDA preferentially transforms into the upright configuration next to existing islands, i.e. the transformation process proceeds in a directed and recurrent manner (reversed domino effect). We also present revised structure models for the relaxed and the compressed NTCDA/Ag(111) monolayer phases.

O 89.11 Thu 17:30 MA 043

**Intramolecular Dipole of Merocyanine Probed by Local Contact Potential Difference Measurements** — •Nils Krane[1], Christian Lotze[1], Xianwen Chen[1], José Ignacio Pascual[1,2,3], and Katharina Franke[1] — [1]Freie Universität Berlin, Berlin, Germany — [2]CIC nanoGUNE, San Sebastián, Spain — [3]Ikerbasque, Basque Foundation for Science, Bilbao, Spain

In gas phase and solution 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran can be switched reversibly by light and temperature to its merocyanine form. This form has been shown to exhibit an intramolecular dipole [1]. When adsorbed on a metal surface the switching back to the spiropyran form is inhibited [2]. Charge redistribution and screening may considerably alter the expected dipole behavior of the merocyanine form. Utilizing combined low-temperature scanning tunneling microscopy and dynamic atomic force microscopy, we characterize the adsorption of merocyanine on Au(111). The intramolecular charge distribution is measured by the local contact potential difference (LCPD) [3]. The vertical and lateral distribution of the LCPD hints at the persistence of an intramolecular dipole.

[1] Lapienis-Grochowska *et al.*, JCS, Far.Trans. **2** 1979, 75, 312
[2] Marten Piantek *et al.*, J. Am. Chem. Soc. 2009, **131**, 12729
[3] Mohn *et al.*, Nature Nanotechnology 2012, **7**, 227-231

O 89.12 Thu 17:45 MA 043

**Force and conductance in a single molecule switch: SnPc on Ag(111)** — Nuala Caffrey[1], Kristof Buchmann[2], Nadine Hauptmann[2], Cesar Lazo[1], •Paolo Ferriani[1], Stefan Heinze[1], and Richard Berndt[2] — [1]Institut für Theoretische Physik und Astrophysik, Christian-Albrecht-Universität zu Kiel, D-24098 Kiel, Germany — [2]Institut für Experimentelle und Angewandte Physik, Christian-Albrecht-Universität zu Kiel, D-24098 Kiel, Germany

Transport in molecular electronic devices is ultimately determined by the properties of the interface between the metallic electrodes and the organic molecule. To understand the interface properties, the relation between structure and conductance needs to be assessed. The combined use of scanning tunneling and atomic force microscopy is an ideal technique as it allows to simultaneously measure interaction forces and conductance between a tip and an adsorbed molecule. Here, we apply it to study Sn-Phthalocyanine (Pc) on Ag(111). This molecule has a shuttle-cock shape and on a surface can acquire one of two possible conformations – either with the central metal atom pointing away from or towards the surface. We have performed conductance and force measurements on both molecular configurations as a function of tip-sample distance. First-principles calculations of the force and conductance curves agree well with the experiment. We find a non-trivial distance-dependence of the force curves which is explained based on the competition of forces acting on different atoms in the molecule.

O 89.13 Thu 18:00 MA 043

**Direct observation of intramolecular H-atom transfer reaction by scanning tunneling microscopy** — •Janina Ladenthin[1], Leonhard Grill[1,2], Jacek Waluk[3], and Takashi Kumagai[1] — [1]Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany. — [2]Department of Physical Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria. — [3]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland.

Intramolecular H-atom transfer reaction, i.e. tautomerization, is an important molecular process in chemistry and biology. More recently tautomerization in free-base phthalocyanine [1] and porphyrin derivatives [2,3] was directly observed and controlled by low-temperature STM. We have studied tautomerization within a single porphycene molecule, which is a structural isomer of porphine but there exist H-bonding interaction in the cavity, adsorbed on Cu(111) by low-temperature STM. After the deposition of porphycene molecule onto the surface at room temperature the adsorption structure and dynamics were investigated at 5 K. The molecules show the thermodynamically favorable trans configuration. A voltage pulse of the STM can induce the unidirectional conversion from the trans to cis configuration, interestingly, which occurs non-locally and the spatial range of the reaction reaches up to ~100 nm from the STM tip position.

[1] P. Liljeroth, J. Repp, G. Meyer, Science 317, 1203 (2007). [2] W. Auwärter et al. Nature Nanotech. 7, 41 (2011). [3] T. Kumagai et al. Nature Chem. 6, 41 (2014).

O 89.14 Thu 18:15 MA 043

**A supramolecular motor at work: Rotation and translation of single atoms** — Robin Ohmann[1,2], •Anja Nickel[1,2], Jörg Meyer[1,2], Jorge Echeverria[3], Maricarmen Grisolia[3], Christian Joachim[3], Gianaurelio Cuniberti[1,2], and Francesca Moresco[1,2] — [1]Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — [2]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [3]GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France

Molecular motors perform rotational and translational movements or undergo conformational changes converting chemical or electrical energy into mechanical energy. Their size can range from large motor proteins to small nanocars or single molecules. While motor proteins are known to transport large intracellular objects, the displacement of a load at the atomic scale by a molecular motor has not been realized so far. Here, we have bound the smallest possible load - a single atom - to a supramolecular motor and, by feeding it with tunneling electrons, we have triggered the motor to move the atom. As a supramolecular motor we use a windmill-shaped supramolecular structure composed of four 4-Acetylbiphenyl molecules which self-assemble on a Au(111) surface. We controllably load the supramolecular motor with single Au adatoms and, by applying voltage pulses with the tip of a STM, we induce the rotation or translation of the motor, thus performing a minute work at the atomic scale, which is enough for the supramolecular motor to move the load.

## O 90: Sensing, Active Structures and other Applications

Time: Thursday 15:00–18:30 Location: MA 144

O 90.1 Thu 15:00 MA 144

**Active Plasmonics using Molecular Switches** — •Malte Grossmann[1], Alwin Klick[1], Christoph Lemke[1], Mehdi Hedayati Keshavarz[2], Ahnaf Usman Zillohu[2], Jacek Fiutowski[3], Arkadiusz Goszczak[3], Jacob Kjelstrup-Hansen[3], Mady Elbahri[2], Franz Faupel[2], Horst-Günter Rubahn[3], and Michael Bauer[1] — [1]Institute for Experimental and Applied Physics, University of Kiel, Germany — [2]Faculty of Engineering, NanoSYD, University of Kiel, Germany — [3]Mads Clausen Institute, NanoSYD, University of Southern Denmark, Denmark

Photochromic molecules have been successfully used in the past to achieve reversible control of optical transmission [1] and plasmonic damping [2] at metal-dielectric interfaces. In this paper we provide experimental evidence that in the same manner also the propagation of surface plasmon polaritons (SPP) can be steered. Switchable metal-dielectric interfaces are prepared from a gold substrate coated with polystyrene films doped with spirophenanthrooxazine molecules. Changes in the SPP dispersion relation at illumination with light of different wavelength are measured using photoemission electron microscopy [3] evidencing a substantial and reversible switching of SPP group and phase velocity. The results imply the realization of non-volatile plasmonic switching units providing new and complex functionalities.

[1] M. Jamali et al., Adv. Materials 23 (2011), 4243.
[2] R.A. Pala et al., Nano Lett.8 ( 2008), 1506.
[3] C. Lemke et al., Appl. Phys. B 116 (2013), 585.

O 90.2 Thu 15:15 MA 144

**Active mid-IR plasmonic metasurfaces: Tunable and switch-**

**able chirality and flat-surface beam steering** — •Xinghui Yin[1], Martin Schäferling[1], Ann-Katrin Michel[2], Andreas Tittl[1], Matthias Wuttig[2], Thomas Taubner[2], and Harald Giessen[1] — [1]4. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart — [2]1. Physikalisches Institut (IA), RWTH Aachen, Sommerfeldstr. 14, 52074 Aachen

The first metamaterials were fully static, i.e., their geometrical and therefore optical properties were predefined by their design. In order to gain greater control over the effective material behavior, it is desirable to introduce handles that allow for subsequent tailoring of certain material properties. In this work, we demonstrate a tunable and switchable mid-IR chiral metamaterial that utilizes the particularly transparent representative Ge3Sb2Te6 (GST-326) of the chalcogenide phase change material family. When this material is brought into proximity with a plasmonic nanoantenna, the difference in the dielectric environment leads to a large spectral shift (19%) of the plasmon resonance position. Hence, a suitable combination of this material with a chiral metamaterial leads to a shifting circular dichroism signal. Additionally, we demonstrate that precise design of a passive bias-type layer superimposed on the active metamaterial achieves the effect of enantiomer switching. Furthermore, we explore plasmonic beam steering using active plasmonic metasurfaces to emphasize the versatility of hybrid metamaterials comprising plasmonic elements and phase change materials.

O 90.3 Thu 15:30 MA 144

**Light-induced field enhancement in polyacenes** — •Luca Bursi[1,2], Arrigo Calzolari[2,3], Stefano Corni[2], and Elisa Molinari[1,2] — [1]Dipartimento di Fisica, Informatica e Matematica, Università di Modena e Reggio Emilia, I-41125 Modena, Italy — [2]Istituto Nanoscienze CNR-NANO-S3, I-41125 Modena, Italy — [3]Department of Physics, University of North Texas, Denton, TX 76203

High attention has been devoted recently to the optical, absorption and plasmonic properties of C-based nanostructures (i.e., graphene-derived), in view of their possible applications as sensors, amplifier antenna and light harvesting devices, alternative to standard metallic systems (e.g. Au, Ag). The way the excitation properties transform, scaling down from macro- to nano-systems, is far from being understood, and it is a field of great current interest.

Using (TD)DFT first-principles approaches, we studied the electric field enhancement in single and coupled polyacene molecules, upon illumination [1]. We demonstrate that optical transitions may generate oscillating dipolar response charge, giving rise to an induced electric field near the molecule, which thus acts as a plasmon-like nanoantenna. While the field amplification in the vicinity of single acenes is rather small and decreases when the size of the system is increased, it may be selectively enhanced in the case of acenes' assemblies. This paves the way for the design of more complex C-based architectures explicitly conceived to improve the amplification factor.

[1] L. Bursi et al., ACS Photonics, 1, (2014) 1049.

O 90.4 Thu 15:45 MA 144

**Tunable and switchable thin film Faraday rotation in magnetoplasmonic waveguides: experiments and coupled oscillator model** — •Dominik Floess[1], Thomas Weiss[1], Sergei Tikhodeev[2], and Harald Giessen[1] — [1]4th Physics Insitute and Research Centre SCOPE, University of Stuttgart, 70569 Stuttgart, Germany — [2]A. M. Prokhorov General Physical Institute, Russian Academy of Sciences, 119991 Moscow, Russia

A static magnetic field can alter the optical response of materials. For instance, an external magnetic field is capable of changing the rotation of polarization by a layer of magneto-optical material, which is termed Faraday effect in transmission geometry and polar Kerr effect in reflection geometry. Faraday rotators are of high practical interest because of their application in magnetic field sensing, optical modulation and, most importantly, as core elements in optical isolation devices. The highly demanded miniaturization of such devices is usually limited by insufficient rotation capabilities of available magneto-optical materials. We experimentally and theoretically demonstrate the enhancement of thin-film Faraday rotation in EuSe-Au nanostructures exhibiting waveguide-plasmon-polaritons. A rotation tuning range of 8.4 deg is achieved for magnetic fields of 5 T at 30 K. The waveguide material EuSe provides strong magnetooptical response and simple fabrication which is desirable for further studies in the emerging field of magnetoplasmonics. Using a classical harmonic oscillator model, we are able to obtain profound understanding of the magneto-optical response of the hybrid structures.

O 90.5 Thu 16:00 MA 144

**Correlation between near-field distribution and enhanced magneto-optical Kerr effect in a patterned magnetoplasmonic Ni sample** — •Markus Rollinger[1], Evangelos Papaioannou[1], Philip Thielen[1], Pascal Melchior[1], Björn Obry[1], Emil Melander[2], Erik Östman[2], Vassilios Kapaklis[2], Mirko Cinchetti[1], and Martin Aeschlimann[1] — [1]Physics Department and OPTIMAS, University of Kaiserslautern, Germany — [2]Department of Physics and Astronomy, Uppsala University, Sweden

The combination of magnetic and plasmonic nanostructures can be used to modify magneto-optical properties leading to an enhancement of the observed polar and transverse magneto-optic Kerr effect (MOKE) [Opt. Expr. 19,23867]. Thin metallic film with a periodic array of holes are a commonly used structure exhibiting extraordinary optical properties due to the presence of plasmonic excitations [Nature 391,667].

We investigate Si / Ti (2 nm) / Ni (100 nm) / Au (2 nm) samples that are patterned with a two-dimensional hexagonal array of holes (anti-dots) with a diameter of d = 275 nm and a pitch size of a = 470 nm. The magnetic Ni layer gives rise to a MOKE signal while the periodic nanopattern in principle supports surface propagating plasmons (SPP). We show the correlation between the enhanced MOKE signal and the electric near-field distribution, which is spatially detected by photoemission electron microscopy (PEEM) for different excitation wavelengths and polarization directions with respect to the anti-dot lattice geometry.

O 90.6 Thu 16:15 MA 144

**Plasmonic chirality and chiral sensing: effects and limitations** — •Maxim Nesterov, Xinghui Yin, Martin Schäferling, Thomas Weiss, and Harald Giessen — 4th Physics Insitute and Research Centre SCoPE, University of Stuttgart, 70550 Stuttgart, Germany

Objects which cannot be superimposed with their mirror image are called chiral. Many bio-molecules such as, e.g., the essential amino acids are chiral. One common method to probe their chiral nature is the interaction with circularly polarized light, which leads to a difference in the absorption depending on both the handedness of the molecule and that of the light. However, this so-called circular dichroism (CD) signal is small for most molecules, which renders such analysis rather challenging, especially when small volumes should be probed.

It has been suggested to use plasmonic structures to enhance the light-matter interaction of the chiral analyte. Following this approach, we present thorough numerical investigations of the electrodynamic interaction between chiral media and chiral plasmonic structures in planar as well as in three-dimensional configurations. We find that chiral plasmonic resonances can significantly enhance the chiral response of bio-molecule solutions. A detailed analysis of the CD enhancement mechanisms shows the dominating role of induced chirality.

O 90.7 Thu 16:30 MA 144

**Poly-peptide sensing with nanoantenna-assisted surface-enhanced infrared spectroscopy** — •Rostyslav Semenyshyn[1], Frank Neubrech[1], Felix Weiher[1], Christoph Stanglmair[2], Claudia Pacholski[2], and Harald Giessen[1] — [1]4th Physics Institute and Stuttgart Research Center SCoPE, University of Stuttgart — [2]Department of New Materials and Biosystems, Max Planck Institute for Intelligent Systems, University of Stuttgart

Surface-enhanced infrared absorption (SEIRA) which uses the enhanced electromagnetic near-fields of resonantly excited metal nanoantennas is a powerful technique to detect minute amounts of molecular substances based on their material-specific vibrations. We used mercaptoundecanoic acid (MUA) functionalized nanoantennas in order to selectively bind poly-l-lysine to gold surface and covered other nanoantennas with specially designed collagen peptides. A tailored flow cell was used to allow for the control of molecular adsorption on the nanostructures and in-situ SEIRA in aqueous solutions. For antennas with different lengths the plasmonic resonance coincides with the amide I and amide II bands of the poly-peptides. Depending on the ratio of the vibrational and plasmonic excitation we observe differently enhanced vibrational amide signals with Fano-type line shapes, confirming the plasmonic nature of the enhancement. In comparison to conventional infrared spectroscopy, such vibrational signals are enhanced by up to four orders of magnitude. This opens up the pathway towards studies of single layers of proteins and their folding behavior.

