

O 36: Posters: Bio/organic Molecules on Surfaces, Graphene, Solid/liquid interfaces, Metal Substrates, Electronic Structure Theory

Time: Tuesday 18:30–22:00

Location: P1

O 36.1 Tue 18:30 P1

Coverage-dependent metalation and dehydrogenation of tetraphenylporphyrin on Cu(111) — ●MICHAEL RÖCKERT, MATTHIAS FRANKE, QURATULAIN TARIQ, MICHAEL STARK, STEFANIE DITZE, HUBERTUS MARBACH, HANS-PETER STEINRÜCK, and OLE LYTKEN — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

The coverage-dependent metalation and dehydrogenation of tetraphenylporphyrin (TPP) on Cu(111) was investigated with XPS, STM and TPD under UHV conditions. 2HTPP has two distinct adsorption structures on Cu(111) [1]: At low coverages (< 0.36 molecules/nm²) 2HTPP adsorbs in a disordered structure, but as the coverage is increased a checkerboard-like structure is formed and saturates at 0.55 molecules/nm². As 2HTPP layers on Cu(111) are heated, three distinct reactions take place: metalation, resulting in CuTPP, a partial dehydrogenation of the outer porphyrin-sphere, linking most likely the pyrrole and phenyl rings together, and upon further heating complete dehydrogenation [2]. The two first reactions, metalation and partial dehydrogenation, strongly depend on the structure of the 2HTPP layer. At low coverages, the temperatures for both processes are very close to each other, while at higher coverages metalation shifts down and dehydrogenation up in temperature.

[1] Stark, M. et al. *Langmuir* 2013, 29, 4104-4110. [2] Xiao, J.; Ditze, S. et al. *J. Phys. Chem. C* 2012, 116, 12275-12282.

O 36.2 Tue 18:30 P1

Self organization driven structure formation of DIP molecules on Cu(111) — HAZEM ALDAHAK, ●WOLF GERO SCHMIDT, and EVA RAULS — Theoretische Physik, Universität Paderborn

Thin films of organic molecules like diindenoperylene (DIP) on metal substrates are of great interest for the further miniaturization of organic optoelectronic devices. DIP molecules show an interesting behavior on different terraces. While step edges have rare influence on the azimuthal molecular orientation of DIP-molecules on Cu(100) [1], they control the molecular crystallographic directions on Au(111) independently of the underlying surface symmetry [2]. On Cu(111), the self-assembly depends on the terrace width. On narrow terraces (< 15 nm), 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. Special focus is put on the role of step-edges to initiate the molecular self-assembly depending on the terrace width. Based on our investigations, we deduced a model which explains the experimental observations.

[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 36.3 Tue 18:30 P1

STM Study of the structural formation of crystal violet on Au(100) and Au(111) surfaces — ●PATRICK MEHRING, LOTHAR BROSDA, and CARSTEN WESTPHAL — Fakultät Physik - Technische Universität Dortmund, Otto-Hahn-Str. 4, D 44221 Dortmund

The selective modification of metal surfaces offers a large variety of possible applications in different fields. Thus, the understanding of the adsorption and structural formation of molecules with well-known properties attracted large attention for different applications in the last years. Crucial parameters having strong influence on the assembly mechanism are the molecular coverage, temperature, and substrate interaction which are topics of many studies. The adsorption and structural formation of crystal violet on Au(100) and Au(111) was investigated by means of scanning tunneling microscopy for different coverages ranging from submonolayer to multilayer regime. The molecules are found forming ordered structures near a closed monolayer on both surfaces. Thus, the phases show similar structural features on both substrate orientations. Overall, two different molecule orientations can be identified. A structure model is presented for both Au(100)

and Au(111) surfaces. When reaching the multilayer regime the long range order decreases and only isolated areas with alternating molecule orientation are found.

O 36.4 Tue 18:30 P1

On the dynamics of molecular processes: STM investigations of porphyrins on Cu(111) — ●STEFANIE DITZE, MICHAEL STARK, MARTIN DROST, FLORIAN BUCHNER, 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 Erlangen

For the controlled fabrication of molecular nanostructures it is important to understand dynamic processes such as surface diffusion, molecular rotation, conformational changes or chemical reactions on well-defined surfaces. Herein, we show that scanning tunneling microscopy (STM) can be a powerful tool to study the dynamics of porphyrins on Cu(111) under UHV conditions. The results of corresponding isothermal measurements at different temperatures are used for an Arrhenius type analysis to finally extract the energetics of the process. Following this route, the kinetic parameters for 2D surface diffusion and 2D molecular rotation of 2H-5,10,15,20-tetraphenylporphyrin (2HTPP) [1], the activation energy for the self-metalation reaction of 2HTPP with Cu substrate atoms [2] and finally even the energetics to conformational switch an individual 2H-5,10,15,20-tetrakis(3,5-di-tert-butyl)-phenylporphyrin can be determined.

This work has been funded by the DFG through SFB 583.

[1] F. Buchner et al., *J. Phys. Chem. C* 115 (2011) 24172-24177.

[2] S. Ditze et al., *Angew. Chem., Int. Ed.* 51 (2012) 10898-10901.

O 36.5 Tue 18:30 P1

Coverage dependent adsorption behavior of Ni-TPBP on Cu(111): A scanning tunneling microscopy study — ●MICHAEL LEPPER, LIANG ZHANG, MICHAEL STARK, 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

In order to design self-assembled supramolecular architectures with specific functional properties it is necessary to understand the adsorption behavior of molecular building blocks on well-defined substrates. One very versatile class of adsorbates in this regard are porphyrins which offer not only a rigid molecular framework but also ligand functionality to bind metals. In this study, we investigate the coverage dependent supramolecular arrangement of Ni(II)-tetraphenylbenzoporphyryl (NiTPBP) on Cu(111) with scanning tunneling microscopy at room-temperature (RT) in ultra-high vacuum (UHV). At low coverage, we observed adsorption of the porphyrin molecules at the steps. By increasing the coverage island formation of NiTPBP is promoted. Interestingly, we were able to monitor three different molecular appearances of the NiTPBP islands at the same coverage and temperature.

O 36.6 Tue 18:30 P1

Atomic Force Microscopy: The qPlus sensor applied to molecules on metal surfaces — ●ROBIN OHMANN^{1,2}, ANJA NICKEL^{1,2}, JÖRG MEYER^{1,2}, FRANCESCA MORESCO^{1,2}, and GIANAU-RELIO CUNIBERTI^{1,2} — ¹Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, Dresden, Germany — ²Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

Atomic force microscopy invented in 1986 allows measuring forces between a probing tip and the surface. In 1998 the qPlus sensor was developed by Franz J. Giessibl which is comprised of a tuning fork found in watches and operates in frequency modulation mode (FM-AFM). By attaching a conducting tip on one of the prongs of the fork it allows to combine scanning tunneling microscopy and atomic force microscopy leading to atomic resolution images of the surface. In our lab, we have set up such an STM/AFM system operating at low temperatures (5 K) under ultra-high vacuum conditions. Our goal is to investigate single molecules and supramolecular structures on metal surfaces with the qPlus sensor. In this poster, I will present our first

measurements on molecules on metal surfaces.

O 36.7 Tue 18:30 P1

Vibrational properties and dynamic charge transfer of the CuPc/Ag(111)-system — ●SEBASTIAN THUSSING und PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany

The vibrational properties and thermal evolution of ultra thin films of copper-phthalocyanine (CuPc) grown on Ag(111) have been investigated using Fourier-transform infrared absorption spectroscopy (FTIRAS), spot-profile-analysis low energy electron diffraction (SPA-LEED) and thermal desorption spectroscopy (TDS). Thereby, various phases in the submonolayer regime could be distinguished and characterized. Bilayer and multilayer are largely decoupled from the Ag(111) substrate and display a distinctly different spectroscopic signature. Mono- and bilayers are orientated parallel to the Ag(111) surface whereas a slightly inclined geometry prevails for the multilayers. The monolayer phases are subject to a pronounced interfacial dynamical charge transfer (IDCT). Interestingly, this process is attenuated upon growth of the bilayer. TDS spectra reveal an incomplete desorption for the CuPc monolayer from the Ag(111) surface. At about 600K a second pathway becomes dominant with fragments desorbing in variable amounts.

O 36.8 Tue 18:30 P1

Large pores and multiple active sites: a 2D metal-organic network employing a de-novo synthesized porphyrin linker — ●YUANQIN HE¹, FELIX BISCHOFF¹, KNUD SEUFERT¹, WILLI AUWÄRTER¹, DAPHNÉ STASSEN², DAVIDE BONIFAZI², and JOHANNES BARTH¹ — ¹Technische Universität München, Department of Physics, E20, Garching, Germany — ²University of Namur, Department of Chemistry, Namur, Belgium

Exploring principles for future single-molecule devices and developing new materials for catalysis using functional molecular building blocks are motivations for molecular nanoscience. Herein, the bottom-up fabrication of metal-organic networks is a promising approach, notably regarding temperature stability or controllable and tunable assembly protocols. We present a low-temperature scanning tunneling microscopy study of the de-novo synthesized porphyrin linker (5,10,15,20)tetra[4-(4-pyridyl)phenyl]porphyrin on Ag(111). This free-base tetrapyrrole species forms nanoporous, metal-organic networks via N-Cu-N coordination bonds when adding Cu atoms. Networks with large openings stabilized by directional coordination interactions present metal atoms as possible catalytically active sites, porphyrin macrocycles as "chemical pockets" and open pores for host-guest chemistry.

O 36.9 Tue 18:30 P1

STM of functionalized platform molecules on Au(111) — ●TORBEN JASPER-TÖNNIES¹, SANDRA ULRICH², RAINER HERGES², and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel — ²Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel

The coupling to a metal substrate affects the electronic and geometric structure of molecules. To preserve their intrinsic properties it may be desirable to decouple functional groups from the substrate. This can be achieved by supporting a molecule by a molecular platform, conceivably via a spacer group. Using low temperature scanning tunneling microscopy we investigate the trioxotriangulenium (TOTA) platform molecule with various functional groups. In contrast to the similar platform molecule triazatriangulenium (TATA), functionalized TOTA can be thermally evaporated due to its higher thermal stability. Depending on the functional groups attached to the TOTA molecules we observe varying degrees of fragmentation. This will be discussed in terms of electronic properties of the functional groups. Financial support by the Deutsche Forschungsgemeinschaft via SFB 677 is gratefully acknowledged.

O 36.10 Tue 18:30 P1

Surface Control of Alkyl Chain Conformations and Chiral Amplification — ●KATHARINA SCHEL¹, NADINE HAUPTMANN¹, THIRUVANCHERIL G. GOPAKUMAR², FRANZISKA L. OTTE³, CHRISTIAN SCHÜTT³, RAINER HERGES³, and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany — ²Department of Chemistry Indian Institute of Technology Kanpur, Uttar Pradesh 208

016, India — ³Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

For alkyl substituents and alkane chains in thin layers on surfaces it was found that adjacent alkyl chains align parallel to each other. We investigated Trioctyl-functionalized triazatriangulenium (TATA) deposited on Au(111) and Ag(111) surfaces by electrospray ionization using low-temperature scanning tunneling microscopy. The molecules surprisingly adsorb with a bent geometry of the octyl groups making them chiral with eight possible configurations. When arranged in hexagonal networks however only one configuration was found making islands homochiral. We suggest a model of the geometry and a mechanism leading to the observed chiral amplification. Financial support by the Deutsche Forschungsgemeinschaft via the SFB 677 is gratefully acknowledged.

O 36.11 Tue 18:30 P1

Cyano-Functionalized Triarylamines on Au(111): Competing Intermolecular versus Molecule/Substrate Interactions — ●STEFANO GOTTARDI¹, KATHRIN MÜLLER¹, JUAN CARLOS MORENO-LÓPEZ¹, HANDAN YILDIRIM³, UTE MEINHARDT², MILAN KIVALA², ABDELKADER KARA³, and MEIKE STÖHR¹ — ¹Zernike Institute of Advanced Materials, University of Groningen, AG, Groningen, The Netherlands — ²Chair of Organic Chemistry 1, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Erlangen, Germany — ³Department of Physics, University of Central Florida, Orlando, FL, USA

The self-assembly of cyano-substituted triarylamine derivatives on Au(111) is studied with scanning tunneling microscopy and density functional theory calculations. Two different phases, each stabilized by at least two different cyano bonding motifs are observed. In the first phase, each molecule is involved in dipolar coupling and hydrogen bonding, while in the second phase, dipolar coupling, hydrogen bonding and metal-ligand interactions are present. Interestingly, the metal/ligand bond is already observed for deposition of the molecules with the sample kept at room temperature leaving the herringbone reconstruction unaffected. It is proposed that for establishing this bond, the Au atoms are slightly displaced out of the surface to bind to the cyano ligands. Despite the intact herringbone reconstruction, the Au substrate is found to considerably interact with the cyano ligands affecting the conformation and adsorption geometry, as well as leading to correlation effects on the molecular orientation.