O 90.8 Thu 16:45 MA 144

**Resonant optical antennas for directional Raman studies of carbon nanotubes** — •Nicola Paradiso, Fatemeh Yaghobian, Christoph Lange, Tobias Korn, Christian Schüller, Rupert Huber, and Christoph Strunk — Institut für Experimentelle und Angewandte Physik, University of Regensburg

We use optical nano-antennas in order to manipulate light on the subwavelength scale. These nanoplasmonic excitations allows us to fully control both amplitude and polarization direction for the incident and scattered light in micro-Raman experiments. Our directional antennas are particularly promising when applied to carbon nanotubes (CNTs), owing to the stronlgy anisotropical optical behavior of CNTs. In particular nano-antennas enable the Raman characterization of individual CNTs that would be otherwise not optically detectable. Our experimental results are discussed together with numerical simulations which reproduce the observed amplification and rotation of the incident optical field.

O 90.9 Thu 17:00 MA 144

**Plasmonic copper nanodisks for monitoring electrochemical redox-reactions** — •Venla Manninen, Nikolai Strohfeldt, Florian Sterl, and Harald Giessen — 4th Physics Institute and Research Center SCoPE, University of Stuttgart, 70550 Stuttgart, Germany

Oxidation of copper under air-exposure has been studied well in colloidal films. As a noble metal, copper nanoparticles can produce strong localized surface plasmon resonances (LSPRs) when illuminated at the resonance frequency. Thus, a few reports have shown that the oxidation of copper nanoparticles can be monitored as changes in the spectral position and intensity of their LSPR.

Furthermore, electrochemical redox-reactions of copper in alkaline solutions have been studied in colloidal films. We therefore fabricated copper nanodisks with a very narrow homogeneous size distribution via colloidal hole-mask lithography on conductive substrates. The plasmonic behaviour of these structures was investigated via absorption and scattering spectroscopy in a bright field microscope. The changes in the LSPR of our copper nanodisks were monitored during their electrochemical oxidation and reduction reactions.

Since copper is widely used as catalyte in various chemical reactions, it is highly interesting to investigate the plasmonic response to (photo-)chemical reactions taking place on the surface of single particles, observable in dark-field microscopy. Potential applications of this principle include the plasmonic detection of electrochemically induced reactions on metal catalytes.

O 90.10 Thu 17:15 MA 144

**Bimetallic plasmonic nanosensors: DNA self-assembly and core-shell nanocrystals** — •Andreas Tittl[1], Na Li[2], Domenico Paone[1], Song Yue[3], Chen Song[2], Justus Back[4], Sabine Ludwigs[4], Baoquan Ding[2], Na Liu[3], and Harald Giessen[1] — [1]4th Physics Institute and Research Center SCOPE, University of Stuttgart, Germany — [2]National Center for Nanoscience and Technology, Beijing, China — [3]Max Planck Institute for Intelligent Systems, Stuttgart, Germany — [4]IPOC - Functional Polymers, University of Stuttgart, Germany

We present DNA-assembled bimetallic plasmonic nanostructures and demonstrate their application for the all-optical detection of hydrogen. Gold (Au) nanorods are functionalized with DNA strands, which serve both as linkers and seeding sites for the growth of palladium (Pd) nanocrystals and facilitate reliable positioning of Pd satellites around a Au nanorod at an ultrashort spacing in the nanometer range. Dark-field scattering spectra of single Au-DNA-Pd nanorods were recorded during controlled cycles of hydrogen gas exposure, and an unambiguous concentration-dependent optical response was observed. Our method enables, for the first time, the all-optical detection of hydrogen-induced phase-change processes in sub-5 nm Pd nanocrystals at the single-antenna level. By substituting the Pd satellites with other functional materials, our sensor platform can be extended to plasmonic sensing of a multitude of chemical and biological reagents, both in liquid and gaseous phases. Furthermore, we demonstrate core-shell Au-Pd nanocrystals with hydrogen-induced spectral shifts exceeding 100 nm.

O 90.11 Thu 17:30 MA 144

**Magnesium for UV plasmonics and chemical reaction sensing** — •Florian Sterl, Andreas Tittl, Nikolai Strohfeldt, Ramon Walter, and Harald Giessen — 4th Physics Institute and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany

Plasmonic structures with resonances in the visible and NIR region can be fabricated from various metals and have been investigated extensively. However, fabricating structures with resonances in the blue and UV region presents a much more challenging task. A promising candidate for UV plasmonics is magnesium, with predicted resonances below 350 nm at intensities comparable to those found for silver. For this reason, we fabricated magnesium nanoantennas via colloidal hole-mask etching as well as electron beam lithography and subsequent electron beam physical vapour deposition. The plasmonic behaviour of these structures was investigated via absorption and scattering spectroscopy. Since Mg is a highly reactive metal, it is highly interesting to investigate the plasmonic response to chemical reactions taking place on the particle surface. To do this experimentally, we continuously record the spectrum of Mg particles during exposure to controlled environments with varying atmospheric contaminants. In this way, we are able to monitor, over extended periods of time, the modification of Mg structures due to oxidation, carbonization, water absorption from humid air, and hydrogen uptake. Potential applications of this principle include the plasmonic detection of various atmospheric compounds.

O 90.12 Thu 17:45 MA 144

**Strip Gratings for Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS)** — •Tobias Mass[1], Tao Wang[1], Vu Hoa Nguyen[2], Uwe Schnakenberg[2], and Thomas Taubner[2,3] — [1]I. Institute of Physics (IA), RWTH Aachen University — [2]Institute of Materials and Electrical Engineering I, RWTH Aachen University — [3]Fraunhofer Institute for Laser Technology (ILT)

Metallic nanoantennas efficiently couple light into a region of subwavelength size. Antenna arrays designed for surface enhanced infrared absorption spectroscopy (SEIRA) enable the detection of molecular vibration with high sensitivity [1-3]. In a previous publication we demonstrated the spectral tuning of gold strip grating resonances by changing the period and demonstrated significant enhancement of a PMMA absorption band [4]. In this contribution, the spectral response as well as the local near field enhancement of the gratings are analysed via FTIR spectroscopy and FDTD simulations, respectively. Especially the dependence of local field enhancement on the strip width of the gratings as well as the influence of different incident angles is investigated.

[1] Adato et al. *PNAS* **2009** 106(46), 19227-19232
[2] K. Chen et al. *ACS Nano* **2012** 6, 7998-8006
[3] Neubrech et al. *Phys. Rev. Lett.* **2008** 101, 157403
[4] Wang et al. *Opt. Express* **2013** 21(7), 9005-9010

O 90.13 Thu 18:00 MA 144

**Fabrication of plasmonic nanoantennas by femtosecond direct laser writing lithography - effects of near field coupling on SEIRA enhancement** — •Frank Neubrech, Shahin Bagheri, Ksenia Weber, Timo Gissibl, and Harald Giessen — 4th Physics Insitute and Research Centre SCOPE, University of Stuttgart, Germany

We demonstrate the use of femtosecond two-photon direct laser writing lithography (2D printing) for fast and homogeneous large-area fabrication of plasmonic nanoantennas on a substrate by creating patterned polymer as an etch mask. Subsequent Argon-ion beam etching provides nanoantennas with feature sizes below the diffraction limit of the laser light, exhibiting tunable high quality plasmon resonances in the mid-infrared spectral range which are ideally suited for surface-enhanced infrared absorption (SEIRA). In the present work, we demonstrate the reliable and simple fabrication of a wide variety of antenna arrays and examine particularly the influence of plasmonic coupling between neighboring antennas on the SEIRA enhancement effect. More specifically, we measure the enhanced infrared vibrational bands of a 5 nm thick 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) layer evaporated on arrays with different longitudinal and transversal spacings between antennas. An optimum SEIRA enhancement per antenna of four orders of magnitude was found close to the collective plasmon excitation in the nanoantenna array. This ideal distance is giving higher signals than simply the highest antenna density.

O 90.14 Thu 18:15 MA 144

**Fast SEIRA Detection on Nanoantenna Arrays with Various Geometry on One Chip** — •Anton Hasenkampf, Niels Kröger, Arthur Schönhals, Wolfgang Petrich, and Annemarie Pucci — Universität of Heidelberg, Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, 69120 Heidelberg, Germany

The main tool for surface-enhanced infrared absorption (SEIRA) spectroscopy was the Fourier transform infrared (FTIR) spectrometer with a globar source. It allows spectroscopy of a sample over a broad spectral range, which in our case covers 1 $\mu$m to 20 $\mu$m. The disadvantage of this system is very low spectral power density of the globar. This can be partially compensated by long measurement times. In this work, we present a setup with a tunable quantum cascade laser as the light source in mid-infrared range. The $10^8$ times higher spectral power density as compared to a globar reduces measurement time drastically. The combination of the quantum cascade laser with a microbolometer array for infrared light enables to map an area $2.8 * 3.1mm^2$ with a spatial resolution of about 9 $\mu$m, a bandwidth from 1170 to $1300cm^{-1}$, and a spectral resolution of $2.5cm^{-1}$ within 5 minutes versus 16 hours using the conventional FTIR microscope with a comparable spatial and spectral resolution.

## O 91: Annual General Meeting of the Surface Science Division

Time: Thursday 19:00–19:30 Location: HE 101

**Report of the Chairman; Presentation of the Gerhard Ertl Young Investigator Award; Miscellaneous**

## O 92: Post-Deadline Session

Time: Thursday 19:30–20:30 Location: HE 101

**Contributed Post-Deadline Talks**

## O 93: Overview Talk (Wolf Widdra)

Time: Friday 9:30–10:15 Location: HE 101

**Invited Talk** O 93.1 Fri 9:30 HE 101
**Ternary oxides: New surfaces structures and surprising interface properties** — •Wolf Widdra — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Oxide heterostructures are a novel materials class with a variety of applications. In the easiest cases, the bulk properties define the thin film characteristics. However, oxide interfaces and surfaces can add interesting new concepts and properties. This will be shown here for barium titanate (BTO), a well-studied material in the class of ferroelectric perovskites. For BTO(001) single-crystal surfaces and well-ordered (001)-oriented thin films, the surface-specific ferroelectric properties will be discussed as determined by photoemission electron microscopy and in-situ piezo-force microscopy [1]. A dynamic coupling of the dipolar response with phonons leads to surface-specific phonon-polaritons dominating high-resolution electron energy loss spectra. The characteristic phonon frequencies can identify different oxide phases and different film strain for epitaxial films due to lattice mismatch for different substrates. However, the frustration between cubic BTO and a threefold substrate can also lead to fully new materials: On Pt(111), BTO forms a two-dimensional oxide quasicrystal that is characterized by a brilliant 12-fold diffraction pattern with atomic tiling pattern of triangular, quadratic and rhombic elements [2].

[1] A. Höfer et al., Phys. Rev. Lett. 108, 087602(2012).
[2] S. Förster et al., Nature 502, 215 (2013).

## O 94: Frontiers of Electronic Structure Theory: Many-body Effects on the Nano-scale

Time: Friday 9:30–12:15 Location: H 0105

**Invited Talk** O 94.1 Fri 9:30 H 0105
**Excitations and charge transfer phenomena in C based systems** — •Elisa Molinari — University of Modena and Reggio Emilia, Modena, Italy — CNR, Istituto Nanoscienze, Modena, Italy

Excitonic effects control excitations and optical spectra in graphene-based nanostructures and related polymers [1], as well as in interacting C-based molecular systems of relevance for photovoltaics [2]. I will show results from ab-initio many body perturbation theory and discuss their implications for spectroscopies and for a realistic description of ultrafast charge separation phenomena.

[1] R. Denk et al, Nat Commun 5, 4253 (2014); A. Batra et al, Chem Sci 5, 4419-4423 (2014); L. Massimi et al, J. Phys. Chem C, in press. [2] S. M. Falke et al, Science 344, 1001-1005 (2014).

**Invited Talk** O 94.2 Fri 10:00 H 0105
**Towards optimal correlation factors for many-electron perturbation theories** — •Andreas Grüneis — Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany — Universität Wien, Vienna, Austria

Many electron perturbation theories such as the coupled-cluster method form a hierarchy of increasingly accurate approximations to the electronic ground state wave function. This presentation will overview recent progress in applying coupled-cluster methods to solids and techniques to reduce their computational cost such as explicit correlation methods [1,2]. Furthermore applications to archetypal solid state systems as well as the uniform electron gas model system will be discussed [3].

[1] G. H. Booth, A. Grüneis, G. Kresse and A. Alavi, Nature 493, 365-370 (2013).
[2] A. Grüneis, J.J. Shepherd, A. Alavi, D.P. Tew, G.H. Booth, The Journal of chemical physics 139 (8), 084112 (2013).
[3] J.J. Shepherd, A. Grüneis, Physical Review Letters 110 (22), 226401 (2013).

**Invited Talk** O 94.3 Fri 10:30 H 0105
**Towards an ab-initio description of high temperature superconductivity** — •Garnet Chan — Department of Chemistry, Princeton University, United States NJ08544

I will describe our continued efforts in developing ab-initio many-body theory in the condensed phase with a view to a first principles description of a cuprate phase diagram.

**Coffee break**

**Invited Talk** O 94.4 Fri 11:15 H 0105
**Correlation effects in unconventional superconductors: from micro- to nano- and macroscales.** — •Roser Valenti — Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, 60438 Frankfurt am Main, Germany

The combination of ab initio density functional theory with dynamical mean field theory (DFT+DMFT) has been proven to be a powerful approach for describing correlation effects in solid state systems at the microscopic level. In this talk we will focus on recent progress on this method and its application to unconventional superconductors such as Fe-pnictides, organic charge-transfer salts as well as correlated Dirac metals [1,2,3]. Further, we shall discuss the manifestation of such effects at the nano- and macroscales.

[1] I. I. Mazin *et al.* Nature Communications 5, 4261 (2014)

[2] S. Backes *et al.* New J. Phys. 16, 083025 (2014)
[3] J. Ferber *et al.* Phys. Rev. B 89, 205106 (2014)

**Invited Talk** O 94.5 Fri 11:45 H 0105
**Stochastic density functional and GW theories scaling linearly with system size** — •Roi Baer[1], Daniel Neuhauser[2], and Eran Rabani[3] — [1]Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Israel. — [2]Department of Chemistry and Biochemistry, University of California, Los Angeles Los Angeles, CA 90095-1569 USA. — [3]Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720 USA.

Kohn-Sham density functional theory (KS-DFT) is formulated as a statistical theory in which the electron density is determined from an average of correlated stochastic densities in a trace formula. Method allows reliable estimates of the electronic band structure, forces on nuclei, density and moments etc. "Self-averaging" leads to sublinear scaling. An embedded fragment stochastic DFT greatly decreases statistical fluctuations. Based on stochastic DFT a GW method is developed scaling linearly with system size. We demonstrate the results on silicon nanocrystals and large water clusters. References: *Phys. Rev. Lett. 111, 106402 (2013). *Phys. Rev. Lett. 113, 076402 (2014). *J. Chem. Phys. 141, 041102 (2014).

## O 95: Metallic nanowires on the atomic scale (DS with O)

Time: Friday 9:30–13:15 Location: H 2032

**Invited Talk** O 95.1 Fri 9:30 H 2032
**From 2D to 1D: Honeycomb crystals and their nanoribbons** — •Friedhelm Bechstedt — Friedrich-Schiller-Universitaet Jena, Germany

Metal-induced quantum wires are usually prepared on Si and Ge surfaces. Novel two-dimensional (2D) sheet crystals silicene, germanene and stanene as well as their functionalized counterparts are prototypes to study such atomically-thin layer systems.