O 36.12 Tue 18:30 P1

Adsorption of HTMGT on Au(111): Influence of Surface Roughness — ●JAN PISCHEL¹, ANNA LEBKÜCHER², HANS-JÖRG HIMMEL², and ANNEMARIE PUCCI¹ — ¹Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, D-69120 Heidelberg — ²Institut für anorganische Chemie, Im Neuenheimer Feld 270, D-69120 Heidelberg

Hexakis(tetramethylguanidinyl)triphenylene (HTMGT) is a guanidiny-functionalized aromatic compound (GFA) recently synthesized in the group of H.-J. Himmel in Heidelberg. GFAs are strong electron donors and can be linked to semiconducting polymers under formation of coordinative bonds mediated, e.g., by copper and iodine [1]. Furthermore, due to appropriate HOMO and LUMO levels (calculation), HTMGT is an interesting material for application in active layers of organic field effect transistors.

We show here an infrared (IR) reflection absorption spectroscopic investigation of its adsorption on the Au(111) surface and focus especially on the influence of surface roughness. Roughness in the submonolayer region is introduced in a well-defined manner by evaporation of gold onto the pristine Au(111) surface cooled to 40K. The different regimes of substrate roughness are determined by using carbon monoxide as a probe for IR spectroscopy.

[1] H.-J. Himmel, Z. Anorg. Allg. Chem., **639**:1940–1952, 2013.

O 36.13 Tue 18:30 P1

Exploring the cerium-directed assembly of porphyrin derivatives on Ag(111) — ●FELIX BISCHOFF, WILLI AUWÄRTER, KNUD SEUFERT, DAVID ECIJA, SARANYAN VIJAYARAGHAVAN, and JOHANNES BARTH — Technische Universität München, Department of Physics, E20, Garching, Germany

In the field of molecular nanoscience considerable effort is put in the bottom-up synthesis of novel interfacial compounds and architectures. In this domain, rare-earth metal complexes are particularly interesting regarding their function as single-molecule magnets, field effect transistors or molecular rotors. Among the series of rare-earth complexes,

those incorporating cerium are especially versatile because cerium can be in a +III or +IV oxidation state. Here we assess the metal-directed assemblies afforded by adsorbed porphyrin derivatives (2H-TPP and 2H-P) and Cerium atoms on Ag(111) in an STM study. Depending on the preparation procedure, observed products were, amongst others, modified single molecules, highly ordered cerium-porphyrinato islands, extended double-decker chains and even triple-deckers. The multiple reaction products reveal that the understanding and control of the reaction parameters is a prerequisite for well-defined products. Thus we explored routes for the controlled synthesis of distinct cerium-porphyrinato arrangements.

O 36.14 Tue 18:30 P1

Spontaneous change in molecular orientation at order-disorder transition of tetracene on Ag(111) — ●TOMOKI SUEYOSHI¹, MARTIN WILLENBOCKEL¹, MICHAEL NABOKA², ALEXEI NEFEDOV², SERGUEI SOUBATCH¹, CHRISTOF WÖLL², and STEFAN TAUTZ¹ — ¹Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich, Germany — ²Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Germany

Molecular orientation is not only correlated closely to the electronic properties of molecular layers but also related directly to formation of various molecular phases composed of the identical molecule(s). Here, we investigate the molecular orientation of tetracene in ordered and disordered layers on Ag(111) using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy [1]. Quantitative analysis of NEXAFS intensities reveals that the compact monolayer α -phase at 150 K consists of essentially flat-lying molecules with an average tilt angle $\alpha < 9^\circ$ with respect to the Ag(111) surface. At room temperature the tetracene monolayer is dynamically disordered with $\alpha = 15 \pm 4^\circ$ (α' -phase). The increase in the average tetracene tilt angle indicates that orientational degrees of freedom perpendicular to the surface drive the order-disorder transition in the tetracene monolayer on Ag(111). We argue that the phase transition can be explained by a delicate balance between the interfacial enthalpy and the orientational entropy.

[1] T. Sueyoshi, M. Willenbockel, M. Naboka, A. Nefedov, S. Soubatch, C. Wöll, and F. S. Tautz, *J. Phys. Chem. C* **117**, 9212 (2013).

O 36.15 Tue 18:30 P1

Self-assembling and electronic structure of metallocenes on Pb(111) and Pb(100) — ●WIBKE BRONSCH, BENJAMIN HEINRICH, and KATHARINA FRANKE — Freie Universität Berlin, Germany

Metallocene molecules are promising candidates for future spintronic applications. However, in contact to metallic leads their stability has recently been discussed [1,2]. Employing low-temperature scanning tunneling microscopy, we show that ferrocene on Pb(111) and Pb(100) forms self-assembled islands, in which the molecular axis is almost parallel to the surface normal. Dissociation of the molecules occurs when the molecules are forced to closer distance, as e.g. at dislocation lines or higher molecular coverages. Tunneling spectroscopy reveals that the HOMO and LUMO are mainly localized on the cyclopentadienyl rings. In agreement with the spin singlet state of the free molecule, we do not find any indication of magnetic interaction with the substrate.

[1] Braun, K.-F. et al., *Phys. Rev. Lett.* **96**, 246102 (2006)

[2] Heinrich, B. W. et al., *Phys. Rev. Lett.* **107**, 216801 (2011)

O 36.16 Tue 18:30 P1

Structural and optical investigation of K doping induced changes of PTCDA on Ag(111) — ●CHRISTIAN ZWICK, MARCO GRUENEWALD, ROMAN FORKER, and TORSTEN FRITZ — Friedrich-Schiller University, Institute of Solid State Physics, Max-Wien-Platz 1, Jena 07743, Germany

We report on the impact of potassium doping on highly-ordered ultra-thin layers of the dye molecule 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on a Ag(111) surface under ultra-high vacuum conditions. The thin films were characterized optically by *in situ* differential reflectance spectroscopy (DRS) [1,2] as well as structurally by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Depending on the doping concentration, distinct optical spectra could be observed. Except for one all could be assigned to the optical fingerprints of ionized PTCDA, showing different doping states ranging up to tetraanions. For the first three doping levels of PTCDA we were able to study the corresponding structures, which significantly differ from each other, referencing directly to the influence of the doping, i.e., doping induced phase transitions and the adsorption sites occupied by the dopants.

References:

[1] R. Forker *et al.*, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, **2012**, *108*, 34-68.

[2] R. Forker and T. Fritz, *Phys. Chem. Chem. Phys.*, **2009**, *11*, 2142-2155.

O 36.17 Tue 18:30 P1

Understanding the peptide folding on surfaces in UHV by electrospray ion beam deposition (ES-IBD) — ●SABINE ABB¹, GORDON RINKE¹, STEPHAN RAUSCHENBACH¹, LUDGER HARNAU^{2,3}, and KLAUS KERN^{1,4} — ¹Max-Planck-Institute for Solid State Reserach, Heisenbergstr. 1, Stuttgart — ²Max-Planck-Institute for Intelligent Systems, Heisenbergstr. 3, Stuttgart — ³IV. Institute for Theoretical Physics, University Stuttgart, Pfaffenwaldring 57, Stuttgart — ⁴Ecole Polytechnique Fédérale de Lausanne, Switzerland

Specific functionality of peptides and proteins is reached by folding into a unique secondary and tertiary structure which is steered by intramolecular interactions as well as metal coordination. A new route to investigate the properties and structural formation of amino acid sequences on surfaces in low dielectric environments (e.g. in vacuo) is possible with our home-built ES-IBD instrument which allows in-situ STM characterization of (bio)molecules. It also gives additional modes of control, for instance by using selected charge states and generating metal-peptide complexes which already form in solution.

Here we show preliminary results of STM investigations of the eight-amino acid peptide angiotensin II on various metal surfaces. We observe dimer to multimer self-assembled structures and present preliminary structural models. For a deeper understanding of the ongoing processes, special attention is paid to the structural differences and similarities between the protonated and coordinated angiotensin II as well as the comparison to the nine-amino acid peptide Bradykinin.

O 36.18 Tue 18:30 P1

Ion beam-induced nanoscale surface modulations and their effect on protein-surface adsorption — ●ALEXANDER VON MÜLLER, JANA SOMMERFELD, and CARSTEN RONNING — Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Helmholtzweg 3, 07743 Jena

Under specific experimental conditions, the irradiation of solid surfaces with ions can result in periodic surface modulations at the nanoscale. This effect of ripple formation is widely discussed in the literature and has been observed on many different types of materials - e.g. semiconductors, amorphous materials, graphite, and metals [1,2]. We will present results of experiments in which we have tested the biocompatibility of such ion beam-induced surface morphologies by studying their effects on the surface adsorption behaviour of human plasma fibrinogen (HPF) proteins. The nanopatterned surfaces have been created by irradiation of different substrates with low-energy ions (< 20 keV). Both the effects of the irradiations and the adsorption of the proteins have been studied by means of atomic force microscopy (AFM).

[1] Nanostructuring surfaces by ion sputtering, U. Valbusa, C. Boragno, F. Buatier de Mongeot, *J. Phys: Condens. Matter*, **2002**, *14*, 8153-8175

[2] Ion-Induced Nanoscale Ripple Patterns on Si Surfaces: Theory and Experiment, A. Keller, S. Facsko, *Materials*, **2010**, *3*, 4811-4841

O 36.19 Tue 18:30 P1

STM and XPS Investigation of Ethylene Carbonate Monolayers on Cu(111) and Co-Adsorption of Lithium — ●MARAL BOZORGCHENANI^{1,2}, FLORIAN BUCHNER¹, HANIEH FARKHONDEH^{1,2}, BENEDIKT UHL^{1,2}, and R. JÜRGEN BEHM^{1,2} — ¹Helmholtz Institute Ulm (HIU), Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, Ulm, Germany

Ethylene Carbonate (EC) and Lithium (Li) are major components in Li-ion battery electrolytes. An understanding of the solid-electrolyte interphase (SEI) at a molecular level would be highly desirable to improve Li-ion batteries. The co-adsorption of both components, as a model system, is topic of the present work and will be investigated to mimic the situation at the SEI. In a first step, adsorption of the two materials on a Cu(111) surface was studied independently: (1) The adsorption behaviour of EC on Cu(111) was investigated by scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum (UHV) conditions. At sub-monolayer coverage, the STM images show highly ordered 2D EC islands around 100 K. Evidence for intact EC adsorbed on Cu(111) is provided by the XP C1s and O1s core level spectra. Temperature induced structural and chemical changes will be highlighted. (2) After deposition

of Li atoms on Cu(111) held at 80 K, objects with a circular shape were identified. The adsorption behaviour and interaction mechanism is discussed. Co-deposition of both materials together on Cu(111) will be explored in forthcoming experiments.

O 36.20 Tue 18:30 P1

Comparison of the adsorption behavior of the ionic liquids [EMIM][TFSA] and [OMIM][TFSA] on Au(111) and Ag(111) — ●BENEDIKT UHL^{1,2}, HSINHUI HUANG¹, DOROTHEA ALWAST^{1,2}, FLORIAN BUCHNER², and R. JÜRGEN BEHM^{1,2} — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-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; e.g., 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 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide ([EMIM][TFSA]) and 1-octyl-3-methylimidazolium-bis(trifluoromethyl-sulfonyl)imide ([OMIM][TFSA]) with Au(111) and Ag(111) was investigated by scanning tunneling microscopy (STM) under UHV conditions at temperatures between 80 K - 293 K. Since both ILs differ only in the length of their alkyl chains, differences in structure formation on the same surface can solely be caused by this. For Au(111) as well as for Ag(111), both ILs show a very similar behavior: long-range ordered (2D crystalline) domains/islands coexist with a short-range ordered (2D glass) phase. The 2D crystalline structures of both IL adsorbates showed the same space requirement per adsorbed molecule, which points to an adsorption geometry of the molecule with the alkyl chain sticking up from the surface.

O 36.21 Tue 18:30 P1

Molecular Aggregates for Photoemission Electron Microscopy (PEEM) — ●HANNES HARTMANN, INGO BARKE, KARL-HEINZ MEIWES-BROER, and SYLVIA SPELLER — University of Rostock, Institute of Physics, 18051 Rostock, Germany

Molecular aggregates are of significant interest for applications in organic electronics and for photovoltaics. Our experiments aim at spatial and energy-resolved studies of excitations in molecular aggregates. The primary method is photoemission electron microscopy (PEEM), in combination with fluorescence- and scanning probe microscopy. The PEEM system is equipped with energy filters and different excitation sources. For time-resolved measurements a pump-probe setup is under construction. The current state of affairs is presented and discussed.

O 36.22 Tue 18:30 P1

Structure and Fluorescence of Molecular Crystals — BJÖRN VOGLER¹, HANNES HARTMANN¹, KAI WARDELMANN¹, HEINRICH BEHLE¹, J.A.A.W. ELEMANS², INGO BARKE¹, and ●SYLVIA SPELLER¹ — ¹University of Rostock, Institute of Physics, 18051 Rostock, Germany — ²Institute for Molecules and Materials, RU Nijmegen, NL

We study the influence of the local environment on the excitation and transport of Frenkel excitons in molecule crystals. Metallo-porphyrin aggregates [1] are prepared by dropcasting on graphite. We use AFM, STM, and Fluorescence Microscopy to study morphology and the spatial distribution of fluorescence. The mesoscopic structure shows molecular strands branching into finer structures. The fluorescence intensity is spatially varying along the strands and appears enhanced at junctions. We discuss possible origins for the observed variations.

[1] M.J.J. Coenen, et al., Phys. Chem. Chem. Phys. 15, 12451 (2013)

O 36.23 Tue 18:30 P1

Photon emission from the tunneling contact of a low temperature STM for pristine and adsorbate covered metal substrates — ●EBRU ÖZEN, MAREN C. COTTIN, TOBIAS ROOS, DETLEF UTZAT, DORIS STEEGER, WILLY PLATZ, ROLF MÖLLER, and CHRISTIAN A. BOBISCH — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

STM-induced light emission (STM-LE) has been a emerging field in scanning tunneling microscopy in the past years [1]. STM-LE experiments on organic molecules are of particular interest, since they can provide information about energy loss in certain organic molecules [2]. We find that Ag(111) terraces show a plasmonic excitation in

the tunneling contact of a silver covered Pt-Ir tip for positive and negative sample bias. In addition experiments on Ag(111) surfaces partially covered by different organic molecules were performed. It is found that the organic molecules perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), copper-phthalocyanine (CuPc) and the carbon-molecule C₆₀ reduce or completely suppress the emission of photons. Photon maps of molecularly resolved C₆₀ islands show a periodic modulation of the light intensity by the adsorbed C₆₀.

- [1] R. Berndt and J. K. Gimzewski, Phys. Rev. B 48 4746 (1993).
[2] C. Chen et al., Phys. Rev. Lett. 105, 217402 (2010).

O 36.24 Tue 18:30 P1

Decoupling in organic heterostructures of PTCDA and CuPc on single crystalline silver — ●TINO KIRCHHUEBEL¹, MARCO GRUENEWALD¹, JULIA PEUKER¹, TIMOTHY VAJAS², ROMAN FORKER¹, and TORSTEN FRITZ¹ — ¹Friedrich Schiller University, Institute of Solid State Physics, Max-Wien-Platz 1, Jena 07743, Germany — ²The Ohio State University, Department of Physics, 191 West Woodruff Ave, Columbus, OH 43210

Here we report on organic heterostructures of highly-ordered ultrathin layers of the dye molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and copper-phthalocyanine (CuPc) grown on Ag(111) and characterized by LEED and LT-STM as well as optically by in-situ differential reflectance spectroscopy (DRS) [1].

The heterostructure consisting of CuPc on top of one monolayer PTCDA on Ag(111) is stable, and the DRS spectra show a clear monomeric behavior of CuPc as likewise observed on an inert mica substrate. In contrast, by LT-STM and DRS measurements we found that one monolayer of CuPc on Ag(111) is thermodynamically not stable when PTCDA is deposited on top. Besides of decoupling aromatic molecules from a metal by an organic interlayer the passivation is also possible by depositing thin films of alkali metal halides on top of the metallic surface [2]. Preliminary results for PTCDA on KCl/Ag(111) and CuPc on KCl/Ag(100) will also be discussed.

References: [1] R. Forker et al., Annu. Rep. Prog. Chem., Sect. C: Phys. Chem., 2012, 108, 34-68. [2] M. Müller et al., Surface Science, 2011, 605, 1090-1094.

O 36.25 Tue 18:30 P1

Electronic “chirality” of transition metal phthalocyanine molecules adsorbed to noble metal surfaces — ●JACOB SENKPIEL, JENS KÜGEL, PIN-JUI HSU, and MATTHIAS BODE — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

We have investigated the transition metal phthalocyanine (TM-Pc) molecules MnPc and CuPc on Cu(001) and Ag(001) by means of low-temperature scanning tunneling microscopy and spectroscopy measurements ($T \approx 5$ K). It is well-known that the symmetry axes of the adsorbed TM-Pc molecules are rotated with respect to the four-fold symmetry axis of noble metal (001)-surfaces. Symmetry considerations suggest that this should generally lead to chiral electronic distortion, which has been ascribed to charge transfer between the TM-Pc and the substrate. However, chirality was clearly observed only for some molecules, such as ZnPc on Cu(001) [1] and CuPc/NiPc on Ag(001) [2], while the topography of others appeared to be almost unaffected [2]. In this contribution we will present a detailed investigation of the molecular shape and the resulting electronic structure. Our results suggest that chirality is indeed a general phenomenon for TM-Pc's on four-fold symmetric substrates.

- [1] Chen *et al.*, Appl. Phys. Lett. 100, 081602 (2012)
[2] Mugarza *et al.*, Phys. Rev. B 85, 155437 (2012)

O 36.26 Tue 18:30 P1

Reversible conformational changes in manganese porphyrin molecules — ●XIANWEN CHEN¹, CHRISTIAN LOTZE¹, PAUL STOLL¹, NILS KRANE¹, JOSÉ I. PASCUAL^{1,2}, and KATHARINA J. FRANKE¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Germany — ²CIC nanoGUNE San Sebastián, and Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Using scanning tunneling microscopy and spectroscopy at 7 K, we investigate manganese tetra-pyridine-porphyrin (Mn-TPyP) molecules adsorbed on a Cu(111) surface. The molecules show notable structural flexibility, which leads to two adsorption states. The different adsorption configurations are characterized by two distinct orbital alignments. Noncontact Atomic Force Microscopy images indicate that the pyridine rings can lie in two meta-stable tilting angles on the surface.

We can induce a reversible rotation of single legs or pairs of legs by the tip of the scanning tunneling microscope with a threshold voltage around 2V.

O 36.27 Tue 18:30 P1

Biomolecules at metal interfaces: a novel force field approach including polarization — ●ISIDRO LORENZO¹, HADI RAMEZANI-DAKHEL², HENDRIK HEINZ², and MARIALORE SULPIZI¹ — ¹Johannes Gutenberg University Mainz, Staudinger Weg 7 55099 Mainz — ²Department of Polymer Engineering, University of Akron, Ohio 44325

Increasing interest in bio-interfaces for medical and bio-technological applications calls for microscopic understanding and control of protein-surface interactions. In particular here we aim to provide a characterization of peptide / gold interactions at a molecular level in order to explain and interpret recent surface experimental results [1] and to fill the gap between fundamental science and real applications. Atomistic simulations have been performed with the GROMACS package using available force field parameters such as CHARMM27 using 12-6 Lennard-Jones potentials [2] force field. A novel scheme is devised to include the metal polarization (image charge effect) induced by the adsorbed molecules. Extensive tests have been performed for the force field validation and comparisons with quantum mechanics (QM) density functional theory (DFT) are also discussed. Results for the di- and tri-peptide of the insulin-like growth factor on gold are presented.

[1] Anne Vallee, Vincent Humblot, and Claire-Marie Pradier *Acc. Chem. Res.*, 2010, 43 (10), pp 1297306

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O 36.28 Tue 18:30 P1

Hybridization and Charge Transfer of Planar Pt(II) Triplet Emitters at the metal organic Interface — ●ALEXANDER TIMMER, PASCAL RAPHAEL EWEN, JAN SANNING, CHRISTIAN ALEJANDRO SRASSERT, DANIEL WEGNER, HARRY MÖNIG, and HARALD FUCHS — Physikalisches Institut, Westfälische-Wilhelms Universität Münster, Deutschland

The physical and chemical properties of organic molecules on surfaces are strongly influenced by the coupling mechanisms involved. We examined the electronic structure and the adsorption behavior of the interfaces formed between electroluminescent Pt(II) complexes and various metal surfaces using photoelectron spectroscopy (PES) and scanning tunneling microscopy (STM). Furthermore we performed PES measurements on multilayer structures of these Pt(II) complexes to gain information about energy level alignment and possible charge transfer processes in stacks of such planar triplet emitters. In addition we methodically changed the substituent of the organo-metallic complexes, which in essence varied the adsorbate substrate distance, or in case of the multilayer structures alters the intermolecular stacking distance, respectively. Our results may provide further insight into the coupling and hybridization mechanisms of these molecular systems with electrodes, which are essential for the design of electroluminescent devices, such as organic light emitting diodes (OLEDs) or light emitting electrochemical cells (LEECs).

O 36.29 Tue 18:30 P1

STM/STS investigation of ionic liquids adsorbed at metal surfaces — ●THOMAS GROSS, MATTHIAS STOCKER, and BERNDT KOSLOWSKI — Institut für Festkörperphysik, Universität Ulm, D-89081 Ulm

In the last years, ionic liquids (ILs) gained more and more interest in the fields of, e.g., catalysis, electrolytes, liquid crystals, electro-elasticity etc. We employ scanning tunneling microscopy and spectroscopy (STM and STS) at low temperature to investigate the properties of such ILs being adsorbed at metal surfaces. We therefore deposited 1-butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)-imide (BMP-TFSA) and 1-ethyl-3-methylimidazoliumtrifluoromethanesulfonate (EMIM-TFSA) on Ag(111) in the sub-monolayer range. Preliminary results are reported as follows: The ILs form stable islands frequently bound by steps in the substrate. The resolution within the islands depends strongly on the state of the tunneling tip. Enhanced resolution is achieved with an IL molecule adsorbed at the tip. The surface state of Ag(111) prevails underneath the IL monolayer and shifts by about +100 meV towards the unoccupied states. We derive the charge state

of the adsorbed molecules by determining the differential barrier height thus discriminating the anions and cations at the surface.

O 36.30 Tue 18:30 P1

Exploring coherent transport through π -stacked systems in molecular electronic devices — ●QIAN LI¹, GEMMA SOLOMON¹, GEDIMINAS KIRSANSKAS², KARSTEN FLENSBERG², and MARTIN LEIJNSE³ — ¹Nano Science Center and Department of Chemistry, University of Copenhagen, Denmark — ²Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, Denmark — ³The Division of Solid State Physics, Lund University, Sweden

Understanding electron transport across π -stacked systems will help to elucidate intermolecular tunneling in molecular junctions and in the design of effective molecular devices. Here we show how conjugation length and substituent groups influence the electron transport and thermoelectric response in the π -stacked structures by investigating five representative stacked molecular junctions. We found that a π -stacked system of two substituted anthracenes exhibit good thermopower and a high power factor, suggesting that increased conjugation can enhance thermoelectric response. The fully eclipsed structure of quinydrone exhibits high power factor at the minimum energy structure and could be a better candidate in a thermoelectric device, compared with the other π -stacked systems considered.

O 36.31 Tue 18:30 P1

Light-induced ring opening of a submonolayer nitrospiropyran electronically decoupled from a Cu(100) surface — ●FABIAN NICKEL¹, MATTHIAS BERNIEN¹, QINGYU XU^{1,2}, and WOLFGANG KUCH¹ — ¹Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — ²Southeast University, Department of Physics, Nanjing 211189, P. R. China

The electronic properties of spiropyran (SP) molecules are known to change enormously after a ring opening to merocyanine (MC). Current research focuses on the isomerization of molecules in direct contact with a surface. These systems might have a great potential for applications to switch properties by external stimuli such as light. In this work the adsorption of SP on a Cu(100) surface covered by a double layer of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) was studied by near-edge x-ray absorption fine structure (NEXAFS). PTCDA adsorbs planar on the Cu(100) surface and is supposed to reduce the interaction of the overlying molecular layer with the metal substrate. At a temperature of 200 K, the SP molecules are physisorbed in the closed-ring conformation. A ring opening by illumination with UV light could be achieved for this system. A change in the out-of-plane nitrogen x-ray absorption can clearly be assigned by density functional theory to the switching of SP to the zwitterionic MC mesomere. Polarization-dependent spectra of the nitrogen and oxygen K edge show a slight change of the angle dependence due to a possible tilting of the molecule.

This work is supported by the DFG through Sfb 658.

O 36.32 Tue 18:30 P1

Honeycombenes: A novel class of hydrocarbon macrocycles made by surface-assisted synthesis — ●MIN CHEN¹, JIAN SHANG², YONGFENG WANG², KAI WU², QITANG FAN³, CICI WANG³, YONG HAN³, JUNFA ZHU³, JULIAN KUTTNER¹, GERHARD HILT¹, and J.MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²College of Chemistry and Molecular Engineering, Peking University, China — ³National Synchrotron Radiation Laboratory, University of Science and Technology of China, China

Surface-assisted synthesis provides an elegant route to molecules that cannot be synthesized in solution or that are too large for vapor-deposition. Both factors apply for [n]-honeycombenes, a novel class of planar hydrocarbon macrocycles of hexagonal geometry. [18]-Honeycombene or hyperbenzene (C₁₀₈H₇₂) consists of 18 phenyl rings and was made by surface-assisted Ullmann reaction from 4,4''-dibromo-m-terphenyl (DBTP) on Cu(111). The molecules arrange in long-range ordered islands with hexagonal unit cell. [30]-Honeycombene (C₁₈₀H₁₂₀), a hexagon with 30 phenyl rings, was made on Ag(111) from 4,4''''-dibromo-m-quinquephenyl (DBQP). DBQP gives also access to strained rings of heptagonal (C₂₁₀H₁₄₀), pentagonal (C₁₅₀H₁₀₀) and square (C₁₂₀H₈₀) shape. Using STS, the electronic structure along the ring perimeter and the confinement of surface state electrons trapped inside the macrocycles were studied. The large diameters of >2 nm and >3.5 nm make [18]- and [30]-honeycombene promising candidates for nanotroughs that can host other molecules or nanoparticles.