Their exotic properties are studied using modern electronic-structure methods and discussed in the light of available experiments:

(i) Despite partial $sp^3$-bonding Dirac cones appear in their band structure similar to the $sp^2$-bonded graphene.

(ii) The infrared absorbance is given by the Sommerfeld fine-structure constant.

(iii) Chemical functionalization opens significant fundamental gaps. Excitons occur with giant binding energies.

(iv) A quantum spin Hall phase is due to spin-orbit interaction.

According to recent predictions one-dimensional structures, i.e., nanoribbons, should conduct electricity with 100% efficiency at room temperature with zero resistance along their edges. The predictions are critically discussed. The influence of magnetic ordering of edge states and external electric fields are investigated.

O 95.2 Fri 10:00 H 2032
**Impurity-mediated early condensation of an atomic layer electronic crystal: oxygen-adsorbed In/Si(111)-(4x1)/(8x2)** — •Stefan Wippermann[1], Wolf Gero Schmidt[2], Deok Mahn Oh[3], and Han Woong Yeom[3] — [1]Max-Planck-Institut für Eisenforschung GmbH, D-40237 Düsseldorf, Germany — [2]Universität Paderborn, D-33098 Paderborn, Germany — [3]Pohang University of Science and Technology, Pohang 790-784, Korea

While impurities have been widely known to affect phase transitions, the atomistic mechanisms have rarely been elucidated. The self-assembled In/Si(111)-(4x1) nanowire array is an extremely popular model system for one-dimensional electronic systems and features a reversible temperature-induced phase transition into a charge density wave (CDW) ordered state, a representative electronic phase.

We present a joint experimental and *first principles* study, demonstrating oxygen impurity atoms to condense the In/Si(111) nanowire array locally into its CDW ordered ground state, even above the transition temperature. Interestingly, CDW ordering is not induced by single impurities, but instead by the cooperation of multiple impurities. The mechanism is explained as a coherent superposition of the local impurity-induced lattice strain, stressing the coupled electronic and lattice degrees of freedom for CDW ordered phases.

O 95.3 Fri 10:15 H 2032
**Transport in spatially confined anisotropic systems** — •Frederik Edler[1], Ilio Miccoli[1,2], Herbert Pfnür[1], and Christoph Tegenkamp[1] — [1]Institut für Festkörperphysik, Univ. Hannover, DE — [2]Dept. Innovation Engineering, Univ. Salento, IT

Atomic chain ensembles are 1D-prototype systems with intriguing electronic properties, e.g. Peierls driven metal-insulator transitions (MIT). While such inherent instabilities can be probed smartly by surface transport, details of the phase transitions depend crucially on atomic-sized imperfections. In order to correlate such imperfections (including finite size effects) with transport properties, a spatial constriction of the electron paths is mandatory, e.g by using appropriately designed templates.

The In/Si(111) system reveals a strong anisotropy and has been comprehensively studied of the last years. We used it here as a benchmark system to investigate systematically the effects of confinement as well as of different contact geometries which is finally important to deduce correctly the resistivity components from resistance measurements. While spatial constrictions were achieved using Si(111)-mesas structures, various 4-point probe geometries could be realized by means of a 4-tip STM/SEM system. The anisotropy of the In-$4\times1$ has been quantified by rotating the tips gradually in squared configuration. Indeed, the sensitivity was increased by one order of magnitude by performing the transport experiments on confined areas. Furthermore, first studies of the MIT tuned by adsorption of, e.g. oxygen, have been performed and will be discussed.

O 95.4 Fri 10:30 H 2032
**Ultrafast dynamics of (quasi-1D) Pb overlayers grown on flat and vicinal Si(111)** — •Abdul Samad Syed[1], Vesna Mikšić Trontl[1], Manuel Ligges[1], Mathias Sandhofer[1], Ishita Agarwal[1], Isabella Avigo[1], Daniel Lükermann[2], Christoph Tegenkamp[2], Herbert Pfnür[2], and Uwe Bovensiepen[1] — [1]Fakultät für Physik, Universität Duisburg-Essen — [2]Institut für Festkörperphysik, Leibniz Universität Hannover

Due to real space anisotropy of the vicinal Si(111) surfaces, hot electrons can be expected to exhibit different dynamics along and perpendicular to the steps [1] as compare to the Si(111) flat surface. We made a comparative study of Pb overlayer structures grown on vicinal Si (557) and flat Si (111) using femtosecond time- and angle-resolved two-photon photoemission. We mapped the unoccupied electronic band structure near Γ and find that both systems have two unoccupied states at $E-E_F$=3.3 and 3.5 eV. In pump-probe experiments combined with a position sensitive electron time of flight spectrometer we analyze the ultrafast momentum dependent electron dynamics along two in plane directions. On vicinal surfaces we observe a specific, momentum dependent population dynamics which are absent on the flat surface. This signature shows a delay in population build up of 5 fs as a function of angle with respect to the terrace direction. We assign this behavior to step-induced scattering. We gratefully acknowledge funding by the DFG through FOR1700.

[1] Roth et al., Phys. Rev. Lett. 88, 096802 (2002)

O 95.5 Fri 10:45 H 2032
**Observation of correlated spin-orbit order in a strongly anisotropic quantum wire system** — •Christian Brand[1], Monika Jäger[1], Herbert Pfnür[1], Gabriel Landolt[2,3], Hugo Dil[2,4], Stefan Muff[2,4], Tanmoy Das[5], and Christoph Tegenkamp[1] — [1]Institut für Festkörperphysik, Leibniz Universität Hannover, Germany — [2]Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland — [3]Physik-Institut, Universität Zürich, Switzerland — [4]Institute of Condensed Matter Physics, École Polytechnique Fédérale de Lausanne, Switzerland — [5]Theoretical Division, Los Alamos National Laboratory, USA

The surface of 1.31 ML Pb on Si(557) reveals a highly anisotropic wire ensemble structure becoming insulating in the direction across the wires when cooling below 78 K (2D/1D transition) as seen by surface transport. The delicate interplay between the superlattice structure, band filling, and extremely large Rashba type spin-orbit interaction results in a highly correlated entangled spin- and charge-state. The spin texture close to the Fermi surface is found to be alternating and equidistant, thus Fermi nesting occurs in between bands with the opposite helicity. Furthermore, the interwire coupling has been gradually changed by adsorption of excess Pb nucleating preferentially at the step edges. The analysis of spin-resolved momentum distribution curves shows that Fermi nesting is preserved up to 0.2 ML. Both the spin-dephasing seen in ARPES as well as the increase of the spin-orbit scattering rates from former magneto transport measurements is quantitatively explained in the framework of a spin-orbit density wave.

O 95.6 Fri 11:00 H 2032

**Tuning the Playground for Spin-Polarization in Au-Induced Atom Chains on High-Index Silicon Surfaces** — •Julian Aulbach[1], Joerg Schaefer[1], Steven C. Erwin[2], and Ralph Claessen[1] — [1]Physikalisches Institut and Röntgen Center for Complex Materials Systems (RCCM), Universität Würzburg, Germany — [2]Naval Research Laboratory, Washington DC, USA

Atomic wires on semiconductor substrates allow direct access to spectroscopic studies of the low-temperature ground state of quasi-one-dimensional systems, such as a charge density wave or a Tomonaga-Luttinger liquid. A particularly intriguing concept is the use of high-index silicon surfaces of the type Si(hhk), providing tunability with respect to terrace width and adatom coverage. As a specific representative, stabilization of the Si(553) surface by Au adsorption results in two different atomically defined chain types, one made of Au atoms and one of Si. The latter, situated at the step edges, forms a honeycomb nanoribbon. At low temperature these silicene-like ribbons develop a period tripling, previously attributed to a Peierls instability. Here we report evidence from scanning tunneling microscopy that rules out this interpretation [1]. On the contrary, our results are in excellent agreement with density functional calculations [2], which reveal an antiferromagnetic ordered state, where every third Si atom at the step edge hosts a single electron [1]. Additionally we will also address the consequences for this spin ordering by varying the high index substrate.

[1] J. Aulbach et al., Phys. Rev. Lett. 111, 137203 (2013).

[2] S. C. Erwin and F. J. Himpsel, Nature Commun. 1, 58 (2010).

O 95.7 Fri 11:15 H 2032

**Vibrational properties and optical anisotropy of lead nanowires on Si(557)** — •Eugen Speiser[1], Arne Baumann[1], Sandhya Chandola[1], Jochen Räthel[1], Daniel Lükermann[2], Christoph Tegekamp[2], and Norbert Esser[1] — [1]Leibniz-Institut für Analytische Wissenschaften - ISAS - e. V., Department Berlin, Schwarzschildstrasse 8, 12489 Berlin, Germany — [2]Institut für Festkörperphysik, Appelstraße 2, 30167 Hannover, Leibniz Universität Hannover, Germany

We use Raman spectroscopy and Reflectance Anisotropy Spectroscopy (RAS) to investigate the vibrational properties and anisotropic optical response of Pb nanowires on Si(557). This model system, which shows quasi-1D conductance below 78 K, consists of 1.31 ML of Pb on the Si(557) surface. The adsorption of Pb induces a refacetting of the surface into evenly stepped (223) facets, decorated by one Pb nanowire each. Above 78 K the 2D coupling between the individual wires increases and allows conductivity perpendicular to them. RAS measurements of the Si(557) surface before and after Pb deposition show that the adsorption of Pb clearly induces a reorganization of the surface. Both phases exhibit a strongly anisotropic optical conductance behavior and anisotropic optical transitions which can be associated with the Pb induced reformation of the surface. The Raman spectra show surface vibrational modes which are only present after Pb deposition. With theoretical calculations it is possible to elucidate the relation of the surface vibrational modes with atomic structure and propose structural models for the high and low temperature phases.

**15 min. break.**

O 95.8 Fri 11:45 H 2032

**Doping Induced 1D Plasmons in Ag Monolayer Stripes on Si(557)** — •Timo Lichtenstein, Ulrich Krieg, Christoph Tegenkamp, and Herbert Pfnür — Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany

We demonstrate here by testing the plasmonic properties for the system Ag/Si(557) that the interaction between adsorbate layers of transition metal atoms and strongly anisotropic surfaces can lead to various quasi-1D signatures, which, however, are not all necessarily metallic. Using low energy electron diffraction in combination with scanning tunneling microscopy and electron energy loss spectroscopy, we correlate the structure with the properties of low dimensional collective excitations, as measured with momentum and energy resolving electron loss spectroscopy. Semiconducting structures with double periodicity along the chains are formed for Ag coverages below 0.3 ML. At higher coverages, coupled with the onset of $\sqrt{3} \times \sqrt{3}$ order, metallic wires are formed. This is evident from the appearance of plasmonic losses, which show 1D dispersion only along the wires. This 1D property even persists up to 1 ML, where a densely packed array of metallic $\sqrt{3} \times \sqrt{3}$ stripes is formed. We show evidence that the metallic property is induced by an extrinsic doping process of excess Ag atoms localized at the step edges, which can be reversibly removed and added. With this system we were able to explicitly show that the 1D plasmon frequency depends on the electron density proportional to $\sqrt{n_e}$ also in the 1D case, and that the confinement of the electrons on the wires is also dependent on doping concentration.

O 95.9 Fri 12:00 H 2032

**Optical and electronic properties of quasi-1D gold nanowires on Si(553) surfaces** — •Sandhya Chandola[1], Eugen Speiser[1], Conor Hogan[2], Svetlana Suchkova[1], Jochen Räthel[1], Julian Plaickner[1], and Norbert Esser[1] — [1]Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Department Berlin, Schwarzschildstrasse 8, 12489 Berlin, Germany — [2]Institute for Structure of Matter, CNR-ISM, Via Fosso del Cavaliere, 00133 Rome, Italy

The structures of many 1D metallic nanowire systems have not yet been sufficiently clarified, such as gold nanowires on vicinal Si surfaces. Such structures are intrinsically anisotropic and can be investigated by Reflection anisotropy spectroscopy (RAS) which is a powerful optical technique for probing electronic states of surfaces. The optical response of the Si(553)-Au and hydrogenated Si(553)-Au surfaces are measured with RAS and compared with density functional theory simulations. Good agreement between experiment and theory is obtained. Local structural elements such as the Si honeycomb chains and the gold atomic wires, yield distinctive features in the optical spectra. By comparing the optical response of the freshly prepared and hydrogenated Si(553)-Au surfaces, the spectral features can be directly attributed to particular structural elements on the surface. This combination of experiment and theory is very useful in identifying specific structural sites on the surface, which generate distinctive features in the optical response. The surface will be used to attach molecules such as 3,4-toluenedithiol. The ordered array of the molecules could act as a template for further functionalization.

O 95.10 Fri 12:15 H 2032

**Vibrational properties of Au nanowires on Si(553) and Si(111) surfaces** — •Sergej Neufeld[1], Simone Sanna[1], Jochen Räthel[2], Norbert Esser[2], and Wolf-Gero Schmidt[1] — [1]Lehrstuhl für Theoretische Physik, Universität Paderborn — [2]Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Berlin

Metallic nanowires on semiconducting substrates such as silicon and germanium have been attracting considerable interest in the last decade. Besides various potential applications as non ohmic conductors, they are candidate systems for the demonstration of the basic concepts of one-dimensional physics such as electron correlation and Luttinger liquid behavior. In particular, the phase transitions observed on these systems have been controversially discussed and are still poorly understood. Self organizing gold chains at vicinal surfaces such as the Si(553) and Si(111) are of particular interest, as the use of stepped templates allows to vary the geometric parameters and, thus, tune the inter-chain coupling. While well-established microscopic structural models of Au nanowires on various Si surfaces based on density functional theory are available in the literature, few is known about their vibrational properties. In this work, the phonon eigenmodes and eigenfrequencies of the Au/Si(553) and Au/Si(111) wires are calculated from first-principles at the center of the Brillouin zone. Several surface localized phonon modes are found, whose phonon frequencies can be directly compared with the spectra obtained by Raman measurements. Raman scattering efficiences are calculated in order to facilitate the comparison between experiment and theory.

O 95.11 Fri 12:30 H 2032

**Plasmonic excitations in Au/Si(553) and Au/Si(775)** — •Timo Lichtenstein[1], Julian Aulbach[2], Jörg Schäfer[2], Christoph Tegenkamp[1], and Herbert Pfnür[1] — [1]Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany — [2]Physikalisches Institut and Röntgen Center for Complex Materials Systems (RCCM), Universität Würzburg, 97074 Würzburg, Germany

Si(553) and Si(775) surfaces are highly stabilized by Au adsorption resulting in chain reconstructions of Au and Si atoms. For low temperatures the chains develop a change in periodicity not because of a Peierl's transition but because of frozen spin-polarization. Therefore, they remain metallic at low temperature. Here we study the metallicity of these systems by investigating the plasmons of the spin-split bands.

The sample quality was controlled with SPA-LEED. The plasmon dispersion was then investigated via a combination of EELS and SPA-LEED setup providing both high energy and momentum resolution. Measurements were carried out at room temperature and at 77 K.

Similar to Au/Si(557) [1], the dispersion for Au/Si(553) and Au/Si(775) is also linear for $k_{||} > 0.07\,\text{Å}^{-1}$, a typical signature in 1D. Compared to Au/Si(557) the slope is decreased by a factor of about 2, reflecting the lower electron density of $1 \times 10^7\,\text{cm}^{-1}$. For lower $k_{||}$ the dispersion relations saturate at 200 meV (150 meV) for Au/Si(553) (Au/Si(775)), indicative of quantum well states perpendicular to the steps expected for electronically well separated wires [2].

[1] T. Nagao et al., Phys. Rev. Lett. 97(11), 116802 (2006).