O 36.33 Tue 18:30 P1

Electrospray deposition of Mn₁₂ and Fe₄ single molecule magnets — ●PHILIPP ERLER¹, EVA-SOPHIE WILHELM¹, NICOLE BARTH¹, SAMUEL BOUVRON¹, PETER SCHMITT², STEFAN AMBRUS², ULRICH GROTH², LUCA GRAGNANELLO¹, and MIKHAIL FONIN¹ — ¹Fachbereich Physik, Universität Konstanz — ²Fachbereich Chemie, Universität Konstanz

Single molecule magnets (SMMs) have attracted significant interest during the past decades due to their unique magnetic properties like hysteresis of purely molecular origin and the possibility to observe quantum tunneling of magnetization. This material class allows for basic studies on quantum effects of magnetism at the molecular scale and is furthermore a promising candidate for preliminary studies aiming at ultrahigh density data storage devices or quantum computing applications. However, progress in this field is hindered by the difficulty of depositing intact SMMs on surfaces.

We have implemented electrospray ionization for the deposition of Mn₁₂-acetate SMMs on various substrates under ultra high vacuum conditions. The magnetic properties of thin films of Mn₁₂-acetate were investigated with SQUID magnetometry, whereas the structural and electronic properties of sub-monolayers and individual molecules were studied by means of low temperature scanning tunneling microscopy and spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). Furthermore, first attempts have been made for the electrospray deposition of Fe₄ SMMs, which offer the advantage of an enhanced redox stability of the magnetic core.

O 36.34 Tue 18:30 P1

Temperature induced dehydrogenation and substrate-mediated hydrogen transfer of tetra(*p*-hydroxyphenyl)porphyrin - a photoelectron spectroscopy study — ●LARS SMYKALLA¹, PAVEL SHUKRYNAU¹, MICHAEL HIETSCHOLD¹, CAROLA MENDE², HEINRICH LANG², and DIETRICH R. T. ZAHN³ — ¹Technische Universität Chemnitz, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany — ²Technische Universität Chemnitz, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany — ³Technische Universität Chemnitz, Institute of Physics, Semiconductor Physics, D-09107 Chemnitz

We present photoelectron spectroscopy investigations of 5,10,15,20-tetra(*p*-hydroxyphenyl)porphyrin (H₂THPP) molecules adsorbed on Au(111) and Ag(110). Directly after deposition of the molecular layer, coexistence of H₂THPP molecules with the cationic form H₄THPP is found. Annealing leads to the dissociation of the central hydrogen atoms in the molecules. On Au(111) after annealing to high temperatures, subsequently, both H₂THPP and its doubly dehydrogenated form THPP are observed. On the other hand, on the more reactive Ag(110) surface after annealing to 300 °C, partial dissociation of the hydroxyl groups followed by diffusion and rebonding of hydrogen to the central nitrogen atoms and with this the formation of a zwitterionic species is found. Furthermore starting at this temperature, on both substrates partial C–H bond breaking at the pyrrole rings is observed, which affects the whole electronic structure of the molecule as shown in the valance band spectra.

O 36.35 Tue 18:30 P1

Towards the formation of extended polycyclic aromatic hydrocarbons doped with nitrogen — ●TIM SANDER¹, MAXIMILIAN AMMON¹, PHILIPP HOFMANN¹, NATALIE HAMMER², MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany

The formation of extended polycyclic aromatic hydrocarbons (PAHs) by on-surface synthesis on metal surfaces has recently attracted increased interest owing to the current developments in the field of building new carbon allotropes in a bottom-up approach. We used planarized triarylamine molecules functionalized with diphenylmethylene side groups and end groups of different types (e.g. alkylchains and trialkylsilyl moieties) as molecular building blocks. We investigated the potential of the functionalized triarylamine molecules to undergo a cyclodehydrogenation reaction on the Au(111) and Cu(111) surface to create novel extended PAHs doped with nitrogen heteroatoms. The thermal-stability of the different functional side and end groups as well as the adsorption configuration of the individual molecules will be discussed in detail by means of low temperature scanning tunneling microscopy under ultra-high vacuum condition.

O 36.36 Tue 18:30 P1

Intramolecular Dipole of Merocyanine probed by Local Contact Potential Difference Measurements — ●NILS KRANE¹, CHRISTIAN LOTZE¹, XIANWEN CHEN¹, JOSÉ I. PASCUAL^{1,2}, and KATHARINA J. FRANKE¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Germany — ²CIC nanoGUNE, San Sebastián, and Ikerbasque, Basque Foundation for Science, Bilbao, Spain

The merocyanine form of the molecular switch 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran exhibits an intramolecular dipole in gas phase and solution [1]. When adsorbed on a metal surface, charge redistribution and screening may considerably alter the expected dipole behaviour. Using a combined low-temperature scanning tunneling microscope/atomic force microscope, we investigate the adsorption and intramolecular charge distribution of merocyanine on Au(111). The lateral and vertical distribution of the local contact potential difference (LCPD) hint at the persistence of an intramolecular dipole.

[1] D. Lapienis-Grochowska *et al.* Journal of the Chemical Society, Faraday Transactions 2 75, 312 (1979)

O 36.37 Tue 18:30 P1

STM Investigations of Spirobifluorene Tripodal Molecules on Au(111) — ●KEVIN EDELMANN¹, LUKAS GERHARD¹, MARCIN LINDNER¹, MICHAL VALASEK¹, LEI ZHANG¹, HILBERT VON LÖHNEYSEN^{1,2,3}, ELKE SCHEER⁴, MARCEL MAYOR^{1,3,5}, MAYA LUKAS¹, and WULF WULFHEKEL^{1,6} — ¹Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe — ²Physics Institute and Institute for Solid State Physics, Karlsruhe Institute of Technology (KIT), D-76049 Karlsruhe — ³DFG Center for Functional Nanostructures (CFN), D-76049 Karlsruhe — ⁴Physics Department, University of Konstanz, Universitätsstraße 10, D-78457 Konstanz — ⁵Department of Chemistry, University of Basel, CH-4056 Basel — ⁶Physikalisches Institut, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe

Decoupling molecular functional electronic units from a metallic substrate in a controllable manner is a major challenge for the investigation of the electronic properties of single molecules by STM. A promising approach is to use a tripodal molecule as a platform that carries the actual molecular wires or functional unit. [1]. Before functionality is integrated into this tripodal stand, the positioning and coupling of the platform to the substrate needs to be characterized thoroughly. To this end, we investigated spirobifluorene tripodal molecules. Different deposition techniques were used to deposit the molecules onto a Au(111) surface (from solutions or sublimation in UHV). We report on the morphology and electronic properties of these molecules by STM measurements. [1] Lukas *et. al.*, ACS Nano 2013 7 (7), 6170-6180

O 36.38 Tue 18:30 P1

Investigation of the Hydrogenation of Graphene on Ni(111) via Temperature Programmed X-Ray Photoemission Spectroscopy and Temperature Programmed Desorption — ●FLORIAN SPÄTH, WEI ZHAO, KARIN GOTTERBARM, CHRISTOPH GLEICHWEIT, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

The fundamental understanding of the reaction of hydrogen with graphene is of paramount importance for hydrogen-based energy storage and for tailoring the properties of graphene through chemical modification, and thus for future applications in hydrogen storage and semiconductor industries. Low defect graphene is prepared on Ni(111) by chemical vapor deposition; subsequent exposure to atomic hydrogen yields hydrogenated graphene. The hydrogenation process is thoroughly investigated with X-Ray Photoelectron Spectroscopy to gain insight in the chemical modification. The dehydrogenation process is investigated with Temperature Programmed X-Ray Photoemission Spectroscopy and Temperature Programmed Desorption. We gain detailed mechanistic insights and observe a two-step dehydrogenation independently with both methods. Furthermore, we determined the hydrogen saturation coverage, which corresponds to a full single-side hydrogenated layer. Additionally, we present a model for both the hydrogenation and dehydrogenation, and deduce a strong dependency of the hydrogen storage capacity on the substrate. A comparison to quasi free-standing graphene will be discussed.

O 36.39 Tue 18:30 P1

Modeling catalytic reactions: graphene-supported Pd nanoclusters studied with high-resolution X-ray photoelectron spectroscopy — ●KARIN GOTTERBARM, CARINA BRONNBAUER, UDO

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In our study, graphene was grown on a Rh(111) single crystal surface by chemical vapour deposition of propylene at elevated temperatures. The corrugated graphene layer serves as a template for the evaporation of Pd nanoclusters with a narrow size distribution. The growth of the clusters and their interaction with adsorbates was investigated by fast X-ray photoelectron spectroscopy (XPS) performed at the synchrotron facility BESSY II. We found a cluster-by-cluster growth mode. Upon annealing, we observe restructuring and agglomeration of the clusters. At temperatures above 850 K, intercalation of the palladium under the intact graphene sheet is observed. The interaction of the Pd particles with CO and O₂ was investigated in all relevant core levels in a temperature range from 150 up to 500 K. The adsorbate coverage varies with temperature and shows a strong dependency on the structure of the clusters.

O 36.40 Tue 18:30 P1

Transport properties of epitaxially grown graphene nanoribbons — ●JENS BARINGHAUS¹, FREDERIK EDLER¹, CHRISTIAN SEIDEL¹, CLAIRE BERGER², WALTER A. DE HEER², and CHRISTOPH TEGENKAMP¹ — ¹Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany — ²Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA

For graphene nanoribbons with zig-zag type edges the existence of topologically protected electronic edge states is theoretically predicted. Hence, exceptional transport phenomena such as ballistic transport with a mean free path in the μm range become accessible. The experimental realization of such nanoribbons requires a gentle patterning avoiding any damaging of the edges. For this purpose, we use a selective graphitization process on SiC mesa structures which allows the direct growth of graphene nanoribbons without post-processing. The electronic properties of the ribbons are investigated with scanning tunneling spectroscopy. A local density of states typical for a zig-zag type edge is observed, revealing features corresponding to the two topologically protected zeroth subbands. The transport properties of the ribbons are further analyzed by means of a 4-tip STM system. Extremely robust ballistic transport with a mean free path up to 10 μm is observed for temperatures up to room temperature. Transport in just one or both zeroth subbands can be detected depending on the probe spacing. Transport data of around 50 different ribbons are analyzed statistically, showing the reliability and reproducibility of the observed phenomena.

O 36.41 Tue 18:30 P1

HRTEM characterization of epitaxially grown graphene nanoribbons — DENNIS LAUBE¹, ●JENS BARINGHAUS¹, ATASI CHATTERJEE¹, EBERHARD BUGIEL², and CHRISTOPH TEGENKAMP¹ — ¹Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany — ²Leibniz Universität Hannover, Institut für Materialien und Bauelemente der Elektronik, 30167 Hannover, Germany

The fabrication of well-ordered graphene nanostructures is essential for any kind of graphene based device. Since standard lithography methods typically induce a large amount of defects at the edges the so produced nanostructures do not exhibit the theoretically expected transport behavior such as a width dependent bandgap (armchair edges) or ballistic transport (zig-zag edges). We use a three-stepped selective graphitization process on SiC mesa structures to grow graphene nanostructures directly in the desired shape to avoid any damaging post-processing. First, the mesa structure is patterned into the SiC substrate. In the second step, the substrate is heated at temperatures slightly below the graphitization temperature to induce a refaceting process of the mesa edges. In the last step, the sample is heated to 1350 °C for the graphitization which starts at the facets due to the much weaker bonding of silicon atoms. The fabrication process is monitored by means of high resolution TEM. Parameters such as the angle of the SiC facets (which predetermines the width of the nanostructure) were deduced. Finally, the graphene grown on the facets is studied with respect to local bonding as well as interface properties.

O 36.42 Tue 18:30 P1

Local transport properties of epitaxially grown graphene — ●FREDERIK EDLER¹, JENS BARINGHAUS¹, CHRISTOPH NEUMANN², CHRISTOPH STAMPFER², STIVEN FORTI³, ULRICH STARKE³, and CHRISTOPH TEGENKAMP¹ — ¹Institut für Festkörperphysik, Leibniz

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Transport properties of graphene are strongly affected by imperfections. A promising approach to large-scale graphene films which could be used in electronic circuits or new device structures is the epitaxial growth of graphene on SiC. For a better understanding of defect parameters, the epitaxial growth of graphene on a 6H-SiC(0001) substrate was stopped before the completion of large scale graphene areas which results in patches of different graphene perfection and transport regimes. By means of a four-tip STM/SEM system we were able to gently contact our sample on a nanometer scale without inducing strain to the graphene films. This allowed us to correlate the local morphology of monolayer graphene (as seen in SEM and STM images) with spatially resolved transport measurements. Further supporting spectroscopic characterizations were done by ARPES, Raman and STS measurements. Our detailed analysis of temperature dependency and variation of probe spacings clearly reveals two-dimensional transport regimes of Anderson localization as well as diffusive transport.

O 36.43 Tue 18:30 P1

Thermolubricity of Xe monolayers on graphene — MATTEO PIERNO¹, ●LUCA BIGNARDI^{2,3}, MARIA CLELIA RIGHI⁴, LORENZO BRUSCHI¹, STEFANO GOTTARDI², MEIKE STÖHR², PIER LUIGI SILVESTRELLI^{1,5}, PETRA RUDOLF², and GIAMPAOLO MISTURA¹ — ¹Dept. of Physics and Astronomy, University of Padova, Padova, Italy — ²Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands — ³Physikalisches Institut, University of Münster, Münster, Germany — ⁴CNR and Dept. of Physics, University of Modena and Reggio, Modena, Italy — ⁵IOM-CNR, Trieste, Italy

The nanofriction of Xe monolayers deposited on graphene was explored with a quartz crystal microbalance (QCM) at temperatures between 25 and 50 K. Graphene was grown by chemical vapour deposition and transferred to the QCM electrodes with a polymer stamp. At low temperatures, the Xe monolayers are fully pinned to the graphene surface. Above 30 K, the Xe film slides and the coverage beyond which the film starts sliding decreases with temperature. Similar measurements repeated on bare gold show an enhanced slippage of the Xe films and a decrease of the depinning temperature below 25 K. Nanofriction measurements of krypton and nitrogen confirm this scenario. This thermolubric behaviour is explained in terms of a recent theory of the size dependence of static friction between adsorbed islands and crystalline substrates.

O 36.44 Tue 18:30 P1

AFM and Raman investigations of epitaxial graphene nanoribbons — ●MALTE HALBAUER¹, JENS BARINGHAUS¹, CHRISTOPH NEUMANN², ANDRÉ MÜLLER², CHRISTOPH STAMPFER², and CHRISTOPH TEGENKAMP¹ — ¹Leibniz Universität Hannover, Institut für Festkörperphysik, 30167 Hannover, Germany — ²JARA-FIT and II. Institute of Physics A, RWTH Aachen University, 52074 Aachen, Germany

The synthesis of graphene nanoribbons (GNR) with well-oriented edges on a wafer-scale is a challenging task for the development of graphene based devices. Lithographic processing of graphene leads to a high amount of defects especially at the edges which destroy easily envisaged properties, e.g. ballistic edge channels. Hence, a self-organized growth of graphene nanoribbons is highly desirable. For this purpose we use the selective graphitization of refaceted SiC mesa structures. In order to reveal ideal growth parameters, the annealing processes have been studied and monitored by AFM as well as Raman spectroscopy. All heating steps have been performed in a face-to-face resistive heater. While AFM provides inside into the morphology of the mesa and facet structure, EFM has been used to record the local work function of the surface which is indicative for a selective growth of graphene nanostructures. The results correlate nicely with mappings of the 2D Raman signal indicating a successful growth of graphene nanoribbons. Best GNR structures have been obtained by annealing to 1200 °C for 20 min. For longer annealing times debunching of the initial MESA structure has been found as well as graphitization in between the ribbons.

O 36.45 Tue 18:30 P1

Chemical and Electronic Modification of Graphene via Reactive Landing of Hyperthermal Molecular Ion Beams — ●GIRJESH DUBEY¹, STEPHAN RAUSCHENBACH¹, ROBERTO URCUYO¹,

MARKO BURGHARD¹, and KLAUS KERN^{1,2} — ¹Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, Stuttgart — ²Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Tailoring the electronic properties of graphene by surface modification is of interest for switching devices and logic applications. However, chemical modification of graphene at stoichiometric densities is generally difficult, due to its low reactivity. One unique solution to this challenge is to collide energetic molecular ion beams (10-200 eV) at the surface of the *sp*²-hybridized basal plane. Upon impact, hyperthermal ion beams with energies considerably larger than that of a covalent bond (1-10 eV) are able to produce surface defects and create reactive fragments, leading to chemisorption. In this work, an electrospray ion beam deposition (ES-IBD) system is employed to carry out the modification in high vacuum. Singly charged cations of 4,4'-azobis(pyridine) are shown to reactively land on mechanically exfoliated and chemical vapor deposited graphene at moderate to high coverage. The resulting morphology, electronic transport properties, and vibrational spectra of the pyridine-functionalized surfaces are presented. These experiments highlight a facile approach for the controlled modification of graphene with a range of new molecules otherwise unreactive toward graphene by existing conventional methods.

O 36.46 Tue 18:30 P1

All-carbon vertical van der Waals heterostructures: Non-destructive functionalization of graphene for electronic applications — MIROSLAW WOSZCZYNA¹, ●ANDREAS WINTER², MIRIAM GROTHE¹, ANNIKA WILLUNAT², STEFAN WUNDRACK¹, RAINER STOSCH¹, THOMAS WEIMANN¹, FRANZ AHLERS¹, and ANDREY TURCHANIN² — ¹Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany — ²Faculty of Physics, University of Bielefeld, 33615 Bielefeld, Germany

We present a route to non-destructive functionalization of graphene via assembly of vertical all-carbon van der Waals heterostructures. To this end, we employ single-layer graphene (SLG) sheets grown by low-pressure methane CVD on Cu foils and large-area dielectric ~ 1 nm thick amino-terminated carbon nanomembranes (NH₂-CNMs) generated by electron-beam-induced crosslinking of aromatic self-assembled monolayers. We encapsulate SLG sheets on oxidized silicon wafers with NH₂-CNMs via mechanical stacking and characterize structural, chemical and electronic properties of the formed heterostructures by Raman spectroscopy and X-ray photoelectron spectroscopy as well as by electric and electromagnetic transport measurements. We unambiguously show that functional amino groups are brought in close vicinity of the SLG sheets and that their transport characteristics are not impaired by this functionalization; moreover, we demonstrate a functional response of the heterostructure devices to the protonation of the amino groups in water.

O 36.47 Tue 18:30 P1

Plasmons in graphene bilayers — ●PHILLIPP RECK¹, SAM SHALLCROSS², and OLEG PANKRATOV² — ¹Institut für Theoretische Physik, Universität Regensburg — ²Lehrstuhl für Theoretische Festkörperphysik, FAU Erlangen

Plasmons are the fundamental collective excitations in the electron system which underlie various many-body phenomena. In two dimensions, plasmons have a square root dispersion. For a double layer system an additional linear branch arises which features a finite gap at $q=0$ which is due to the interlayer tunneling [1]. Multilayer graphene stacks offer an interesting possibility for realizing such systems. Moreover, stacks with mutually rotated layers present a novel 2D system which is periodically modulated due to the moiré pattern [2]. It was found [3] that the moiré potential alters the one particle spectrum and induces Anderson-type localization at certain energies.

Our work aims at exploring the many-particle effects in these moiré systems, where at first we investigate plasmons in the RPA, using the low energy, homogeneous Mele Hamiltonians [4]. We find qualitatively the same results as in 2DEG. To include the inhomogeneity effects of the moiré potential we shall accordingly adopt the RPA scheme by including the most important coupling reciprocal vectors of the moiré periodicity [3].

[1] S. Das Sarma and E. H. Hwang, Phys. Rev. Lett. 81, 4216 (1998)

[2] S. Shallcross et al, PRB 81, 165105 (2010)

[3] S. Shallcross et al, PRB 87, 245403 (2013)

[4] E. J. Mele, PRB 81, 161405(R) (2010)

O 36.48 Tue 18:30 P1

"white graphene" on Ag(001) — ●SAMUEL GRANDTHYLL, KARIN JACOBS, and FRANK MÜLLER — Saarland University, Experimental Physics, D-66041 Saarbrücken

Monolayers of boron nitride (white graphene/h-BN) were grown via chemical vapor deposition of borazine on Ag(001) and characterized by X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). "The growth of h-BN on Ag(001) is the same as previously demonstrated for Ag(111), giving evidence that for weakly interacting transition metal surfaces the surface symmetry has no distinct impact on the h-BN growth." [1]

[1] F.Müller, S.Grandthyll, Surf. Sci. 617 (2013) 207.

O 36.49 Tue 18:30 P1

Hybrid heterostructures of zero-dimensional and two-dimensional carbon — ZHIKUN ZHENG^{1,2}, XIANGHUI ZHANG¹, ●CHRISTOF NEUMANN¹, ANDREAS WINTER¹, HENNING VIEKER¹, WEI LIU³, MARGA LENSEN², ARMIN GÖLZHAUSER¹, and ANDREY TURCHANIN¹ — ¹Faculty of Physics, University of Bielefeld, 33615 Bielefeld — ²Department of Chemistry, Technical University of Berlin, 10623 Berlin — ³Physical Chemistry and Electrochemistry, Technical University of Dresden, 01062 Dresden

Van der Waals heterostructures of free-standing two-dimensional (2D) materials open many avenues in the experimental physics and materials science of nanomaterials as they reveal unusual properties and phenomena. Here we present the fabrication of novel hybrid 0D/2D carbon-based heterostructures consisting of ~ 1 nm thick bifacial Janus Nanomembranes (JNMs) selectively functionalized with fullerenes (C60) or gold nanoparticles (AuNP) on one or both faces. We characterize the physical and chemical properties of the JNM/(C60-JNM)_n stacks with n=1, 2, 3 and 4 and individual C60-JNM-AuNP sheets in their supported and free-standing states by optical microscopy, helium ion microscopy (HIM), X-ray photoelectron spectroscopy (XPS) as well as by bulge tests with an atomic force microscope (AFM). We discuss these results and the possible application areas of the engineered hybrid heterostructures in nanotechnology.

O 36.50 Tue 18:30 P1

Ion Beam Characterisation with Graphene — ●IGOR ZAGORANSKIY, ROLAND KOZUBEK, OLIVER OCHEDOWSKI, and MARIKA SCHLEBERGER — Universität Duisburg-Essen, Duisburg, Deutschland

In ion irradiation experiments material modifications due to ion impacts are often studied as a function of fluence. A precise knowledge of the beam homogeneity and the spot size of the beam is therefore of utmost importance for the experiment. While the spot size analysis can be performed using a Faraday cup, the homogeneity has to be determined using a spatially resolving detector. These detectors are expensive and not applicable for every experimental setup. In our contribution we demonstrate that CVD graphene in combination with μ -Raman spectroscopy mapping can be applied as an ion beam detector which can be used to determine the fluence and beam homogeneity on the micron scale.

As an example we present data from an experiment where we irradiated a CVD graphene sample with an ion beam of highly charged Xe³⁵⁺ particles (260 keV). By analysing the D-band originating from the ion induced defects, the beam homogeneity, spot size and the actual size of the ion-induced defects can be determined.

O 36.51 Tue 18:30 P1

Damage in graphene and single layer hexagonal boron nitride due to electronic excitation induced by highly charged ions — ●ROLAND KOZUBEK, JOHANNES HOPSTER, OLIVER OCHEDOWSKI, and MARIKA SCHLEBERGER — Universität Duisburg-Essen, Duisburg, Deutschland

In this work, we demonstrate that single layers of exfoliated graphene sustain significant damage from irradiation with slow highly charged ions of different charge states ($q = 28-42$). By atomic force microscopy in lateral force mode we have observed nontopographical frictional defects induced by single ion impacts. To compare these results, we have repeated the experiment with single layers of hexagonal boron nitride (SL-hBN), which is an insulator with a bandgap of 5.5 eV. One can see, that the threshold potential energy for defect creation in graphene is much smaller than in SL-hBN, which can be explained by the classical over-the-barrier model. Here, the time of flight of the ion above the surface is the key parameter, which is varied in further studies by using different projectile velocities. From these experiments we expect

to be able to create large defective areas at low kinetic energies. In order to achieve this, a novel deceleration system was installed and tested at our setup.

O 36.52 Tue 18:30 P1

Two-photon photoemission study of gold-intercalated graphene on Ir(111) — ●DAVID NOBIS, DANIEL NIESNER, and THOMAS FAUSTER — Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen, Germany

We have investigated gold-intercalated graphene on Ir(111) as well as gold on clean Ir(111) using UV photoelectron spectroscopy (UPS) and two-photon photoemission (2PPE). Up to 5 monolayers (MLs) of gold were intercalated at several temperatures.

The measured work function of the Au/Ir system approaches the value of Au(111) after the deposition of 4 MLs of gold. In the graphene-covered case the work function (4.88 eV with 5 MLs gold) remains larger than expected [1]. The UPS spectra of Au/Ir(111) show a gold-related, upward-dispersing surface state around 0.47 eV below the Fermi level.

In the 2PPE spectra two image-potential states (IPS) are found. The second IPS shows a resonant transition from the Au surface state. The energetic positions of the IPS in combination with the large work function is evidence for incomplete intercalation of the gold. From the energetic spacing of the IPS the local work function of the intercalated areas is extrapolated to 4.69 eV which agrees with the calculated value of 4.74 eV [1]. With this local work function the binding energies of the first two IPS (0.85 eV and 0.21 eV) agree well with those measured on other graphene-covered noble-metal surfaces [2].