[2] U. Krieg et al., J. Phys.: Condens. Matter 25(1), 14013 (2013)

O 95.12 Fri 12:45 H 2032

**Structural Fluctuations on Si(553)-Au** — •Ingo Barke[1], Stefan Polei[1], Paul C. Snijders[2], and Karl-Heinz Meiwes-Broer[1] — [1]University of Rostock, Institute of Physics, 18051 Rostock, Germany — [2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

The (1x3) reconstruction on Si(553)-Au can be excited to a (1x2) structure by charge injection from the tip of a scanning tunneling microscope [1,2]. Time-resolved measurements enable access to the system's dynamics revealing rapid fluctuations due to a competition between excitation and decay. In this contribution we focus on the time-dependent response to the specific charge injection site. Two distinct locations of high excitation efficiency are identified. This site specific behavior is also found in spatially resolved current-distance curves which are further employed for a quantitative analysis of the current-dependent structural transition of this system. The results are discussed in view of structural and electronic ground state properties of Si(553)-Au.

[1] S. Polei, P.C. Snijders, S.C. Erwin, F.J. Himpsel, K.-H. Meiwes-Broer, and I. Barke, Phys. Rev. Lett. 111, 156801 (2013).

[2] S. Polei, P.C. Snijders, K.-H. Meiwes-Broer, and I. Barke, Phys. Rev. B 89, 205420 (2014).

O 95.13 Fri 13:00 H 2032

**Tb silicide nanowires on Si(001) - a one-dimensional metal?** — •Stephan Appelfeller, Martin Franz, Christopher Prohl, Jan Grosse, Zeno Diemer, and Mario Dähne — Inst. f. Festkörperphysik, TU Berlin, Hardenbergstr. 36, 10623 Berlin

Rare earth metals are well known for their formation of metallic bulk silicides with low Schottky-barrier heigths to *n*-type Si. Using appropriate preparation conditions, some rare earth metals, e.g. Tb, are forming silicide nanowires on Si(001) by self-assembly, which have widths of only a few nanometers and lengths of several hundred nanometers. Here, the structural and electronical properties of Tb silicide nanowires are elucidated.

The structural information gained by scanning tunneling microscopy indicates that the Tb silicide nanowires consist of metallic hexagonal $TbSi_2$. Scanning tunneling spectroscopy confirms this finding by showing metallic behavior. Furthermore, angle resolved photoemission data obtained at the UE56/2 PGM1 beamline of BESSY clearly reveal a one-dimensional metallic band structure without dispersion perpendicular to the nanowire main axis. Thus, Tb silicide nanowires are promising for future investigations of unique phenomena of one-dimensional metals, such as the Peierls transition.

This work was supported by the DFG, FOR 1700, project E2. We kindly acknowledge the support of K. Horn and coworkers and of BESSY.

## O 96: Ultrafast Electron Dynamics at Surfaces and Interfaces

Time: Friday 10:30–12:45 Location: MA 004

**Invited Talk** O 96.1 Fri 10:30 MA 004

**Ultrafast electron dynamics at oxide surfaces: How metallic is a semiconductor?** — •Julia Stähler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dept. of Physical Chemistry, Faradayweg 4-6, 14195 Berlin, Germany

Light absorption in a semiconductor creates non-equilibrium conditions that relax by a multitude of pathways involving electron dynamics on femto- and picosecond timescales. These can be monitored in real time using time-resolved one- and two-photon photoelectron spectroscopy of the occupied and unoccupied electronic structure, respectively. On ZnO(10$\bar{1}$0), hydrogen adsorption causes the formation of a charge accumulation layer through downward surface band bending. Despite this metallicity, highly stable sub surface-bound excitons form within only 200 fs after above band gap photoexcitation. Strong excitation close to the Mott limit enhances the screening of the Coulomb interaction (CIA) and reduces the exciton formation probability [1]. On the other hand, in the case of the strongly correlated electron material $VO_2$, strong photoexcitation even leads to an *instantaneous collapse* of the band gap, followed by hot carrier relaxation within 200 fs. In conjunction with many body perturbation theory, these results show that the photoinduced semiconductor-to-metal transition is caused by photohole doping at the top of the $VO_2$ valence band: The significantly enhanced screening of the CIA through low-energy intraband transitions causes the drastic band gap renormalization [2].

[1] J.-C. Deinert et al., *Phys Rev Lett* **113**, 057602 (2014)

[2] D. Wegkamp, M. Herzog et al., *Phys Rev Lett* **113**, 216401(2014)

O 96.2 Fri 11:00 MA 004

**Electron dynamics across the charge-transfer gap of NiO ultrathin films** — •Konrad Gillmeister[1], Mario Kiel[1], and Wolf Widdra[1,2] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

NiO is known as a prototype system for a strongly correlated oxide. Despite of numerous scientific investigations of its electronic structure, studies of the electron dynamics of NiO are rare. This contribution deals with the unoccupied Ni 3*d* states at the upper edge of the charge-transfer gap. For the study, ultrathin well-ordered films from 1–20 monolayers (ML) thickness have been grown on Ag(001) via molecular beam epitaxy.

The unoccupied Ni 3*d* states have been investigated by time-resolved two-photon photoemission spectroscopy. While interface effects dominate the electronic structure for films up to 3 ML, films of 4 ML and beyond show bulk-like behavior. For these thicknesses we find the upper Hubbard band (UHB) at 2.5 eV above $E_F$. Electrons excited into the UHB decay on a timescale of less than 15 fs. The surprisingly short lifetimes are explained by correlation effects within the oxide film. Ultrafast decay via additional intra-gap states and strong electron-phonon coupling is also considerable.

O 96.3 Fri 11:15 MA 004

**Charge Transfer Dynamics at the Buried GaP/Si(001)-Interface Studied by Means of Time-Resolved SHG** — •Alexander Lerch, Kristina Brixius, Andreas Beyer, Kerstin Volz, Wolfgang Stolz, and Ulrich Höfer — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität,D-35032 Marburg

Epitaxially grown GaP on Si(001) is a technologically important and structurally well characterized model system for a polar/nonpolar semiconductor interface. We have employed time-resolved optical second-harmonic generation (SHG) to investigate the ultrafast carrier dynamics at the buried GaP/Si interface. The experiments were conducted using 800-nm 45-fs pump and probe pulses in a non-collinear geometry where the SHG response of bulk GaP is suppressed. The samples exhibit characteristic SHG transients on a 5-ps time-scale which are attributed to the build-up of an electric field via charge transfer across the interface. From the linear dependence of the transients on the pump fluence we exclude direct excitation of both GaP and Si bulk with direct band gaps of 2.8 eV and 3.4 eV, respectively. Instead we propose a direct excitation of electronic states at the interface by the 1.55-eV pump pulses which is consistent with a rise-time of the SHG signal faster than 30 fs. We also show, how different SHG components of the interface can be distinguished phase-sensitively by utilizing interference between SHG from GaP bulk and the transients, and discuss the influence of the lattice temperature on the dynamics via electron-phonon scattering.

O 96.4 Fri 11:30 MA 004

**One-step theory of pump-probe photoemission** — •Jürgen Braun[1], Roman Rausch[2], Michael Potthoff[2], Jan Minár[1], and Hubert Ebert[1] — [1]Dept. Chemie, LMU Universität München, Germany — [2]I. Institut für Theoretische Physik, Universität Hamburg, Germany

A theoretical frame for the description of pump-probe photoemission is presented. The approach is based on a general formulation using the Keldysh formalism for the lesser Green function to describe the real-time evolution of the electronic degrees of freedom in the initial state after a strong pump pulse that drives the system out of equilibrium. The final state is represented by a time-reversed low-energy electron diffraction (LEED) state. Our one-step description is related to Pendry's original formulation of the photoemission process as close as possible. The formalism allows for a quantitative calculation of the time-dependent photocurrent in particular for simple metals where a picture of effectively independent electrons is assumed as reliable. The theory is worked out for valence- and core-electron excitations [1]. As a first application, the theoretical description of two-photon photoemission for real systems within the KKR-approach is introduced [2].

1. J. Braun, R. Rausch, M. Potthoff, J. Minàr, H. Ebert, submitted to Phys. Rev. B (2014)
2. H. Ebert et al., The Munich SPR-KKR package, version 6.3, http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR (2012)

O 96.5 Fri 11:45 MA 004

**Attosecond delays in the photoemission from layered materials** — Sergej Neb[1], Fabian Siek[1], Matthias Hensen[1], Sebastian Fiechter[2], Hugo Dil[3], Norbert Müller[1], •Walter Pfeiffer[1], and Ulrich Heinzmann[1] — [1]Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany — [2]Helmholtz Zentrum Berlin, Institut für Solare Brennstoffe, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — [3]Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

The availability of single attosecond (as) XUV pulses allows investigating ultrafast electron dynamics on the as time scale by recording slight temporal shifts of the photoelectron streaking in a simultaneously present strong IR field. The physical origin of the observed small delays is not yet understood and controversial theoretical models coexist demonstrating our still limited understanding of the fundamentals of the photoemission process. We report delays for core level emissions from different layered materials with and without inversion symmetry. This provides a larger data base for testing the various theoretical models. In particular solids with defined layers of different chemical composition allow an investigation of the influence of propagation effects and of photoelectron wave phase shifts.

O 96.6 Fri 12:00 MA 004

**Ultrafast charge transfer across the 5P-pyridine/ZnO($10\bar{1}0$) interface** — •Jan-Christoph Deinert[1], Clemens Richter[1], Lea Bogner[1], Yves Garmshausen[2], Stefan Hecht[2], Martin Wolf[1], and Julia Stähler[1] — [1]Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — [2]Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

The functionality of hybrid inorganic organic systems (HIOS) is governed by the interfacial electronic coupling and the resulting charge transfer (CT) dynamics. To gain direct insight into these dynamics we use femtosecond time-resolved two-photon photoemission (2PPE) to investigate the hybrid system 5P-pyridine on ZnO($10\bar{1}0$). The molecules form an ordered layer on the mixed-terminated ZnO surface, accompanied by a strong reduction of the work function by up to 1.8 eV. We optically excite electrons from just below the Fermi level $E_\mathrm{F}$ at the ZnO surface with 2.5 eV photons, leading to transient formation of a CT state by population of the molecular LUMO (1.7 eV above $E_\mathrm{F}$). This CT state is used to observe the *pure* interfacial electron transfer from the LUMO to the ZnO conduction band, which occurs on an ultrafast timescale of 90 fs. This is in contrast to previous results on interfacial CT processes on ps timescales at ZnO interfaces where photoexcitation is used to create *excitons* in the organic film. [1] Our results show that the purely electronic coupling at the interface is significantly stronger in the absence of the photohole.

[1] K. R. Siefermann et al., *J. Phys. Chem. Lett.* **5**, 2753–2759 (2014)

O 96.7 Fri 12:15 MA 004

**Theoretical Study of Ultrafast Electron Transfer in Alkanethiolate Self-Assembled Monolayers at the Au(111) Surface** — •Veronika Prucker[1], Pedro B. Coto[1], Michel Bockstedte[1], Haobin Wang[2], and Michael Thoss[1] — [1]Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 7/B2, D-91058 Erlangen, Germany — [2]Department of Chemistry, University of Colorado, Denver, CO 80217, USA

The dynamics of ultrafast electron transfer (ET) processes in self-assembled monolayers consisting of nitrile substituted short-chain alkanethiolate molecules on gold substrates is investigated. Employing a model Hamiltonian, which is parametrized by first principles electronic structure calculations [1], and dynamical simulations, we analyze the basic mechanism underlying the ET process. The results show, in accordance with experiments [2,3], a dependence on the molecular chain length and on the symmetry of the donor states [4]. Additionally, we discuss the influence of partly occupied substrate states at the Fermi edge on the ET process.

[1] I. Kondov *et al.*, J. Phys. Chem. C 111, 11970 (2007).
[2] F. Blobner *et al.*, J. Phys. Chem. Lett. 3, 436 (2012).
[3] P. Kao *et al.*, J. Phys. Chem. C 114, 13766 (2010).
[4] V. Prucker *et al.*, J. Phys. Chem. C 117, 25334 (2013).

O 96.8 Fri 12:30 MA 004

**Dynamics of exciton formation and decay in SP6 films on ZnO(10-10)** — •Lea Bogner, Laura Foglia, Jan-Christoph Deinert, Clemens Richter, Martin Wolf, and Julia Stähler — Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Zinc oxide (ZnO) is a promising transparent electrode material for various optoelectronic applications. On the ZnO surface, the spirofluorene derivative SP6 forms smooth amorphous films from which, after resonant excitation, charge transfer to the ZnO conduction band has been observed [1]. We investigate the electronic properties and the excited states dynamics of 20 nm thick SP6 films adsorbed on ZnO(10-10) using time-resolved two-photon photoemission (2PPE). In this system, optical spectroscopy showed that resonant excitation of the SP6 molecules leads to the formation of an excitonic state which relaxes vibrationally (2-6 ps) and decays on a timescale of 200-300 ps [2]. Complementarily, time-resolved 2PPE provides access to absolute binding energies and fast electron dynamics on fs timescales, which we attribute to exciton formation. Photon energy and repetition rate-dependent measurements indicate a strong intermolecular coupling of the excited states leading to electron emission from a long-lived dark state (1 eV above $\mathrm{E}_F$) due to energy transfer rather than photoemission by the probe pulse. Possible energy transfer mechanisms such as intermolecular Coulombic decay or Förster resonance energy transfer will be discussed.

[1] S. Blumstengel et al., Phys. Rev. B 77, 085323, 2008
[2] L. Foglia et al., to be published

## O 97: Nanostructure at Surfaces: Structures and Properties

Time: Friday 10:30–12:45 Location: MA 005

O 97.1 Fri 10:30 MA 005

**Thin diamond-like carbon (DLC) coatings on bio plastic films of polyhydroxybutyrate (PHB)** — •Christian B. Fischer and Stefan Wehner — Department of Physics, University Koblenz-Landau, 56070 Koblenz, Germany

Bio generated and biodegradable polymers represent a promising alternative for conventional petroleum-based plastics. These bio plastics are ideal for packaging in food industry, agricultural usage or in the medical field. In many cases parent plastic material suits mechanical requirements but exhibits poor surface features, leading to bacterial adhesion, for instance. This can be avoided by appropriate surface modifications. One frequently used technique is the coating of parent material with thin films of diamond-like carbon (DLC) via PECVD. The surface morphologies of a 50 $\mu$m thick foil of polyhydroxybutyrate (PHB) coated with two different DLC-types of various thicknesses are examined by SEM and AFM. The r-type is sp3-enriched which results in a more robust layer, and the f-DLC is sp2-enriched, making it more flexible. Layers of r-type up to around 450 nm are intact, further deposition results in cracking and exfoliation of the DLC coating due to increasing internal stress. Furthermore, the effect of an improved understanding of hard DLC and soft PHB material is part of the present work.

O 97.2 Fri 10:45 MA 005

**novel structures and phenomena in ultrathin films** — •rajib batabyal and bhupendra nath dev — indian association for the cultivation of science, kolkata, india

Nanostructures and thin films on well-defined substrate surfaces, their stability and exploration of new physical phenomena are important aspects not only for the development of future nanoscale devices but also for the advancement of basic physics research.