[1] Khomyakov, P. A. *et al.*, Phys. Rev. B **79** (2009) 195425

[2] Nobis, D. *et al.*, Phys. Rev. B **88** (2013) 195435

O 36.53 Tue 18:30 P1

Doping on Epitaxial Graphene on SiC with Molecular Adsorbates — ●MARTINA WANKE¹, ANTON TADICH², MARK EDMONDS³, LOTHAR LEY⁴, FELIX FROMM¹, YAOU SMETS³, CHRISTIAN RAIDEL¹, CHRISTIAN HEIDRICH¹, ZORAN MAZEJ⁵, JOHN RILEY³, CHRIS PAKES³, and THOMAS SEYLLER¹ — ¹TU Chemnitz, Institut für Physik, Germany — ²Australian Synchrotron, Soft-X-ray-Beamline, Clayton, Victoria, Australia — ³La Trobe University, School of Physics, Bundoora, Victoria, Australia — ⁴FAU Erlangen-Nürnberg, Institut für Festkörperphysik, Erlangen, Germany — ⁵Joseph Stefan Institute Ljubljana, Slovenia

Molecular doping of epitaxial graphene and quasi-freestanding graphene on SiC(0001) was used to tune the doping type character. Epitaxial graphene on SiC shows a strong intrinsic n-type character [1, 2]. It was possible not only to achieve charge neutrality as it was shown for F4-TCNQ [3,4], but to effectively p-type dope graphene by using of C60F48. While quasi-freestanding graphene is already p-type doped, it was possible to increase the amount of p-type doping. Angle-resolved photoemission was used to determine the amount of doping [3,4,5,6].

[1] T.Ohta, *et al.*, Science 313,951(2006). [2] J.Jobst, *et al.*, PRB 81,195434(2010). [3] W.Chen, *et al.*, JACS 129,10418(2007). [4] C.Coletti, *et al.*, PRB 81,235401(2010). [5] A.L.Walter, *et al.*, APL 98,184102(2011). [6] A. Tadich, *et al.*, APL 102, 241601 (2013).

O 36.54 Tue 18:30 P1

The Effects of Disorder and Defects on the Electronic Structure of Graphene — ●JONATHAN PARNELL¹, SINA HABIBIAN¹, KLAUS KERN^{1,2}, and CHRISTIAN AST¹ — ¹Max Planck Institute for Solid State Research, D-70569 Stuttgart — ²Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

A high electron mobility is one of the hallmarks of the two-dimensional graphene system. However, disorder and defects reduce the electron mobility, which places constraints on the different ways graphene can be modified. We simulate the effects of disorder and defects within graphene lattices on the electronic structure. For this we employ a simple real space tight-binding model. These simulations allow us to directly correlate theory and experiment by comparing the calculated results with angular resolved photo-emission data. In this way we can make a quantitative assessment of the density of the different types of defects with their signatures in the electronic structure.

O 36.55 Tue 18:30 P1

many-body interactions in the sigma band of graphene — ●FEDERICO MAZZOLA¹, JUSTIN WELLS¹, ROSITZA YAKIMOVA², SOREN ULSTRUP³, JILL MIWA³, RICHARD BALOG³, MARCO BIANCHI³, MATS

LEANDERSSON⁴, JOHAN ADELL⁴, PHILIP HOFMANN³, and THIAGARAJAN BALASUBRAMANIAN⁴ — ¹Department of Physics, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway — ²Department of Physics, Chemistry, and Biology, Linköping University, S-581 83 Linköping, Sweden — ³Department of Physics and Astronomy, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark — ⁴MAX IV Laboratory, Lund University, P.O. Box 118, 221 00 Lund, Sweden

Contrary to the case of Graphene's pi band structure, the deeper lying sigma bands have attracted little attention. Here we present a detailed study of the sigma band structure using angle resolved photoemission spectroscopy (ARPES). Graphene is prepared on different substrates and it is compared with graphite and quasi free standing graphene (graphene which is lifted up by oxygen intercalation after growth on Ir(111)). We find that such bands hide an unexpected large interaction close to the Gamma-bar point. A 'kink' deviates the band from the expected dispersion of a non-interacting band, and a corresponding broadening of the line width is seen. The experiment is supported by a numerical simulation of the many-body interaction, such that the nature of the kink can be probed. We conclude that electron phonon coupling plays a significant role and can satisfactorily account for the observed strong kink.

O 36.56 Tue 18:30 P1

An STM-study on the Electronic Properties of epitaxial Graphene using Thermovoltage Effects — ●PHILIP WILLKE¹, THOMAS DRUGA¹, ALEXANDER SCHNEIDER², and MARTIN WENDEROTH¹ — ¹IV. Physikalisches Institut, Georg-August Universität Göttingen, Germany — ²Lehrstuhl für Festkörperphysik, FAU Erlangen, D-91058, Germany

We study the electronic properties of epitaxial-grown mono- and bilayer graphene on SiC by locally mapping the thermovoltage: This quantity is obtained by compensating a finite current present due to the temperature difference between sample and tunneling tip by adjusting the tip-sample voltage. According to theory, this property is sensitive to the change in LDOS at the Fermi level. [1] Recently, it was demonstrated that thermovoltage experiments on epitaxial-grown graphene can be used to distinguish between different domain structures induced by wrinkles. [2] By mapping the thermovoltage in a low-temperature STM operating at 6 K, we can confirm the theoretical predictions given in [1] by comparing high-resolution spectroscopy and thermovoltage measurements. Moreover, we obtain information on the electron scattering behaviour on monolayer and bilayer graphene with the help of Fourier spectroscopy and we can also identify irregularities in the interface layer. This work was supported by SPP 1459 "Graphene".

[1] J. A. Stovng and P. Lipavsky, Phys. Rev. B 42, 9214-9216 (1990)

[2] J. Park *et al.*, Nanoletters 13(7) 3269-3273 (2013)

O 36.57 Tue 18:30 P1

An influence of parallel electric field on the dispersion relation of graphene - a new route to Dirac logics — JAKUB SOŁTYS¹, STANISŁAW KRUKOWSKI^{1,2}, JOLANTA BORYSIUK^{3,4}, and ●JACEK PIECHOTA¹ — ¹ICM, University of Warsaw, ul. Pawińskiego 5a, 02-106 Warszawa, Poland — ²Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warsaw, Poland — ³Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland — ⁴Faculty of Physics, University of Warsaw, ul. Hoza 69, 00-681 Warsaw, Poland

Ab initio density functional theory (DFT) simulations were used to investigate an influence of an electric field, parallel to single and multilayer graphene, on its electron dispersion relations close to the K point. It was shown that for both single layer and AAAA stacking multilayer graphene under an influence of a parallel field the dispersion relations transform to nonlinear ones. The effect, associated with the hexagonal symmetry breaking, opens a new route to high speed transistors and logical devices working in the Dirac regime. The implementation of such a device is presented.

O 36.58 Tue 18:30 P1

Study of Spin-Polarized Behaviour in Cobalt Decorated Graphene — ●EAMON MCDERMOTT¹, PAUL BAZYLEWSKI², GAP SOO CHANG², and PETER BLAHA¹ — ¹Institute of Materials Chemistry, Vienna University of Technology, Austria — ²Department of Physics & Engineering Physics, University of Saskatchewan, Canada

Advances in sub-monolayer PVD deposition of metals on graphene have allowed us to consider the possibility of decorating graphene with magnetic species in the hope of controlling its electronic structure. Density Functional Theory calculations performed using WIEN2k, a scalar-relativistic, all-electron LAPW code, shows an opening of the band-gap of model Co-graphene systems, including those with oxidized Co and Co dimer decoration. When force-relaxed, the graphene layer remains unbuckled, even in the presence of a Co surface underneath the decorating atoms. Additionally, states near the Fermi level become spin polarized, suggesting the possibility of fabricating half-metallic Co-graphene devices.

O 36.59 Tue 18:30 P1

Crystallographic Order and Decomposition of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ SMMs deposited on Various Substrates Analyzed by Means of KPFM and nc-AFM — AARON GRYZIA¹, ●TIMM VOLKMAN¹, ARMIN BRECHLING¹, ULRICH HEINZMANN¹, VERONIKA HOEKE², and THORSTEN GLASER² — ¹Molecular and Surface Physics, Bielefeld University — ²Anorganic Chemistry I, Bielefeld University

$[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ Single-Molecule Magnets (SMMs) consist of seven metal ions in its center and organic compounds and ligands in the periphery. On surfaces such as e.g. mica and HOPG, these organic parts and charge of 3+ play an important role regarding the adsorption of the molecule. For charge neutrality $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ needs thus counterions. The resulting dipole moment of the SMM layer influences the local contact potential difference (LCPD). We are able to determine the LCPD of the sample by using frequency modulated Kelvin Probe Force Microscopy (FM-KPFM) at UHV conditions. By means of molecular resolved nc-AFM we found a two-fold symmetry close to a four-fold symmetry in the structure of the on HOPG adsorbed SMM monolayer. The two lateral dimensions period matches the size of the molecule whereas these layers heights resemble the SMM's height. In addition we also observed layers with half the height of the molecules besides those of the full height. We interpret this observation as decomposition of $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$ into its molecular building blocks. These layers show a higher LCPD than the layers with full molecular height.

O 36.60 Tue 18:30 P1

Bottom-up creation of metal-organic magnetic molecules based on cyclooctatetraene — ●HASMİK HARUTYUNYAN¹ and DANIEL WEGNER² — ¹Westfälische Wilhelms-Universität Münster — ²Westfälische Wilhelms-Universität Münster

Single molecule magnets (SMM) are metal-organic complexes where the spin is mostly carried by transition-metal atoms (3d or 4f), while the coupling is mediated by organic ligands. Due to their large size it is very difficult to deposit SMMs onto a surface under ultrahigh vacuum conditions. An alternative way is the creation of magnetic molecules in a bottom-up fashion. Here we show that single cyclooctatetraene (COT) molecules can be connected to isolated 3d-transition metal atoms (Fe, Co) by self-assembly or via atomic manipulation using a scanning tunneling microscope (STM) at low temperature. Experiments have been performed on a Au(111) and a Ag(100) substrate. We compare the structural and electronic properties as gained from STM and tunneling spectroscopy (STS). The results will also be compared with theoretical predictions, and a strategic route toward COT-based SMMs will be shown.

O 36.61 Tue 18:30 P1

Total Internal Reflection Ellipsometry to detect ultrathin adsorbed films — ●LEI WANG, IGOR SIRETANU, MICHÈL DUITS, and FRIEDER MUGELE — Physics of Complex Fluids, MESA+ Institute for Nanotechnology, University of Twente P.O. Box 217, 7500 AE Enschede, The Netherlands

To understand the adsorption/desorption of polar components of crude oil (model "asphaltene") onto polar (model "rock") substrates, is of great importance for optimizing the enhanced oil recovery (EOR) process via low salinity water flooding. However, much is still unknown from the molecular aspects about this process, and many components have to be screened. Total Internal Reflection Ellipsometry (TIRE) is capable of detecting ions or small molecules adsorbed at solid-liquid interfaces. In this work, the TIRE setup integrated with combinatorial microfluidics, enables parallel measurements on one substrate, making it a fast screening technique. Detection limit of this setup is 0.2 ng/cm², and the sensitivity is demonstrated via the adsorption of Ca²⁺ at silica-water interfaces. Experimental evidences show that these adsorbed calcium ions enable the adsorption of Hexanoic Acid (HA), and the adsorbed HA film desorbs gradually when decreasing

the salinity of flooding solutions, which is in consistent with the observations in EOR.

O 36.62 Tue 18:30 P1

Computational screening of functionalized zinc porphyrins for dye sensitized solar cells — ●KRISTIAN BARUËL ØRNSØ, JUAN MARIA GARCIA-LASTRA, and KRISTIAN SOMMER THYGESEN — Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

The search for sustainable energy sources has been intensified during the past years and Dye Sensitized Solar Cells (DSSC) have since the emergence of the first efficient system in 1991[1] received extensive attention due to the promising nature of these in terms of cost efficiency and flexibility.[2] Commonly, either zinc porphyrins or ruthenium based dyes are used combined with the I-/I₃- redox pair as electrolyte in an acetonitrile solvent. The advantage of the porphyrin based dyes are the large absorption of visible light and the straightforward customizability by introducing side groups. We exploit this feature by presenting the calculated frontier energy levels, orbitals, and optical gaps for 1029 systematically functionalized zinc porphyrin dye candidates. Based on this we investigate trends in the selective tuning of energy levels and orbital shapes and estimate a (loss-less) DSSC level alignment quality of the candidate molecules.[3]

References: [1] B. O'Regan, and M. Grätzel. Nature, 1991, 353, 737-740. [2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson. Chem. Rev., 2010, 110, 6595-6663. [3] K. B. Ørnsø, J. M. Garcia-Lastra, and K. S. Thygesen. Phys. Chem. Chem. Phys., 2013, 15, 19478-19486.

O 36.63 Tue 18:30 P1

Tuning the conductance of an unimolecular organic junction — ●BOGDANA BORCA¹, VERENA SCHENDEL¹, IVAN PENTEGOV¹, ULRIKE KRAFT¹, HAGEN KLAUK¹, PETER WAHL^{1,2}, UTA SCHLICKUM¹, and KLAUS KERN^{1,3} — ¹Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany — ²School of Physics & Astronomy, University of St Andrews, St Andrews, KY16 9SS, UK — ³Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

To improve and realize future molecular based electronic devices, a good understanding of electronic properties at the individual molecular level and possible ways to tune the intrinsic properties of the charge transport through unimolecular junctions are needed. Scanning Tunneling Microscopy and Spectroscopy (STM/STS) represent an ideal tool to characterize and manipulate single atoms and molecules on surfaces. We investigate the behavior of the conductance of pentacene and one of its thioacenes derivatives, thiotetracen, with a low temperature (6.7K) STM. The organic molecules are thermally evaporated under UHV conditions on a clean Cu(111) surface. The submolecular resolution of the STM allows contacting individual molecules at the desired site and measure the flow of the electrical current through this metal-molecular-metal junction. In terms of conductance, a difference is observed between pentacene and the sulfur-containing structure. In addition, the functionalized side of the thiotetracene molecule may be bonded to a metallic adatom or to a molecule, varying the conductance in this way by a gating-like mechanism.

O 36.64 Tue 18:30 P1

Functionalization of 6H-SiC(0001) and quartz surfaces with benzo[ghi]perylene-1,2-dicarboxylic anhydride dye through different organic linker molecules — ●DEB KUMAR BHOWMICK¹, MANFRED BARTSCH¹, LINDA STEGEMANN², CRISTIAN A. STRASSERT², and HELMUT ZACHARIAS^{1,2} — ¹Physikalisches Institut, Westfälische Wilhelms-Universität, 48149 Münster, Germany — ²Center for Nanotechnology (CeNTech), Westfälische Wilhelms-Universität, Münster, Germany

Due to different band gaps of semiconductors which control the electronic interactions between substrates and adsorbates, the hybrid semiconductor-organic interfacial systems have versatile applications like transistors, microelectronics, and biosensor. The covalent functionalization gives the stability to the hybrid system [1]. In this study we have chemically functionalized benzo[ghi]perylene-1,2-dicarboxylic anhydride dye on 6H-SiC and quartz surfaces through three different silane linker molecules, e.g., 11-aminoundecyl triethoxysilane (AU-DTES), 3-aminopropyl triethoxysilane (APTES), para-aminophenyl trimethoxysilane (PAPTMS). These linkers have different electron conductivities [2]. These systems are characterized by ATR-IR and XPS, and are further studied by confocal fluorescence microscopy. These

fluorescence measurements show a gradual decrease of the fluorescence lifetime from 7.6 ns to 1.3 ns from a non-conductive to a conductive linker.

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O 36.65 Tue 18:30 P1

Surface melting of ice — ●M.ALEJANDRA SÁNCHEZ¹, MARC-JAN VAN ZADEL¹, PATRICK BISSON², MARY J. SHULTZ³, MISCHA BONN¹, and ELLEN H.G. BACKUS¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Dartmouth College, Thayer School of Engineering at Dartmouth, Hanover, USA — ³Laboratory for Water and Surface Studies, Chemistry Department, Tufts University, Medford, USA

Although ice is omnipresent on earth and in the atmosphere, its surface is poorly understood. It is well-known that a liquid-like layer is present on the surface of ice far below the bulk melting temperature of ice. However, there is intense debate on the microscopic nature of this interfacial melt. By using single crystal ice samples and Sum Frequency Generation (SFG) surface-specific vibrational spectroscopy, we aim to elucidate the nature of this layer. With SFG we obtain the vibrational spectrum of solely the interfacial molecules. Single Ih crystals rods of 2.5 cm diameter with a length of 20 cm are grown in a homebuilt ice machine based on the Bridgeman-Stockbarger method. By comparing SFG spectra at different temperatures varying from liquid water to ice, we obtain information about the hydrogen bond strength, and thus the nature, of the interfacial water molecules. Preliminary results show that at 258 K the water molecules are more strongly bonded than in liquid water at 293 K. In the future we will perform time resolved-SFG to elucidate the reorientational dynamics of the molecules at different temperatures, which gives additional information about the molecules' binding strength.

O 36.66 Tue 18:30 P1

Experimental and theoretical studies of water orientation at the CaF₂ interface at different pH. — ●MARIA JOSE PEREZ-HARO¹, REMI KHATIB², MISCHA BONN¹, MARIALORE Sulpizi², and ELLEN H.G. BACKUS¹ — ¹Max Planck Inst Polymer Res, D-55128 Mainz, Germany — ²Johannes Gutenberg Univ Mainz, Dept Phys, D-55099 Mainz, Germany

The molecular arrangement of water molecules at solid-aqueous interfaces is important in numerous areas of science. It is very challenging to obtain molecular insights into this type of interfaces. We present here a combined experimental and theoretical approach to obtain those molecular insights into water at the interface between CaF₂ and aqueous solutions at different pH.

The experimental results have been obtained with the surface-sensitive spectroscopy technique Vibrational Sum Frequency Generation (SFG), and the recently developed expansion of this technique: phase-sensitive SFG. The vibrational spectrum of the interfacial water molecules thus obtained with SFG reflects the organization and arrangement of interfacial water. We have unraveled the structure, including the absolute orientation of the water molecules at the interface. We clearly see an orientation inversion, 'flip-flop', of the water molecules as the pH of the aqueous phase is changed from acidic to alkaline. The experimental spectra are compared to calculated spectra obtained from first principles molecular dynamics simulations. This comparison provides new insight in the molecular species present at the interface.

O 36.67 Tue 18:30 P1

Porous glass - epoxy interfaces investigated with an Atomic Force Microscopy — ●ALEKSANDER OSTROWSKI, MARLENA FILIMON, JÖRG BALLER, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg

There has been a great interest in the field of interphases and interfaces in recent years. The understanding of phenomena occurring on the border of two materials is crucial in development of modern compounds. In this work we present the results of investigation performed for the porous glass * epoxy resin systems. The epoxy applied on porous glass penetrates its pores with an extent dependent on the pore size, temperature and epoxy components mixing ratio. Our study presents characterization of porous-glass/epoxy interfaces with the use of Atomic Force Microscopy.

O 36.68 Tue 18:30 P1

Porous glass - epoxy interfaces investigated with an Atomic

Force Microscopy — ●ALEKSANDER OSTROWSKI, MARLENA FILIMON, JÖRG BALLER, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg

There has been a great interest in the field of interphases and interfaces in recent years. The understanding of phenomena occurring on the border of two materials is crucial in development of modern compounds. In this work we present the results of investigation performed for the porous glass - epoxy resin systems. The epoxy applied on porous glass penetrates its pores with an extent dependent on the pore size, temperature and epoxy components mixing ratio. Our study presents characterization of porous-glass/epoxy interfaces with the use of Atomic Force Microscopy.

O 36.69 Tue 18:30 P1

STM and AFM investigations of [OMIm]Tf₂N on Graphite — ●RENE GUSTUS^{1,2}, TIMO CARSTENS¹, OLIVER HÖFFT¹, and FRANK ENDRES¹ — ¹Institut für Elektrochemie, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany — ²Institut für Energieforschung und Physikalische Technologien, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany

Electrochemical reactions can always be explained by the interaction of an electrochemically active solution with a solid surface. Besides aqueous solutions, Ionic Liquids (IL) have become an integral part of scientific research especially in electrochemistry but also in different fields of research like catalysis and solar cells, to name only a few. In this regard the physical and chemical properties of the liquid/solid interface like the adsorption mechanisms or the structure formation of the IL near the solid surface are of great interest. Here we investigated the interaction of [OMIm]Tf₂N with a graphite surface (Highly Ordered Pyrolytic Graphite - HOPG) by means of scanning tunnelling (STM) and atomic force microscopy (AFM). In a first step in-situ STM measurements in an electrochemically controlled environment were performed. In addition we studied the adsorption of monolayers of [OMIm]Tf₂N under UHV conditions. Therefore IL films with different thicknesses were prepared on clean HOPG by evaporation in UHV and were subsequently investigated by STM and AFM using especially force distance curves to study a potential layering of the IL at the interface.

O 36.70 Tue 18:30 P1

Characterization of 1-octyl-3-methyl-imidazolium chloride interfaces with Photoelectron Spectroscopy and Metastable Induced Electron Spectroscopy — ●MARCEL MARSCHEWSKI¹, WOLFGANG MAUS-FRIEDRICH¹, VOLKER KEMPTER¹, ANGELA ULBRICH², STEFAN KRISCHOK², FRANK ENDRES³, and OLIVER HÖFFT³ — ¹Institut für Energieforschung und Physikalische Technologien, TU Clausthal, 38678 Clausthal-Zellerfeld, Germany — ²Institut für Physik und Institut für Mikro- und Nanotechnologien, TU Ilmenau, 98684 Ilmenau, Germany — ³Institut für Elektrochemie, TU Clausthal, 38678 Clausthal-Zellerfeld, Germany

Room temperature Ionic Liquids are a class of materials, which has recently gained enormous interest. Due to the low vapour pressure ionic liquids interfaces can be investigated with photoelectron spectroscopy (UPS/XPS) and metastable induced electron spectroscopy (MIES). In this study we investigate the liquid solid and liquid vacuum interfaces of 1-octyl-3-methyl-imidazolium chloride ([OMIm]Cl). For the analysis of the solid/liquid interface we have prepared monolayers of [OMIm]Cl on Si(100) by vapour deposition at room temperature. The obtained data are compared with results for the multilayer films. The electron spectra of thick [OMIm]Cl films indicate, that the alkyl chain sticks out of the surface. The chlorine induced feature is not detected in the MIES spectra and the anion seems to be completely buried under the alkyl chain. In the monolayer case, due to the visibility of the chlorine feature in MIES, our results indicate a more flat adsorption of alkyl chains of the cation.

O 36.71 Tue 18:30 P1

The evaporation of nanodroplet on a chemically heterogeneous substrate — ●JIANGUO ZHANG, FRÉDÉRIC LEROY, and FLORIAN MÜLLER-PLATHE — Eduard-Zintl-Institut für Anorganische und Physikalische Chemie and Center of Smart Interfaces, Technische Universität Darmstadt, Alarich-Weiss-straße 4, D-64287 Darmstadt, Germany

The pinning phenomenon which causes a constant contact line model (CCL) was often experimentally observed in the evaporation of droplet on a substrate. It is usually believed that the pinning was originated

from the substrate's chemical [1] or/and topographical (rough)[2] heterogeneities. The effect of the topographically heterogeneous surface on the evaporation has been investigated recently by deposited a droplet on a pillared surface[3]. The pinning as well as the CCL model resulted from the roughness was confirmed. However, the chemical heterogeneity effect on the evaporation is still unknown. Here, the evaporation of nanodroplet on a chemically striped substrate has been studied by molecular dynamics simulations. Our results indicate that the chemical heterogeneity can indeed cause pinning and the CCL model when the strip width is larger than 2σ (σ is the atom diameter). Moreover, a slip-jump-stick pattern was observed for the motion of the contact line. The mechanisms for each phase of the pattern have been explored.

[1] P. S. Swain and R. Lipowsky, *Langmuir*, 14(1998), 6772. [2] P. Lenz and R. Lipowsky, *Eur. Phys. J. E* 1(2000), 249. [3] X. Chen, R. Ma, et al, *Phys. Rev. Lett.* 109(2012), 116101.

O 36.72 Tue 18:30 P1

Electrocatalytic activity of structurally well defined AgPt/Pt(111) monolayer 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

Bimetallic surface alloys often show an electrochemical and catalytic behavior very different from that of the respective metal components. This is evident, e.g., in the oxygen reduction reaction (ORR), where Pt is known to be the best single metal catalyst, but modification with transition or noble metals, such as Ni, Co, Cu has been found to result in an improved reactivity.[1]

In this work we report first results on the electrochemical and -catalytic properties of well defined $\text{Ag}_x\text{Pt}_{1-x}$ surface alloys with different amounts of Ag (0% - 100% Ag) on Pt(111). The surface alloys were prepared under ultra high vacuum (UHV) conditions by evaporation of Ag on Pt(111), followed by annealing to 900 K to form a surface alloy. From 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) can be determined. Subsequently the surfaces are characterized in an electrochemical flow cell on their ORR activity in sulfuric acid. Finally structural properties are discussed in comparison with electrochemical activity and theoretical predictions and will be compared to findings for $\text{Au}_x\text{Pt}_{1-x}/\text{Pt}(111)$. [2]

[1] J. Greeley et al., *J.Phys.Chem.* 113 (2009) 4932, [2] S. Brimaud et al., *J.Electroanal.Chem.*, 2013, in press.

O 36.73 Tue 18:30 P1

Atomistic modeling of solid-liquid interface ordering and its effect on the growth kinetics of metallic alloys. — ●MOHAMMED GUERDANE and BRITTA NESTLER — Karlsruhe Institute of Technology (KIT) Institute of Applied Materials - Reliability of Components and Systems (IAM-ZBS)

The structure of solid-liquid interfaces remains an open question in condensed-matter science. Understanding this structure is of particular importance because its crucial influence on various physical phenomena such as freezing, wetting, and capillary osmosis. We illustrate here how local ordering in a metallic melt (NiZr) can transform into a massive in-plane ordering at the surface of a crystal (bcc Zr) when the solute-centered clusters of the melt match the periodic potential of the crystal surface. Linking molecular dynamics simulation to phase-field modeling allows to estimate quantitatively the influence of the surface effect on the growth kinetics. Furthermore, our study suggests a possibility to give experimental evidence for the existence of the structural units of the melt by capturing them at suitable interfaces.