Here we discuss two major aspects of Ag ultrathin films on Si(111)-7x7 surfaces. In the first section, we demonstrate a new phenomenon related to the electronic transport in 2-D to 3-D crossover. By STS measurement we show the dependence of the negative differential resistance (NDR) with film thickness for one-atomic layer to five-atomic layer thick films. The dependence of the onset voltage at which NDR sets in, is shown as a function of ultrathin film thickness. These results are explained via density functional theory (DFT) calculations. In the other section, we report on a novel mechanism in electric filed induced atomic migration and formation of one-atom thick fractal nanostructures. Application of a voltage pulse at an edge of a flat-top Ag island results in migration of Ag atoms from edge to the top of the island and aggregation to form a precisely one-atom thick fractal Ag layer. Diffusion limited aggregation (DLA) appears to be responsible for the formation of fractal nanostructures. We have also determined various fractal dimensions and corelated them to describe the morphology of fractal clusters.

O 97.3 Fri 11:00 MA 005

**Spin-resolved photoelectron spectroscopy of chiral nanostructures** — •Daniel Nürenberg[1], Andrew Mark[2], Matthias Kettner[1], Benjamin Göhler[1], Peer Fischer[2], and Helmut Zacharias[1] — [1]Westfälische Wilhelms-Universität, Münster, Germany — [2]Max-Plank-Institut für Intelligente Systeme, Stuttgart, Germany

Helical molecules on surfaces have been shown to affect the spin polarization of photoelectrons excited from the substrate [1]. Further investigation demands new materials, showing similar effects, which offer more degrees of freedom in designing helical potentials than are possible with molecules. Helical nanostructures are a candidate for this. They can be grown on wafer scale size by glancing angle vapor deposition (GLAD) on a turning silicon wafer seeded with Au nanodots. The nanohelices have lengths of around 100 nm, a pitch of approximately 50 nm and show a circular dichroism at visible wavelengths [2]. We present spin- and polarization-resolved photoelectron studies of such nanostructures made of noble metal and noble metal alloys.

[1] Göhler, B.; Hamelbeck, V.; Markus, T.Z.; Kettner, M.; Hanne, G. F.; Vager, Z.; Naaman, R. and Zacharias, Science, 331, 894-897(2011)

[2] Mark, A.G.; Gibbs, J.G.; Lee, T. and Fischer, P., Nat. Mater.,12, 802-807(2013)

O 97.4 Fri 11:15 MA 005

**Mechanical properties of surfaces at the nanoscale** — •Jörg Buchwald[1] and Stefan G. Mayr[1,2,3] — [1]Leibniz Institute of Surface Modification, Permoserstr. 15, 04318 Leipzig, Germany — [2]Faculty of Physics and Earth Sciences, University of Leipzig, Linnéstr. 5, 04103 Leipzig, Germany — [3]Translational Center for Regenerative Medicine (TRM)Leipzig, Philipp-Rosenthal-Str. 55, 04103 Leipzig, Germany

New experimental techniques like contact resonance atomic force microscopy (CR-AFM) allow for non-destructive testing mechanical properties with nanometer resolution. Mechanical properties of surfaces or nanostructures deviate from bulk material due to surface stresses as well as local relaxations. In experimental indentation based measurements discrimination between physical effects and artifacts - primarily due to variation of indenter contact area and extend of stress field - poses the largest challenge. To calculate the surface sensitivity of the indentation moduli, we performed a computational multiscale approach to study the phenomena on different scales. We utilized abinitio-DFT and molecular dynamics to simulate the mechanical properties, i. e. the surface elastic constants of Si and SrTiO3 ultra-thin films. These results were used to build up a finite-element layer model where the influence of surface stresses in indentation experiments is studied. Additionally, we propose an analytical model that describes the decrease in the moduli due to surface stresses as a function of the contact radius.

O 97.5 Fri 11:30 MA 005

**Efficient conformational sampling of complex adsorbates: Basin Hopping in curvilinear coordinates** — Konstantin Krautgasser[1], •Chiara Panosetti[1], Dennis Palagin[2], Karsten Reuter[1], and Reinhard Maurer[3] — [1]Technische Universität München, Germany — [2]University of Oxford, GB — [3]Yale University, USA

Continuous computational and methodological advances provide first-principles access to ever larger and more complex adsorbate molecules. The vastly increasing configurational spaces of such molecules nevertheless pose an enormous challenge. Local geometry optimizations of a few chemically motivated adsorption modes are inadequate to sample these spaces and need to be replaced by rigorous global optimization techniques. In those, a crucial role is played by the choice of coordinates representing geometries and trial moves. When aiming for sampling in chemically motivated subspaces the most popular, but physically blind choice of Cartesians is often inefficient. Rather than e.g. testing for adsorption modes of the intact adsorbate, Cartesian trial moves may quickly lead to dissociated structures. We address this by presenting a Basin Hopping (BH) scheme employing Delocalized Internal Coordinates (DICs) suitable for covalently bound systems. In the application to two rather diverse systems we indeed find that such DIC trial moves significantly reduce the sampling efficiency: Retinoic Acid on Au(111) and $Si_{16}H_{16}$ clusters in gas-phase and on Si(001).

O 97.6 Fri 11:45 MA 005

**Theoretical study of structure of solid electrolyte interphase** — •Sara Panahian Jand and Payam Kaghazchi — Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany

Solid electrolyte interphase (SEI) is a heterogeneous layer that is formed on the surface of electrodes (e.g. graphite) in Li-ion batteries during the first charging cycles. The SEI layer plays a key role in the safety, irreversible capacity loss, cycle life, and calendar lifetime of Li-ion batteries. Therefore, fundamental understanding of the structure of SEI layer is a prerequisite for developing advanced electrode materials. In this work, we study the structure and growing mechanism of LiF (a main component of a SEI layer) on graphene using density fiunctional theory (DFT) calculations and electrostatic models. DFT calculations show that, independent of being in contact or not with a graphene surface, crystalline-LiF nanoclusters with (100) facets grow in a three-dimensional mode. This result is in agreement with experimental observations [1]. We also find that the stability of LiF nanoclusters can be predicted by a simple electrostatic model [2]. This model can also be used to study other inorganic components of the SEI layer such as $Li_2O$ and $Li_2CO_3$ [3].

[1] S. Chattopadhyay et al., Chem. Mater., 24, 3038 (2012)
[2] S. Panahian Jand and P. Kaghazchi, J. Phys.: Condens. Matter, 26, 262001 (2014)
[3] S. Panahian Jand and P. Kaghazchi, in preparation

O 97.7 Fri 12:00 MA 005

**Linear and Nonlinear excitations of the Plasmonic Nanogap** — Anke Horneber[1], Jan Rogalski[1], Jiyong Wang[1], Anne-Laure Baudrion[2], Pierre-Michel Adam[2], Kai Braun[1], Alfred J. Meixner[1], and •Dai Zhang[1] — [1]Institute of Physical and Theoretical Chemistry, University of Tübingen — [2]Institut Charles Delaunay, Technical University of Troyes

Plasmonic nanogaps of changing geometries, gaps, and material compositions provide tunable model systems to investigate how plasmonic resonance effect participates in the optical or/and electrical excitation of metallic nanoantennas. As the precise control of nanogap distance of less than 10 nm is still a major challenge, pursuing and investigating narrow gaps even down to the quantum regime attract great research interests. We studied the composition-influences on SHG and 2PPL of homo- and hetero- nanodimers [1-3]. By combining scanning probe microscope with a confocal optical microscope, we investigated the linear/nonlinear PL and electroluminescence from narrow plasmonic nanogaps of down to 1 nm. Furthermore, using a fs-scanning near-field optical microscope, we imaged optical gold nanotriangles with less than 30 nm nonlinear resolution based on the different plasmonic nanogaps formed between the scanning tip and different locations at the nanotriangle [4]. References [1] Horneber A., Baudrion A.-L., Zhang, D. et al., PCCP, 2013, 15, 8031. [2] Reichenbach, P., Zhang D., Eng L. et al., Opt. Exp., 2014, 13,15484. [3] Kern A., Zhang D., Meixner A. J. et al., Chem. Soc. Rev., 2014, 43, 965. [4] Horneber A., Braun K., Zhang, D. et al., PCCP, 2014, in revision.

O 97.8 Fri 12:15 MA 005

**A suitable tip for TERS? Find it out with photo-induced force microscopy (PiFM).** — •Michael Ludemann[1], Anne-D. Müller[1], Falk Müller[1], Derek Nowak[2], and Sung I. Park[2] — [1]Anfatec Instruments AG, Melanchthonstr. 28, D-08606 Oelsnitz (V) — [2]Molecular Vista Inc., 6840 Via Del Oro, CA-95199 San Jose (USA)

Tip-enhanced Raman spectroscopy (TERS) pushes down the spatial resolution of the measurement below the tip diameter and thus way beyond the diffraction limit of focused light.

Obtaining reproducible TERS results is difficult even with a proper setup. One key factor is a suitable tip.

PiFM offers the opportunity to characterize the tip at any time of the experiment. Here, the intensity of a linear polarized laser beam is modulated at a frequency in the range of the cantilever resonance. Illuminating the tip with the focused light induces a detectable dipole-dipole force even on non-metallic samples (e.g. glass). If the tip provides an appropriate near-field enhancement, a double lobe structure associated with the axial focal field created by a high-NA inverted objective lens is obtained while scanning the tip in the fixed laser focus. This way, PiFM can be utilized as a tool to validate the optical properties of the tip and the laser alignment.

The talk explains the physical background of PiFM and presents experimental results on differently prepared TERS tips.

O 97.9 Fri 12:30 MA 005

**Background suppression in near-field optical microscopy by generalized lockin detection** — •Susanne Hartmann[1], Falk Müller[1], Yi Huang[2], Abeer Al Mohtar[2], Aurélien Bruyant[2], Michael Ludemann[1], and Anne-D. Müller[1] — [1]Anfatec Instruments AG, Melanchthonstr. 28, 08606 Oelsnitz, V. — [2]Laboratoire de Nanotechnologie et Instrumentation Optique, CNRS (FRE 2671), Universite de Technologie de Troyes, 10010 TROYES cedex, France

A detection scheme is presented that allows to simultaneously measure signal amplitude and phase in near-field optical microscopy (SNOM) with the aid of interferometry. The method is based on a phase modulation of the reference arm inside the interferometer followed by a demodulation of the measured signal with specifically chosen trigonometric functions. The output can be understood as generalized lockin technique (GLIA). The GLIA successfully extracts the signal while suppressing the background. In case of an additional tip oscillation at $f_r$, a further background subtraction is achieved by a preceding amplitude demodulation of the GLIA's input signal at $f_r$. The calculations are verified by measurements on gold discs. The method is a crucial step for background suppression with applications not only in near-field optical microscopy.

## O 98: Graphene: Intercalation

Time: Friday 10:30–12:45 Location: MA 041

O 98.1 Fri 10:30 MA 041

**Keeping Argon under a Graphene Lid - Argon intercalation between Graphene and Ni(111)** — •Florian Späth, Karin Gotterbarm, Christoph Gleichweit, Max Amende, Udo Bauer, Oliver Höfert, Hans-Peter Steinrück, and Christian Papp — Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Graphene with its thickness of only one single atomic layer can be considered as the thinnest membrane or gas barrier. We present a spectroscopic investigation of related properties under well-defined ultra-high vacuum conditions in a surface science experiment: We implant argon into a Ni(111) crystal by sputtering prior to the growth of graphene. Subsequently, when growing graphene on Ni(111), argon diffuses out of the bulk and is caught underneath graphene. We investigate the system with high-resolution in-situ X-ray photoelectron spectroscopy. From the growth behavior of these intercalated argon bubbles during graphene preparation and from temperature programmed XP spectra we are able to deduce a model of the intercalation system (G/Ar/Ni) and estimate the pressure for argon under graphene. Furthermore, we find an increased thermal stability of graphene due to a decoupling of graphene from the Ni(111) substrate. This work was supported by SFB 953 "Synthetic Carbon Allotropes"

O 98.2 Fri 10:45 MA 041

**Intercalation of Gadolinium underneath graphene on SiC(0001)** — •Stefan Link, Stiven Forti, Alexander Stöhr, and Ulrich Starke — Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Investigating the properties of graphene in a highly doped state, such that the Fermi level reaches a saddle point of it's electronic bands is an on-going field. Superconductivity could be one potential effect in this regime. Functionalization with highly reactive species such as alkali and/or earth alkali atoms has been pursued for strong doping effects. However, such systems are prone to fast degradation by environmental influences which needs to be circumvented for any kind of application.

Here, we present a method of doping graphene to such levels and simultaneously making the system stable to temperatures higher than 1000°C as well as to air exposure. This was achieved by the intercalation of Gadolinium atoms underneath the so-called buffer layer on SiC(0001), i.e., the carbon rich $(6\sqrt{3}\times6\sqrt{3})\text{R}30^\circ$ reconstruction of this surface. Significant hybridization effects of the graphene $\pi$-bands with the adatom states are observed in the ARPES data. In addition, evidence for strong electron-phonon scattering is visible. Spectroscopic weight appears in the measurements completely interlinking two Dirac cones through the $\overline{\text{M}}$-point, thus indicating the presence of an electronic topological transition (ETT).

O 98.3 Fri 11:00 MA 041

**Nitrogen Intercalation and Nitrogen-based Molecular Doping of Epitaxial Graphene on 6H-SiC(0001)** — •Nuala Mai Caffrey, Rickard Armiento, Rositsa Yakimova, and Igor Abrikosov — Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden

The thermal decomposition of silicon carbide (SiC) is one of the most promising methods to produce high-quality epitaxial graphene on a wafer scale. Sufficient control has even been achieved to selectively grow monolayer, bilayer and few-layer graphene, rendering it a indispensable technique for the manufacture of graphene-based electronics. A disadvantage of this method is that the first carbon layer is covalently bonded to the surface Si atoms, with only subsequent layers displaying the characteristic electronic features of graphene. Several methods have been proposed to electronically decouple this buffer layer, as well as to reduce the high substrate-induced doping, including intercalation and chemical doping. Understanding such chemical functionalisations is a fundamental first step towards engineering the properties of graphene on SiC. It is clear that the graphene layer, as well as the interface between it and the SiC surface, can be significantly influenced by the growth environment. We consider how common environmental dopants can affect the electronic structure of mono- and bilayer graphene grown on a 6H-SiC(0001) substrate. We show, using first-principles calculations, how nitrogen intercalation and nitrogen-based molecular dopants, such as NO2 and NH3, present a promising route to tailor the properties of this system.

O 98.4 Fri 11:15 MA 041

**Investigation of the electrostatic changes induced by metal islands on graphene/SiC(0001) using field-emission resonance spectroscopy with STM** — •Anastasia Sokolova[1], Alexander Stöhr[2], Stiven Forti[2], Ulrich Starke[1,2], and M.Alexander Schneider[1] — [1]Solid State Physics, Friedrich-Alexander-University Erlangen-Nuremberg, Germany — [2]Max Planck Institute for Solid State Research, Stuttgart, Germany

Using the Scanning Tunneling Microscope in field-emission resonance spectroscopy mode (FRS-STM) it is possible to map changes of the electrostatic potential in front of the graphene surface at the nanoscale [1]. We investigated the properties of 10 nm-sized metal islands on top of epitaxial graphene on SiC(0001) as well as islands intercalated underneath the graphene layer.

For cobalt and palladium islands on top of graphene we observe a spatially localized shift of the 1st field-emission resonance to higher energy strictly occurring at the topographical step. This is consistent with larger work functions of the metals with respect to that of graphene. In the case of intercalated cobalt islands FRS-STM shows a rise of the 1st field-emission resonance energy of only 150 meV and a spatially delocalized transition. Considering the properties of graphene flakes on an extended Co(0001) surface [2] this suggests negative charge of the capping graphene layer and a positive charge on the cobalt island.

[1] S. Bose *et al* 2010 *New Journal of Physics* **12** 023028

[2] D. Eom *et al* 2009 *Nano Letters* **9** 2844-2848

O 98.5 Fri 11:30 MA 041

**Oxygen orders differently under graphene: new superstructures on Ir(111)** — •Antonio J. Martínez-Galera[1], Felix Huttmann[1], Ulrike Schröder[1], Fabian Craes[1], Carsten Busse[1], Vasile Caciuc[2], Nicolae Atodiresei[2], Stefan Blügel[2], and Thomas Michely[1] — [1]Universität zu Köln, II. Physikalisches Institut, Germany — [2]Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich, Germany

Modifying the properties of graphene (Gr) by intercalation of atoms or molecules at the Gr/substrate interface has been proven to be a straightforward and versatile concept. However, the effect of the Gr layer on the ordering of the intercalated material remains much less studied. We present evidence that indeed the Gr cover has a substantial influence on the resulting superstructures of oxygen chemisorbed on Ir(111). As a function of exposure to molecular oxygen and temperature the oxygen adsorbate superstructures on Ir(111) are identified by scanning tunneling microscopy (STM). They are compared to the ones formed by intercalation in between graphene and Ir(111). For bare Ir(111) we observe O-(2x2) and O-(2x1) structures, thereby clarifying a long-standing debate on the existence of these structures and the role of defects for their stability. For Gr/O/Ir(111) with increasing exposure O-(2x2), O-(R3xR3)-R30, O-(2x1) and O-(2R3x2R3)-R30 superstructures referred to Ir(111) are observed. The (R3xR3)-R30 and (2R3x2R3)-R30 structures were not yet reported and they exist only under Gr. Based on density functional theory (DFT) we discuss the origin of the new adsorbate superstructures under graphene.

O 98.6 Fri 11:45 MA 041

**Oxidation of sulfuric acid intercalated graphite: the role of sulfuric acid and permanganate ions** — •Steffen Seiler and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Wet-chemical exfoliation of graphite via Hummers' method [1,2] is a promising route for large-scale graphene production. This solution-based process is carried out in concentrated sulfuric acid and involves several steps: first, graphite is converted into a sulfuric acid–graphite intercalation compound (GIC), then the GIC is transformed into oxidized graphite, graphene oxide (GO) layers are separated in solution by hydrolysis reactions, and finally the GO layers are reduced to graphene [3].

To obtain atomistic insights into the mechanisms of the chemical reactions in liquid sulfuric acid within the confined space between graphene layers we performed Car-Parrinello molecular dynamics (CP-MD) simulations. By changing the coverage of hydroxy and epoxy groups their stabilizing effect on the attack of sulfuric acid (solvent) and $KMnO_4$ (oxidizing agent) molecules was investigated. Furthermore, different carbon atoms on the partly oxidized graphene sheets were attacked to elucidate the most reactive sites.

[1] W. S. Hummers, *J. Am. Chem. Soc.* **80**, 1339 (1958).

[2] D. C. Marcano et al., *ACS Nano* **4**, 4806 (2010).

[3] A. M. Dimiev and J. M. Tour, *ACS Nano* **8**, 3060 (2014).

O 98.7 Fri 12:00 MA 041

**Approaching ideal graphene: The structure of hydrogen- and germanium-intercalated graphene on 6H-SiC(0001)** — •F.C. Bocquet[1,2], J. Sforzini[1,2], T. Denig[3], A. Stöhr[3], T.-L. Lee[4], S. Subach[1,2], U. Starke[3], and F.S. Tautz[1,2] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany — [3]Max Planck Institute for Solid State Research, Heisenbergstraße, 70569 Stuttgart, Germany — [4]Diamond Light Source Ltd, Didcot, OX11ODE, Oxfordshire, United Kingdom

We investigated Quasi-Free-standing Monolayer Graphene epitaxially grown on 6H-SiC(0001) obtained by decoupling the buffer-layer from the Si-terminated surface by hydrogen intercalation (1) or by intercalating one or two monolayers of germanium (2). All three samples show a clear linear dispersion around the K-point, confirming their Quasi-Free-standing character. We used the X-ray standing wave (XSW) technique, combining dynamical diffraction and X-ray photoelectron spectroscopy, to detect the coherent distribution of the chemically different species (Si, C and Ge) at the interface. Based on the lattice parameter of bulk SiC, we accurately determine the vertical height differences between each chemical species. Comparing the overlaps of van der Waals radii between the graphene layer and the topmost intercalating atoms, we conclude on the degree of decoupling of the graphene layers.

O 98.8 Fri 12:15 MA 041

**Bismuth Intercalated Graphene on Iridium Probed by STM and ARPES** — •Jonas Warmuth[1], Matteo Michardi[2], Torben Hänke[1], Marco Bianchi[2], Jens Wiebe[1], Roland Wiesendanger[1], Philip Hofmann[2], and Alexander Khajetoorians[3] — [1]Department of Applied Physics, University of Hamburg, Germany — [2]Department of Physics and Astronomy, University of Aarhus, Denmark — [3]Institute for Materials and Molecules, Radboud University, Nijmegen, Netherlands

We report on the investigation of bismuth intercalated graphene grown on Ir(111) by means of STM and ARPES. The STM measurements reveal a complex periodic structure upon Bi intercalation which we attribute to the formation of a $\sqrt{3}$ Bi surface alloy. We characterize the changes to the band structure using ARPES, including the doping effects and the modification to the Dirac dispersion.

O 98.9 Fri 12:30 MA 041

**Enhancement of many-body effects observed on epitaxial monolayer graphene/Au/SiC(0001)** — •Stiven Forti[1], Stefan Link[1], Alexander Stöhr[1], Yuran Niu[2], Alexei Zakharov[2], and Ulrich Starke[1] — [1]Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart,Germany — [2]Max-Lab, Lund University, Box 118, Lund, S-22100, Sweden

The interaction of graphene with gold atoms has gained high relevance for a series of reasons, from electrical contacts to plasmonics. Here we present the realization of n-type epitaxial monolayer graphene on SiC(0001) via the intercalation of a layer of Au atoms at the heterointerface between the graphene and the SiC substrate. Such a phase exhibits enhanced many-body effects, as observed by ARPES. The plasmaron band is observed and its dispersion is well discernible from the hole-Dirac cone. The effective dielectric constant extracted from the ARPES data is about five times smaller than what is reported in the literature so far. The effectiveness of the intercalation is corroborated by $\mu$LEED measurements, which clearly indicate a suppression of the diffraction spots on the $(6\sqrt{3}\times 6\sqrt{3})$R30° grid, except for spots arising from multiple diffraction. CLPES measurements indicate the presence of a single gold component, namely assigned to gold silicides. The quality of the epitaxial graphene grown on SiC(0001) in Ar atmosphere, together with the aforementioned preparation, makes possible to observe bands of unprecedent sharpness for this system. Dispersive states arising from the 5d orbitals of the interfacial gold are observed as well, as predicted by theory.

## O 99: Semiconductor Substrates: Structure, Epitaxy and Growth

Time: Friday 10:30–12:45 Location: MA 042

O 99.1 Fri 10:30 MA 042

**Surface and step conductivities at Si(111)-(7×7) surfaces investigated by multi-tip STM** — •Sven Just[1], Marcus Blab[1], Stefan Korte[1], Vasily Cherepanov[1], Helmut Soltner[2], and Bert Voigtländer[1] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, and JARA-Fundamentals of Future Information Technology — [2]Central Institute for Engineering, Electronics and Analytics (ZEA-1), Forschungszentrum Jülich

Four point measurements using a multi-tip scanning tunneling microscope (STM) are carried out to determine surface and step conductivities at Si(111)-(7×7) reconstructed surfaces. In a first step, distance dependent linear four point measurements are used to disentangle the 2D surface conductivity from bulk and space charge layer contributions. In order to further disentangle the surface conductivity of the step free surface from the contribution due to steps, the four probe method is applied in a quadratic configuration as function of the rotation angle. In total this combined approach allows to uniquely determine the surface conductivity, as well as the step conductivity at silicon surfaces.

O 99.2 Fri 10:45 MA 042

**Atomic structure of terbium-induced nanostructures on Si(111)** — •Martin Franz, Jan Grosse, Robert Kohlhaas, and Mario Dähne — Technische Universität Berlin, Institut für Festkörperphysik, Berlin

Rare earth metals are known to form a variety of very interesting self-assembled nanostructures on silicon surfaces. Examples are the metallic nanowires that form on the Si(001) and the Si(557) surface. On the planar Si(111) surface, the formation of two- and three-dimensional layers is observed.

Here, we report on a detailed scanning tunneling microscopy study on the growth and the atomic structure of terbium-induced nanostructures growing on the Si(111)7×7 surface for different terbium coverage. At extremely low coverage, the $7 \times 7$ substrate acts as a template for the growth of terbium-induced magic clusters. In the submonolayer regime, a $2\sqrt{3} \times 2\sqrt{3}$ superstructure, a chain-like $5 \times 2$ superstructure, and elongated islands with a $2 \times 1$ reconstruction on top are found. The $5 \times 2$ phase consists of alternating silicon Seiwatz and honeycomb chains with terbium rows in between. The observed different configurations can be explained by registry shifts between neighboring terbium rows or defects within one row. At higher coverage, the two-dimensional $TbSi_2$ monolayer forming a $1 \times 1$ reconstruction and the three-dimensional $Tb_3Si_5$ multilayer forming a $\sqrt{3} \times \sqrt{3}$ reconstruction are found.

This work was supported by the DFG through FOR 1282 project D.

O 99.3 Fri 11:00 MA 042

**Tailoring Si(100) substrate surfaces for GaP growth by Ga predeposition** — •Michael Häberle, Benjamin Borkenhagen, Gerhard Lilienkamp, and Winfried Daum — Clausthal University of Technology, Institute of Energy Research and Physical Technologies, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany

For GaP-on-Si(100) heteroepitaxy, currently considered as a model system for monolithic integration of III-V semiconductors on Si(100), the surface steps of Si(100) have a major impact on the quality of the GaP film. Monoatomic steps cause antiphase domains in GaP with detrimental electrical properties. A viable route is to grow the III-V epilayer on single-domain Si(100) with biatomic steps, but preferably not at the expense of reduced terrace widths introduced by miscut substrates [1]. We have performed in situ investigations of the influence of Ga deposition on the surface terrace dynamics of Si(100) at elevated substrate temperatures by low-energy electron microscopy (LEEM). Starting from nearly equally distributed $T_A$- and $T_B$-terraces of a two-domain Si(100) surface, submonolayer deposition of Ga resulted in a transformation into a surface with prevailing $T_A$-terraces. By increasing deposition rate or decreasing temperature, we induced restructuring of Si(100) into a surface dominated by $T_B$-terraces as reported by Hara et al. [2]. The occurrence and mutual transformations of surface structures with different terrace and step structures in a narrow range of temperatures and Ga deposition rates are discussed.

[1] K. Volz et al., J. Cryst. Growth 315, 37 (2011)
[2] S. Hara et al., J. Appl. Phys. 98, 083513 (2005)

O 99.4 Fri 11:15 MA 042

**Calculated formation energies of charged defects at surfaces from the repeated-slab approach** — •Christoph Freysoldt and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

Defects play an important role for the electrical, optical, and chemical properties of semiconductor surfaces under realistic conditions. In theory, the relevant structures, i.e., surfaces and point defects, are often simulated in the supercell approach. Yet, supercell calculations suffer from artificial interactions between the repeated images that are absent in the physical situation of interest. This is particularly problematic for formally charged defects because of the slow $1/r$ decay of the Coulomb interaction. In this contribution, we suggest a correction for the effect from an analysis of the underlying electrostatics. Screening is taken into account right from the beginning to account for potentially complex screening mechanisms. Yet, the universal long-range behavior limits the complexity to a finite range, allowing for simplified screening models in the end. By using a formulation based on charges and screened potentials, direct contact is made to electronic-structure calculations. The approach will be demonstrated for a model defect at the H-terminated Si(111) surface. The analysis reveals that the electric behavior of defects at surfaces depends on *two* macroscopic parameters (e.g. potential and field far from the surface), rather than *one* as for bulk point defects. Different choices of boundary conditions in charged surface calculations and extrapolation to arbitrary surface charges will be discussed.

O 99.5 Fri 11:30 MA 042

**Nanoscale Structure of Si/SiO$_2$/Organics Interfaces** — •Hans-Georg Steinrück[1], Andreas Schiener[1], Torben Schindler[1], Johannes Will[1], Andreas Magerl[1], Oleg Konovalov[2], Giovanni Li Destri[2], Oliver H. Seeck[3], Markus Mezger[4], Julia Haddad[5], Moshe Deutsch[5], Antonio Checco[6], and Benjamin M. Ocko[6] — [1]FAU, Germany — [2]ESRF, France — [3]DESY, Germany — [4]MPI Mainz, Germany — [5]Bar-Ilan University, Israel — [6]BNL, USA

Single-crystal silicon is by far the most widely used substrate for the deposition of organic thin films. It's surface is invariably terminated by a few nanometer-thick amorphous native $SiO_2$ layer. The structure of the transition layer between the silicon and it's oxide is neither well characterized nor well understood at present.

Using high-resolution x-ray reflectivity measurements of increasingly more complex interfaces involving silicon (001) substrates, we reveal the existence of a low-density, few-angstrom-thick, transition layer at the Si/$SiO_2$ interface [1]. The importance of accounting for this layer in modeling silicon/liquid interfaces and silicon-supported monolayers is demonstrated by comparing fits of reflectivity curves by models including this layer and the widely used Tidswell model [2], which excludes this layer. The 6-8 missing electrons per silicon unit cell area found here support previous theoretical models and simulations of the Si/$SiO_2$ interface [3].

[1] H.-G. Steinrück *et al.*, ACS Nano (2014), DOI: 10.1021/nn5056223.
[2] I. M. Tidswell *et al.*, Phys. Rev. B **41**, 1111 (1990).
[3] Y. Tu and J. Tersoff, Phys. Rev. Lett. **84**, 4393 (2000).

O 99.6 Fri 11:45 MA 042

**Comparative study of Co and Ni germanides growth on Ge(001) substrates** — •Tomasz Grzela[1], Wojciech Koczorowski[2], Giovanni Capellini[1,3], Ryszard Czajka[2], Neil

Curson[4,5], and Thomas Schroeder[1,6] — [1]IHP, Im Technologiepark 25, Frankfurt (Oder), 15236, Germany — [2]Institute of Physics, PUT, Piotrowo 3, Poznan, Poland — [3]Dipartimento di Scienze, Università degli Studi Roma Tre, Roma, Italy — [4]London Centre for Nanotechnology, UCL, London, UK — [5]Department of Electronic and Electrical Engineering, UCL, London, UK — [6]BTU Cottbus, Konrad-Zuse Str. 1, 03046 Cottbus

Extending the performance of existing Si microelectronics beyond the limits faced by either miniaturization (”More Moore”) or available functions (”More than Moore”) requires the integration of new materials. Germanium, due to its superior physical properties with respect to Si in terms of optoelectronics and its CMOS processing compatibility, is one of the most promising materials to further develop the existing Si platform. However, there are challenges to the formation of low resistance metallic contacts to Ge. Different metal/Ge systems present promising electrical properties, but given wide-spread use in Si CMOS technologies in form of their respective silicides-, cobalt- and nickel- germanides are of special importance. In this contribution we focus our attention on the systematic and comparative growth studies of Co- and Ni- germanides on Ge(001) substrates, by means of STM technique. In addition, other measurement technique like TEM-EDX, XPS and LEED were applied to corroborate these STM results.

O 99.7 Fri 12:00 MA 042

**Investigation of the surface termination of BiTeI by combined STM/AFM** — •Julian Berwanger, Florian Pielmeier, and Franz J. Giessibl — Institut für Experimentelle und Angewandte Physik der Universität Regensburg, 93053 Regensburg, Deutschland

Cleaved BiTeI surfaces consist of domains which are either terminated by Te or I [1-3]. The size of these domains depends on the bulk crystallinity of the sample and ranges from 100 $\mu$m [1] to 100 nm [3]. The samples investigated here by a combination of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) also consist of domains with smaller size. We find a similar surface structure as reported in Ref. 3 at 4.5K with plain STM in our room and low temperature STM/AFM experiments. Two different step heights are observed by STM in Ref. 3 and our experiments: 0.7 nm and 0.2 nm. The larger step height corresponds to the height of a -Bi-Te-I-stack. The smaller step height was also suggested to be a structural step caused by a stacking fault [3]. In contrast, the atomically resolved STM/AFM data of the smaller "step" suggests that this is indeed an atomically flat layer. The observed step height in STM is a purely electronic effect due to the different density of states at the Fermi-level of Te- and I-terminated surfaces. [1] Crepaldi et al. Phys. Rev. Letters 109, 096803 (2012) [2] Landolt et al. Phys. Rev. Letters 109, 116403 (2012) [3] Butler et al. Nat. Com. 5, 4066 (2014)

O 99.8 Fri 12:15 MA 042

**Morphology of ultra-thin ZnO on Ag(111)** — •Bjoern Bieniek[1], Patrick Rinke[1,2], Takashi Kumagai[1], Shamil Shaikhutdinov[1], Bo Hong Liu[1], and Matthias Scheffler[1] — [1]Fritz Haber Institut der MPG, Berlin, Germany — [2]Aalto University, Helsinki, Finland

In the context of catalysis and hybrid inorganic/organic systems, metal supported ultra-thin ZnO can be used as model systems. However, the atomic morphology of these films is not well understood [1,2,3]. To investigate the thickness and termination of ZnO adsorbed on Ag we combine experimental techniques with all-electron density-functional theory calculations performed with the FHI-aims code and the PBE functional. PBE *ab initio* thermodynamics calculations predict H terminated $2\times1$-H structures to be most stable for all film thickness and $H_2$ pressures from low to ultra-high vacuum. However, a comparison of relative apparent height differences in calculated and measured scanning tunnelling microscopy (STM) images gives the best agreement for H- and OH-free two layer ZnO films. Further evidence for H- and OH-free unreconstructed ZnO films comes from the absence of OH peaks in infra-red spectroscopy and the comparison of measured and simulated field effect resonances (FER). We attribute this discrepancy to the *ab initio* thermodynamics prediction to kinetic effects such as energy barriers for the dissociation of $H_2$ and $H_2O$. [1] C. Tusche *et al.* PRL **99**, 026102 (2007) [2] Y. Martynova *et al.*, J. Cat., **301**, 227-223 (2013) [3] G. Weirum *et al.* J. Phys. Chem. C, 114 (2010)

O 99.9 Fri 12:30 MA 042

**Adding 3D to conventional SEM or FIB surface imaging information - In situ Surface Sensing and Nanoprofilometry for Focused Electron and Ion Beam Induced Processes Verification** — •Frank Nouvertne[1], Axel Rudzinski[1], Torsten Michael[1], Marc Levermann[1], and Eva Maynicke[2,3] — [1]Raith GmbH, Konrad-Adenauer-Allee 8, Dortmund, 44263, Germany — [2]RWTH Aachen, 2. Phys. Inst., Otto-Blumenthal-Str. 28, 52074 Aachen, Germany — [3]Klocke Nanotechnik GmbH, Pascalstr.17, 52076 Aachen, Germany

Recently, the bandwidth of nanofabrication applications for dedicated nanopatterning tools using Electron Beam Lithography (EBL) or FIB has significantly broadened. Some few latest generation professional and multi-technique electron and ion beam nanolithography tools even facilitate additional resistless, focused electron or ion beam induced in situ processes such as material deposition or gas enhanced etching. The number of variable parameters for such complex processes is nearly ”infinite”, so that an efficient in situ characterization of e.g. material deposition, milling or etching rates becomes crucial for most effective understanding and subsequent optimization of such processes.

We have implemented a nanomanipulator with nanoprofilometric capabilities, which allows efficient in situ characterization of nanostructures in 3D by collecting topographic sample surface information via line scans with approx. 10nm height resolution.

First results of direct in situ growth rate determination of focused electron beam induced material deposition (FEBID) will be presented.

## O 100: Metal Substrates: Adsorption and Reactivity

Time: Friday 10:30–13:00 Location: MA 043

O 100.1 Fri 10:30 MA 043

**Following “hot” adatoms wherever they go: QM/Me with multiple embedding regions** — •Vanessa Jane Bukas[1], Jörg Meyer[2], and Karsten Reuter[1] — [1]Technische Universität München, Germany — [2]Universiteit Leiden, The Netherlands

Exothermic surface chemical reactions may easily release several electron volts of energy. This challenges first-principles based dynamical simulations to account for adequate energy dissipation channels. Focusing on phononic dissipation we recently presented a novel embedding scheme for metallic substrates (QM/Me [1]), in which energy dissipation out of a quantum-mechanically described reaction zone occurs into a computationally undemanding, yet reliably described extended bath. In the application to oxygen dissociation over Pd(100) this predicted translationally “hot” dissociation fragments as a consequence of nonimmediate energy transfer to the metal surface. Here, we advance this approach to include the concurrent treatment of multiple reaction zones centered around individual fragments and dynamically following their motion. This suppresses unphysical interactions between reaction partners through periodic images, allows to use smaller suppercells, and most importantly enables the application to chemical reactions for which the lateral direction of “hot” translational motion is not clear *a priori*. We demonstrate this new functionality by comparing oxygen dissociation at Pd(111) to the previously studied Pd(100). [1] J. Meyer and K. Reuter, Angew. Chem. Int. Ed., **53**, 4721 (2014).

O 100.2 Fri 10:45 MA 043

**Oxygen dissociation and recombination on Au/Ag(110) thin film alloys** — •Martin Schmid[1], Joshua E. Klobas[2], and Cynthia M. Friend[2] — [1]Fachbereich Chemie, Philipps Universität Marburg — [2]Dpt. of Chemistry and Chemical Biology, Harvard University, Cambridge MA, USA

In order to gain insight into the fundamental processes on complex bimetallic catalysts, such as nanoporous gold or bimetallic AuAg nanoparticles, $O_2$ dissociation and recombination on Au/Ag(110) thin film alloys of various compositions were studied with Temperature-Programmed Desorption (TPD). An increasing gold content of the thin film alloys is associated with a linear decrease of the maximum oxygen uptake of the surfaces; the oxygen uptake is completely quenched at gold concentrations higher than 50%. A closer analysis of the TPD signals shows that there is no transfer of oxygen adatoms between Au and Ag sites and that the oxygen chemistry is, in general, dominated by the Ag sites on the alloy surfaces. Apart from passivating the surface against oxygen uptake, gold also leads to a reduction of the recombination temperature of oxygen adatoms by 20 K. These results indicate that there are at least two neighboring Ag atoms required to dissociate oxygen and demonstrate that gold efficiently lowers the amount of adsorbed oxygen and facilitates recombination and release of the remaining oxygen adatoms. The results provide a lower limit for the size of active groups of Ag atoms and show that the bond strength between surface and oxygen adatoms is influenced by the local Au:Ag stoichiometry.

O 100.3 Fri 11:00 MA 043

**Interaction of CO with bimetallic $\mathbf{Pt_xAg_{1\text{-}x}}$/Pt(111) surface alloys** — •Konstantin M. Schüttler, Thomas Diemant, Joachim Bansmann, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

From recent studies, it is known that supported PtAg nanoparticles show enhanced (electro-) catalytic properties compared to pure Pt nanoparticles. In order to understand their chemical properties and to correlate them with their atomic structure, structurally well-defined $Pt_xAg_{1\text{-}x}$/Pt(111) surface alloys, whose structure had been characterized by STM in our institute, were chosen as model system. The interaction of CO as probe molecule with these surface alloys was investigated by temperature-programmed desorption (TPD) and infrared spectroscopy (IRRAS) under UHV conditions.

TPD measurements show a modification of the chemical properties of both components in the surface alloy. For CO adsorbed on Pt sites, the trailing edge first shifts to higher temperature with increasing Ag content, indicating a stabilization of adsorbed CO. At higher Ag content in the surface alloy, an additional desorption feature appears at higher temperature, which is attributed to CO adsorption on smaller Pt ensembles surrounded by Ag atoms. Additionally, a small desorption feature appeared at very low temperature for all surface alloys after CO saturation. This desorption feature is attributed to CO adsorption on Ag defect sites.

O 100.4 Fri 11:15 MA 043

**IRRAS Investigation of Carbon Monoxide Adsorption on Pristine and Roughened Au(111)** — •Jan Pischel and Annemarie Pucci — Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, D-69120 Heidelberg

The behavior of gold nanoparticles which are used, e.g., in surface enhanced spectroscopies [1] or heterogeneous catalysis [2], often critically depends on the properties of their surface.

While scanning tunneling microscopy as a well-suited method to explore the morphology of gold surfaces has already abundantly been applied [e.g. 3], we use infrared reflection absorption spectroscopy (IRRAS) in combination with CO adsorbed at cryogenic temperatures to probe the chemical properties of available sites at the surface. In this context, we present the first IRRAS investigation of CO adsorption on single crystalline Au(111) under ultra-high vacuum conditions. The interaction between CO and the flat surface is shown to differ significantly from that between CO and other types of gold surfaces known from literature. To make the connection, we introduced surface roughness in a well-defined manner by cold-depositing submonolayer amounts of gold onto the surface at 30K. Adsorption of CO on these rough surfaces is shown to result in the IR-response known from literature. A gradual transition between these two limiting cases can be realized by successively annealing the rough substrates.

[1] Neubrech, F. and A. Pucci, *IEEE J. Select. Topics Quant. Electronics* 19(3):4600809, 2013. [2] Haruta, M., *Gold Bulletin* 37(1–2):27, 2004. [3] Rai, A. et al., *Surf. Sci.* 625:97, 2014.

O 100.5 Fri 11:30 MA 043

**Following PtAg/Pt(111) surface alloy formation by CO adsorption** — •Thomas Diemant, Konstantin M. Schüttler, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The influence of the structure of a bimetallic surface on the chemical and catalytic properties is of high interest to further the understanding of the working principles of bimetallic catalysts. In this context, the growth of Ag films on a Pt(111) substrate at room temperature, the formation of PtAg/Pt(111) surface alloys by annealing to higher temperature (up to 900 K) and the consequences of surface alloy formation on the CO adsorption properties were studied by a combination of XPS, TPD and IR spectroscopy (IRRAS) measurements using CO as probe molecule in the two latter methods. Previous STM studies by Röder et al.[1] and in our institute had revealed a change of the atom distribution from extended Ag overlayer islands on the Pt(111) substrate directly after deposition at RT to disperse PtAg surface alloys.

The modification of the electronic properties of the components in the bimetallic surface layer upon alloy formation, which starts at 600 K, is resolved in XPS by a shift of the Ag(3d) peak to lower binding energy. The CO adsorption also starts to change drastically after heating to this temperature. New features in the CO TPD spectra (extra peak at higher desorption temperature) and in the IRRAS (2025 cm$^{-1}$) occur, which we attribute to the formation of isolated Pt sites surrounded by Ag atoms.

[1] Röder et al., Phys. Rev. Lett. 71 (1993) 2086.

O 100.6 Fri 11:45 MA 043

**An ab initio study on the oxidation of Mg-Zn alloys and the $\mathbf{MgZn_2}$ intermetallic compound** — •Su-Ting Cheng, Mira Todorova, and Jörg Neugebauer — Max-Panck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

A first step towards protecting iron from corrosion is galvanization, i.e. coating the iron surface with Zn. Recent experimental investigations have revealed [1], that addition of Mg can significantly improve the corrosion properties of Zn: the loss of weight during electrolysis of the intermetallic compound $MgZn_2$ was reduced by 1/3 compared to results for pure Zn [2]. This seems astonishing in view of the high affinity of Mg to oxidise, which we relate to the appearance of attractive interactions arising between electronegative adsorbates on the Mg(0001) surface [3]. Using density functional theory calculations we investigate clean and oxygen covered Mg-Zn and $MgZn_2$ surfaces and find the formation of a rather compact surface oxide. We will discuss our results in the context of corrosion protection.

[1] R. Hausbrand, M. Stratmann, and M. Rohwerder, Corrosion Science 51 2107 (2009)

[2] E. Diler, S. Rioual, B. Lescop, D. Thierry, and B. Rouvellou, Corrosion Science 65 178 (2012).

[3] S.-T. Cheng, M. Todorova, C. Freysoldt, and J. Neugebauer, Phys. Rev. Lett., 113, 136102 (2014).

O 100.7 Fri 12:00 MA 043

**Correlation between adsorption and strain: a first-principles study of the H/Ir(111) system** — •Anja Michl and Stefan Müller — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

The interaction of hydrogen with Iridium surfaces is relevant for a wide range of catalytic reactions. Straining the catalysts surface has an impact on adsorption energies and energy barriers and thus can be used to tune the catalytic activity.

We use density functional theory (DFT) to study the energetics of hydrogen adsorption on Ir(111). Vibrational frequencies are determined to account for zero-point energy corrections. The most favorable adsorption configurations are identified by using the DFT data to construct a cluster-expansion Hamiltonian, which enables an exhaustive scan of the configuration space. We find that top site adsorption is preferred over the whole coverage range from 0 to 1 ML. At low coverage the distance between adsorbed hydrogen atoms is maximized, while at higher coverage ground states exhibit hydrogen covered stripes of varying width. However, the ordering tendencies of the system are not very pronounced, with energy differences less than 30 meV per 1×1 surface site. Biaxial strain in the surface plane is applied to energetically favorable configurations in order to reveal strain-induced changes in the energetic hierarchy and to determine the coupling strength between adsorption energies and strain.

O 100.8 Fri 12:15 MA 043

**Metallocene adsorption and customization on copper** — •Nicolas Bachellier[1], Maider Ormaza[1], Paula Abufager[2], Roberto Robles[2], Martin Vérot[3], Tangui Le Bahers[3], Marie-Laure Bocquet[3], Nicolas Lorente[2], and Laurent Limot[1] — [1]IPCMS, Université de Strasbourg, UMR CNRS 7504, 67034 Strasbourg, France — [2]ICN2, Campus UAB, 08193 Bellaterra, Spain — [3]ENS Lyon, Université Claude Bernard, CNRS, 69007 Lyon, France

Organometallic molecules offer promising perspectives for improving spintronic devices. Metallocenes wires, in particular ferrocene wires (FeCp2, Cp=C5H5), have been predicted to produce currents with a spin polarization close to 100%. The design and conception of such wires is however hampered by the little and often contradictory knowledge we have concerning the molecule-substrate and molecule-molecule interaction of ferrocene.

By means of low-temperature STM and DFT calculations, we show how associatively adsorbed ferrocene self-assembles on copper surfaces adopting a configuration that is independent of the surface orientation. The stability of the two-dimensional structure is ensured by a combination of vertical and horizontal-lying molecules relative to the surface. We also show that a subsequent exposure of the molecular layer to single magnetic cobalt atoms leads to the formation of upstanding Co-FeCp2 molecules that exhibit the Kondo effect. Through a tip-assisted manipulation, we show that the newly formed molecule consists of ferrocene adsorbed on top of cobalt.

O 100.9 Fri 12:30 MA 043

**The adsorption and recognition of carborane thiols molecules on the Au(111) surface** — •Jan Berger[1], Martin Švec[1], Pingo Mutombo[1], Tomáš Baše[2], Wojciech Kamiński[3], and Pavel Jelínek[1] — [1]Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-16200, Prague, Czech Republic — [2]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Husinec-Rez, c.p. 1001, Czech Republic — [3]Institute of Experimental Physics, University of Wrocław, plac Maksa Borna 9, 50-204 Wrocław, Poland

We present simultaneous qPlus AFM/STM measurements of carborane molecules functionalized by thiol groups (1,2-(HS)2-1,2-C2B10H10) deposited on Au (111) surface. The morphology of different adsorption configurations of molecules on Au (111), depending on surface coverage, was characterized. At low coverage, carboranes adopt a mobile triangle configuration with one molecule up, two molecules down.

Using df(z)/I(z) local spectroscopy we revealed, that two different molecule configuration show distinct transport and mechanical properties. Thus we attribute this observation to different binding mechanism to the substrate. Molecules tend to create multi-domain islands at higher coverage. The STM/AFM experimental findings are complemented - and supported - by state-of-the-art DFT calculations.

O 100.10 Fri 12:45 MA 043

**Carbene-based self-assembly of diamondoids on metal surfaces** — •Bibek Adhikari[1], Sheng Meng[2], and Maria Fyta[1] — [1]Institute for Computational Physics, Stuttgart, Germany — [2]Institute of Physics, Chinese Academy of Sciences, Beijing, China

N-hetero-cyclic carbenes (NHC)s are emerging as the alternative class of molecules to thiol based self-assembled monolayers (SAMs). A gold-sulfur bond is weaker compared to the carbon-gold, which makes the carbene-based self-assembled monolayers much more stable in harsh environmental conditions. The NHCs bind easily to metal surfaces. By attaching diamondoids to the opposite end of these NHCs, we prepare very stable self-assembled monolayers of diamondoids on metal substrates such as gold and silver. Diamondoids are diamond-like cage structures with hydrogen terminations and have excellent electron-emission properties. These have potential applications as field-emission display devices. In this work, we perform quantum mechanical simulations under the frame work of density functional theory (DFT) to reveal the electronic properties of the carbene-based diamondoid SAMs. We focus on the binding possibility, stability and the adsorption sites of these newly formed monolayers on Au/Ag surfaces. We next turn to the investigation of their optical and emission properties in view of their nanotechnological applications.

## O 101: Scanning Probe Techniques: AFM

Time: Friday 10:30–12:45 Location: MA 144

O 101.1 Fri 10:30 MA 144

**Probing higher force gradients with Atomic Force Microscopy on the graphene surface** — •Daniel Meuer, Thomas Hofmann, Alfred John Weymouth, Andrea Donarini, and Franz Josef Giessibl — Universität Regensburg, D-93053 Regensburg

Graphene is a very important material for applications in the future, because of its outstanding material properties. The atomic structure of graphite, graphene and carbo-nanostructures were investigated by Scanning Tunneling Microscopy [1] and with Atomic Force Microscopy [2] in several studies.

In this contribution we analyze the higher harmonics of the cantilever oscillation. The signal of the nth harmonic of the cantilever deflection connects to the nth force gradient [3]. Our hypothesis is that the strong signal is a signature of the two top carbon layers that abruptly rehybridize from sp2 to sp3 by forming and breaking a covalent bond between the graphene layer and the buffer layer beneath.

[1] G. Binnig, et al., Europhysics Lett. (EPL) 1, S. 31-36 (1986); S.-I. Park et al., App. Phys. Lett. 48, S. 112 (1986); D. Tománek et al., Phys. Rev. B 35, S. 7790-7793 (1987);

[2] H. Hölscher, et al., Phys. Rev. B 62, S. 6967-6970 (2000); S. Hembacher et al., Proc. of the Nat. Academy of Sciences 100, S. 12539-42 (2003);

[3] U. Dürig, N. J. Phys. 2, 5.1-5.12 (2000); S. Hembacher, et al., Science 305, 380 (2004)

O 101.2 Fri 10:45 MA 144

**Information in multifrequency AFM data** — •Daniel Platz[1,2], Daniel Forchheimer[2], Erik A. Tholén[3], John E. Sader[4], and David B. Haviland[2] — [1]Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, D-01187 Dresden, Germany — [2]KTH Royal Institute of Technology, Albanova University Center, SE-114 19 Stockholm, Sweden — [3]Intermodulation Products AB, Vasavägen 29, SE - 169 58 Solna, Sweden — [4]The University of Melbourne, Victoria 3010, Australia

In contrast to conventional amplitude or frequency-modulated AFM, multifrequency AFM is characterized by tip motion that contains more than one single oscillation frequency. The additional frequency components might be generated by a nonlinear tip-surface force, a multifrequency drive scheme, or both. Each frequency component is usually considered as an individual channel carrying information about the tip-surface interaction. However, it is generally not understood exactly which information about the tip-surface force is encoded in each of the individual frequency components. We present a clear definition of ”information” in the context of multifrequency AFM, and we introduce a general method, called numerical kernel estimate (NKE), for the analysis of multifrequency AFM spectra. We demonstrate the capabilities of NKE by applying it to the analysis of Intermodulation AFM. This analysis reveals the fundamental limitations of force measurement from spectral data. Moreover, we use NKE also for the design of new multifrequency drive schemes that are optimal for the extraction of a maximum amount of information about the tip-surface force.

O 101.3 Fri 11:00 MA 144

**High Resolution at High Viscosity - Dynamic Force Microscopy at Low Q-Factors** — •Stefan Weber[1,2], Jason Kilpatrick[2], Timothy Brosnan[2], Victor Bergmann[1], Suzanne Jarvis[2], and Brian Rodriguez[2] — [1]Physics of Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany — [2]Conway Institute of Biomedical and Biomolecular Research, University College Dublin, Dublin, Ireland

Atomic force microscopy (AFM) is often used in non-aqueous liquid environments for in situ investigations of processes including chemical reactions, lubrication and molecular ordering. These environments often exhibit a much higher damping, lowering the quality factor (Q) of the cantilever resonance. It is generally expected that AFM operation in such environments will not yield atomic scale resolution due to increased noise resulting in a reduced signal-to-noise ratio (SNR).

Recently, we have demonstrated that true atomic resolution can be obtained in a highly viscous environment. In particular, we imaged the atomic structure of highly ordered pyrolytic graphite (HOPG) and mica surfaces with SNR values comparable to ultra-high vacuum systems (Weber, S.A.L., et al., Nanotech., 2014. 25(17): p. 175701). We also investigated the influence of the Q-factor of a cantilever on the thermal noise of the relevant AFM signals, namely amplitude, phase and frequency shift. This new understanding of the noise contributions to the imaging process opens up a new route to high resolution AFM studies in a wide range of viscous fluids.

O 101.4 Fri 11:15 MA 144

**A sophisticated Feedback Control algorithm for High-Speed AFM** — •Anne-D. Mueller and Falk Mueller — Anfatec Instruments AG, Melanchthonstr. 28, 08606 Oelsnitz.

The need to track surface features in Scanning Probe Applications (SPM) while increasing the scan speed leads to the complication, that the feedback parameters (e.g. Ki and Kp) entered by the user become more difficult to determine. As a result, the surface is not tracked with optimum performance.

This contribution utilizes a control theory approach to determine the microscope's closed loop transfer function in Z. An algorithm to automatically determine the optimum parameter set is presented that considers a scan speed driven bandwidth. As a result, Ki and Kp become system specific, while the strength of the tracking representing the sample roughness is left as the only free user entry. This completely new approach not only simplifies the control of an AFM; it automatically leads to an optimum noise level. Surprisingly, the feature tracking bandwidth can be tuned higher than the system's bandwidth.

With the help of a simulation circuit for contact and dynamic mode AFM operation, the frequency dependence of the feature tracking on the entry parameters is simulated and studied. Finally, the method is applied to real feedback systems demonstrating unexpected performance.

O 101.5 Fri 11:30 MA 144

**Capillary force acting on a particle correlated with the shape of the meniscus** — •Frank Schellenberger, Periklis Papadopoulos, Stefan Weber, Michael Kappl, Doris Vollmer, and Hans-Jürgen Butt — Max Planck Institute for Polymer Research, Mainz, Germany

Capillary bridges play a important role for the stability of colloidal systems. The forces of these bridges strongly correlates with their shape. It is possible to measure capillary forces with an Atomic Force Microscope (AFM), but it is impossible with such a device to image the shape of the capillary bridge at the same time.

Analytical and numerical calculations exist that correlates the force of the capillary bridges with the shape of the liquid . However experimentally capillary bridges could not directly be imaged with the corresponding force in the micrometer range so far. A Laser Scanning Confocal Microscope (LSCM) can visualize the shape of a liquid bridge on solid surface in a three-dimensional form. We built a combined LSCM and AFM device and measured the forces with colloidal probes on liquid surfaces. The combination of force spectroscopy and confocal microscopy allows us to image capillary bridges and simultaneously measure the corresponding force.

With our setup we can now verify the theoretical forces, calculated from the shape of the meniscus, and the corresponding force curves. We present our results of the simultaneous AFM and LSCM measurements of capillary bridges.

O 101.6 Fri 11:45 MA 144

**The contact charging of insulators by atomic force microscopy** — •Monika Mirkowska[1,2], Markus Kratzer[1], Stefan Klima[1,2], Helmut Flachberger[2], and Christian Teichert[1] — [1]Institute of Physics, Montanuniversität Leoben, Austria — [2]Chair of Mineral Processing, Montanuniversität Leoben, Austria

Better understanding of tribocharging and contact electrification of dielectric materials is of great interest for technological applications like tribocharging separation of mineral particles and secondary raw materials. The underlying mechanisms are still not well understood. The charging of calcite single crystal surfaces upon contact with an Atomic Force Microscope (AFM) tip and micrometer sized single calcite particles attached to the end of commercial AFM cantilevers has been investigated using Kelvin Probe Force Microscopy (KPFM). The resulting surface charge depends on the type of charging (static charging, matrix of static charging, rubbing), the load force, and the value of the initial surface potential. A charge decay, within several tens of hours, has been observed. Increasing the sample temperature accelerated this charge decay process. Sequential charging of the same area with opposite sign could be performed, showing that the preceding charging does not alter the charging behavior.Experiments were carried out under various conditions.

O 101.7 Fri 12:00 MA 144

**The Meaning of Temperature in Interferometric Detection Schemes** — •Alexander Schwarz[1], Gotthold Fläschner[1], Kai Ruschmeier[1], Roland Wiesendanger[1], Reza Bakhtiari[2], and Michael Thorwart[2] — [1]University of Hamburg, Institute of Applied Physics, Jungiusstr.11, 20355 Hamburg — [2]University of Hamburg, I. Institute of Theoretical Physics, Jungiusstr. 9, 20355 Hamburg

The force sensitivity of cantilevers used in atomic force microscopy (AFM) scales with $\sqrt{T}$. A convenient way to obtain the temperature $T$ is measuring the power spectral density around the resonance frequency and subsequent application of the equipartition theorem. However, in interferometric detection schemes, where the backside of the cantilever acts as one mirror of a Fabry-Perot cavity, the dynamic of the cantilever motion can be influenced by the light, e.g., due to photothermal effects [1,2]. In this case the so-called *mode temperature* and not the *phonon temperature* is measured.

In our presentation we describe a procedure to determine the phonon temperature of the cantilever for a Fabry-Perot type interferometric detection scheme, if radiation pressure dominates over photothermal effects. Moreover, we also explain how laser noise can influence the cantilever motion. Our analysis shows that the recorded power spectral density are best described by Fano line shapes, which can exhibit a dip instead of a peak at resonance. Indeed, we were able to observe such a peculiar antiresonant behavior experimentally.

[1] C. H. Metzger and K. Karrai, Nature **432**, 1002 (2004).

[2] H. Hölscher et al., Appl. Phys. Lett. **94**, 223514 (2009).

O 101.8 Fri 12:15 MA 144

**Dynamic Friction Force Microscopy at Surface Defects on HOPG** — •Felix Mertens, Thomas Göddenhenrich, and André Schirmeisen — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35392 Gießen

Dynamic friction force microscopy is a valuable scanning probe technique for the detection of friction properties on the nanometer scale. An off-resonance modulation of a sample surface induces non-linear cantilever bending oscillations, where the resonance response is a very sensitive measure of the interaction at the tip-sample contact. Images reveal surface steps and grain boundaries on graphite surfaces. The dynamic response furthermore contains information about elastic properties of surface steps. A signal pulse is applied to the modulation piezo and a fast Fourier transform of the cantilever real-time oscillation exhibits resonance parameters of the oscillation.

O 101.9 Fri 12:30 MA 144

**A Closer Look into Operating Perovskite-Sensitized Solar Cells** — •Stefan Weber[1], Victor Bergmann[1], Javier Ramos[2], Mohammad Nazeeruddin[3], Michael Graetzel[3], Shazada Ahmad[2], and Ruediger Berger[1] — [1]MPI for Polymer Research, Mainz, Germany — [2]Abengoa Research, Seville, Spain — [3]EPFL, Lausanne, Switzerland

Solar cells based on novel hybrid organic-inorganic halide perovskites have recently reached power conversion efficiencies comparable to silicon solar cells. Nevertheless, the exact charge generation mechanism in perovskites is still unclear. The aim of our study is to apply scanning probe microscopy (SPM) for measuring the electrical potential in the different layers of the device under working conditions. Therefore, a SPM setup was equipped with a sample illumination and placed in an inert atmosphere to avoid photo-oxidation of the sensitive materials. We prepared smooth cross sections of the solar cell by means of focused ion beam milling. This way, the internal interfaces between the different materials in the fully functional device were accessible for frequency modulation Kelvin Probe Force Microscopy (FM-KPFM). Our measurements revealed that the investigated perovskite devices have an internal potential distribution that represents a p-i-n type junction solar cell. Upon illumination under short-circuit conditions, we found an unbalanced charge transport inside the device with holes accumulating in the preovskite layer. These results are important for understanding the physics of perovskite solar cells [Bergmann, V.W. et al (2014); Nature Comm. 5, 5001].

## O 102: Overview Talk (Robert Schlögl)

Time: Friday 13:15–14:00 Location: HE 101

**Invited Talk** O 102.1 Fri 13:15 HE 101

**Energiewende: Grenzgänge und Grenzflächen** — •Robert Schlögl — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — Max-Planck-Institut für Chemische Energiekonversion, Mülheim a.d. Ruhr

Die Energiewende wurde 2011 durch einen politischen Impuls ausgelöst. Damals bestand nur eine eingeschränkte Kenntnis über die Folgen eines weiteren Eingriffs in ein System mit verkoppelten soziologisch-ökonomisch-juristischen und technischen Komponenten. Die DPG hat sich intensiv und vertieft mit den resultierenden Herausforderungen befasst. Auf der technischen Ebene besteht ein erheblicher Bedarf für neue Entwicklungen für alle Anwendungsbereiche der Energiewandlung und Nutzung. Der Beitrag zeigt ihre zentrale Rolle auf und belegt an Beispielen, dass die wissenschaftlichen Kerne dieser Technologien überwiegend Grenzflächenprozesse darstellen. Dies erschließt sich von selbst für die Photovoltaik. Weniger klar ist dies für Batterien und oft aus den Augen verloren wird dies für die elektrochemische Wasserspaltung und die Prozesse zur Hydrierung von CO2. Diesen energiewandelnden Großprozessen, die als Beispiele für den Beitrag behandelt werden, stehen viele Prozesse gegenüber, die durch Optimierung von Grenzflächen energieeffizienter werden können. Nehmen wir schließlich die Vielzahl von Grenzflächen in solch komplexen Strukturen wie Displays und LED Lichtquellen hinzu, so wird schnell klar, dass der Titel nicht übertrieben ist.