O 36.74 Tue 18:30 P1

Low-temperature UHV-STM investigation of adsorbed H_2O on metal surfaces — ●MARTIN SCHILLING, ALBERT K. ENGSTFELD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

A better understanding of the elementary electrochemical/-catalytic processes on bimetallic electrode surfaces requires a detailed understanding of the solid-liquid interface, including the water-solid interaction. The latter has been studied in detail earlier, using model systems consisting of ice layers adsorbed on single crystal metal surfaces.[1]

Following these lines, we investigated the interaction of H_2O with catalytically relevant mono- and bimetallic single crystal surfaces. Here we report *in situ* scanning tunnelling microscopy results obtained at variable temperatures (VT-STM, 95 K - RT). Submonolayers of H_2O

were deposited under well defined conditions under ultra high vacuum (UHV) at low temperature (~ 95 K) on single crystal surfaces such as Au(111) or Ru(0001). Depending on the dosing conditions (H_2O pressure, dosing rate, sample temperature), the thermal treatment and the substrate, the deposited H_2O was found to form monolayer and/or multilayer islands or three-dimensional clusters. Correlations between structure and deposition/post-treatment conditions are discussed.

[1] P.A. Thiel and T.E. Madey, *Surf. Sci. Rept.* 7 (1987) 211-385

O 36.75 Tue 18:30 P1

Electrocatalytic activity and stability of Pt nanoparticles on Ru(0001) supported graphene — ●JENS KLEIN, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Pt-based catalysts consisting of carbon supported Pt nanoparticles are widely used, e.g. in fuel cell technology, and it is well known that the performance of these catalysts depends sensitively on the size, density, shape and stability of the Pt nanoparticles.

Here we present results of a model study on the activity and stability of small Pt nanoparticles with narrow size distributions and mean sizes between some 10 - 20 atoms and below 3nm, which were grown on Ru(0001)-supported graphene. The graphene monolayers were prepared under ultra high vacuum (UHV) by ethylene decomposition on Ru(0001) at 1050 K. Pt cluster/nanoparticle arrays with well known particle- and size-distributions were formed by physical vapor deposition of Pt and characterized by scanning tunneling microscopy (STM).[1] The electrodes were subsequently transferred to an electrochemical flow cell attached to the UHV system, to investigate their electrochemical properties and the electrocatalytic activity during CO oxidation. In a last step, the samples were transferred back to the UHV for STM characterization, to evaluate the stability of the particles and correlate the results from the electrochemical measurements with the change in particle sizes and distributions.

[1] Y.Han, A.K. Engstfeld, R.J. Behm, J.W. Evans, *J. Chem. Phys.* 138, 134703 (2013).

O 36.76 Tue 18:30 P1

Preparation of smooth and unreconstructed Pt(100)-(1x1) — ●KLAUS MEINEL¹, FLORIAN SCHUMANN¹, BENJAMIN KÖHLER¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck Institut für Mikrostrukturphysik, Halle, Germany

Pt(100) is known for its Pt(100)-hex reconstruction where a compressed quasihexagonal top layer is formed. For specific applications, the non-reconstructed quadratic (1x1) structure is desired. Surface reconstruction can be lifted by adsorbates. Using HREELS and LEED we show that upon exposure to Ar sputter gas in the presence of electrons an effective C_2H_x adsorption takes place from the background which immediately lifts reconstruction. In STM, the resulting (1x1) surface appears extremely rough due to numerous two-dimensional islands (size 3 nm) formed by the surplus Pt atoms. Surface smoothing by intralayer diffusion at temperatures above 300 °C fails as the surface reconstruction recovers from small islands. Surface smoothing without reconstruction is attained by activating step edge diffusion at temperatures around 100 °C which promotes Smoluchowski ripening of the islands. When the island size increases to about 10 nm, islands no longer promote the surface reconstruction and allow pronounced Ostwald ripening even at temperatures around 450 °C. This yields a smooth surface which displays only large 2D islands. During annealing the surface remains covered by C_2H_x showing after Ostwald ripening a $(\sqrt{2}\times\sqrt{2})R45^\circ$ structure. Final cleaning is attained by annealing in O_2 atmosphere at 150 °C at which adsorbates desorb as CO and H_2O .

O 36.77 Tue 18:30 P1

Setup of a HHG-ARPES experiment with sub-femtosecond XUV pulses — ●JÜRGEN SCHMIDT¹, SABBIR AHSAN², ALEXANDER GUGGENMOS¹, SOO HOON CHEW¹, and ULF KLEINEBERG¹ — ¹LMU Physics Department, Munich, Germany — ²KTH Royal Institute of Technology, Stockholm, Sweden

Attosecond electron streaking spectroscopy from solids using single attosecond XUV pump pulses and few-cycle IR streaking pulses has recently revealed first insight into the temporal dynamics of the photoemission process with unprecedented temporal resolution of 100 as [1]. Due to the inherent nature of the energy streaking of the liberated electrons in the IR polarization field, only electrons emitted perpendicular from the surface have been recorded. Our experimental setup

however aims for both time- and angle-resolving photoelectron spectroscopy (TR-ARPES) revealing information about the sub-fs temporal band structure dynamics in energy and momentum space after transient excitation by few-cycle NIR laser pulses. Especially materials with high correlated electron systems (such as high T_c materials, exchange split materials or topological insulators) give indications for electron dynamics on a sub-fs time scale. As a proof of principle experiment we report about the setup and first measurements on a tungsten (110) surface.

[1] Cavalieri et al, Nature 449, 1029 (2007)

O 36.78 Tue 18:30 P1

Iron surfaces in a sour gas environment — ●MEHMET ALI ILHAN, MIRA TODOROVA, and JÖRG NEUGEBAUER — Department for Computational Material Design, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

Low alloyed steels are particularly susceptible to sour gas corrosion, which leads to the formation of iron sulfides. The developing corrosion products typically do not form protective layers and have no passivating effect. Knowledge of the structure, stability and adhesion of such corrosion products is essential to the evaluation and improvement of their protective properties.

To address these questions we study the interactions of S, H and O with the (100) surfaces of bcc Fe by density-functional theory calculations. We find that the competition between adsorbates can cause H to be pushed below the surface, when S occupies the hollow surface adsorption sites it prefers, while O/H co-adsorption leads to the formation of OH-groups. Increasing S coverage, on the other hand, leads to the formation of a layered structure, with loosely bound interatomic layers, which resembles Mackinawite (tetragonal FeS). The insight we gain from our calculations, regarding the protective behaviour of the forming corrosion products, will be discussed.

O 36.79 Tue 18:30 P1

Adsorbate nanomesh causes lateral periodicity of segregation: Ab-initio study for h -BN on $Pt_{50}Rh_{50}(111)$ — ●WOLFGANG HECKEL¹, TOBIAS C. KERSCHER¹, ROLAND STANIA², IRAKLI KALICHAVA³, JUERG OSTERWALDER², PHIL WILLMOTT³, BERND SCHÖNFELD⁴, THOMAS GREBER², and STEFAN MÜLLER¹ — ¹Hamburg University of Technology, Institute of Advanced Ceramics — ²Universität Zürich, Physik-Institut — ³Paul Scherrer Institut Villigen, Swiss Light Source — ⁴ETH Zürich, LMPT

The segregation profile of Pt–Rh surfaces strongly depends on the presence of adsorbates; e.g., at the top layer, the clean surface favors Pt enrichment, yet a small amount of C adsorbates leads to a significant depletion of Pt there [1]. Pt–Rh also serves as a substrate for self-assembled 2d adsorbate layers such as boron nitride (h -BN). The experiments on h -BN/ $Pt_{50}Rh_{50}(111)$ show a corrugated, honeycombed 11×11 nanomesh adsorbate layer caused by the lattice constant mismatch of substrate and adsorbate. We present an ab-initio study combining DFT data and a cluster–expansion approach with UNCLE [2]. We elucidate the laterally periodic segregation profile of $Pt_{50}Rh_{50}(111)$ caused by h -BN. Our results perfectly confirm the experiment: Beneath the pores of the nanomesh the segregation profile shows a strong Rh enrichment, while beneath the wires the topmost layer favors platinum. By this, the h -BN layer induces a segregation profile with a lateral periodicity according to its honeycombed nanomesh.

[1] Kerschker et al., Phys. Rev. B **86**, 195420 (2012)

[2] Lerch et al., Modelling Simul. Mater. Sci. Eng. **17**, 055003 (2009)

O 36.80 Tue 18:30 P1

Antiferromagnetic coupling in Mn_2 on $Ag(111)$ induced by H attachment — ●TORSTEN SACHSE^{1,2}, NICOLAS NÉEL^{1,3}, RICHARD BERNDT³, WERNER HOFER², and JÖRG KRÖGER¹ — ¹Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau — ²Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool L69 3BX, Britain — ³Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel

Manganese dimers on $Ag(111)$ are investigated with scanning tunneling microscopy (STM) and density functional calculations. Two species of dimers coexist that differ in their apparent height and the absence or presence of submolecular structure. These species can be interconverted by electron and hole injection from the microscope tip. Calculations identify the two kinds of dimers as pristine Mn_2 and Mn_2H and show that hydrogen attachment to Mn_2 leads to marked changes in the

dimer electronic and magnetic structure. Simulated constant-current STM images are in good agreement with the experimental data. The calculations further reveal an antiferromagnetic coupling of Mn magnetic moments in Mn_2H .

O 36.81 Tue 18:30 P1

Image-Potential States on close-packed magnetic surfaces — ●BEATRICE ANDRES, MARC CHRIST, MARKO WIETSTRUK, and MARTIN WEINELT — Fachbereich Physik, Freie Universität Berlin, 14195 Berlin

The close-packed surfaces of ferromagnetic materials exhibit various surface states. One type are image-potential states (IPS). Located in front of the surface with a part of the probability density inside they overlap with the exchange-split bulk bands. This results in a small exchange splitting in the IPS. Due to spin conservation under laser excitation they act as excellent spin-filters in two-photon photoemission (2PPE) reflecting the spin-dependent properties of the bulk band structure.

We use spin- and time-resolved 2PPE to investigate the $n = 1$ IPS on Gd(0001), Ni(111) and Fe(110) thin films all grown *in situ* on a W(110) substrate. We find the exchange splitting of the IPS scales with a factor of 3% to that of the valence bands.

The lifetimes of electrons excited to the initially unoccupied IPS show nearly no spin dependence on Ni(111) but differ by a factor of two on Fe(110) depending on the amount of majority and minority decay channels. The temporal evolution of the spin-dependent linewidths in 2PPE serves as an indicator for quasi-elastic scattering rates which were found to be mediated by magnon emission on Fe(001) while we find no influence of magnons on Ni(111).

O 36.82 Tue 18:30 P1

magnetic properties of iron and cobalt nanostructures fabricated by focused electron induced processing — ●FAN TU, MARTIN DROST, FLORIAN VOLLNHALS, ESTHER CARRASCO, ANDREAS SPÄTH, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058, Erlangen, Germany

Thin film nanostructures have wide-spread potential applications. With our specific approach to focused electron beam induced processing (FEBIP), we are able to fabricate clean nanostructures on surfaces with full lithographic control from adsorbed precursor molecules. With metal-organic precursors such as iron pentacarbonyl ($Fe(CO)_5$) and cobalt tricarbonyl nitrosyl ($Co(CO)_3NO$), we report the fabrication of clean metallic nanostructures with lateral dimensions as small as 15 nm[1]. In this contribution, we investigate Fe, Co and mixed Fe/Co nanostructures using laterally resolved X-ray absorption spectroscopy (XAS) to access the spatial chemical composition, and for the characterization of the magnetic properties X-ray magnetic circular dichroism (XMCD) was employed[2]. The bulk composition and the magnetic properties will be presented and discussed.

Supported by the DFG via grant MA 4246/2-1 and Excellence Cluster "Engineering of Advanced Materials (EAM)" at the FAU Erlangen-Nürnberg and two granted beamtimes at the PoLux instrument at the Swiss Light Source (SLS).

[1] M.M. Walz et al., Angw. Chem. Int. Ed., 49 (2010), 4669;

[2] G. Schütz et al., Phys. Rev. Lett., 58(1987), 737.

O 36.83 Tue 18:30 P1

Magnetic interactions and spin dynamics in one-dimensional ordered alloys at step edges of vicinal Pt surfaces. — ●OLEG P. POLYAKOV^{1,2}, OLEG V. STEPANYUK^{1,2}, DMITRY I. BAZHANOV^{1,2}, ALEXANDER M. SALETSKY¹, and VALERI S. STEPANYUK² — ¹Faculty of Physics, Moscow State University, GSP-1, Lenin Hills, 119991 Moscow, Russia — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

Properties of low-dimensional atomic structures is a subject for intensive experimental and theoretical investigation in recent years. One of the most notable systems for further fundamental investigation are atomic chains and wires deposited on various surfaces [1]. In this work we present the first-principles study of the magnetic behavior in transition metals (TM=Mn, Fe, Co, Ni) based one-dimensional monatomic and alloyed wires on vicinal Pt(111) surfaces which could be deposited at their step edges. We demonstrate that atomic wires can exhibit ferromagnetic or anti-ferromagnetic orderings due to their atomic structure and interatomic exchange interactions between different atoms and atom types (TM-TM, TM-Pt) at step edges. We find that the value of exchange interaction between TM atoms in atomic wires can be drastically changed or switch a sign by Pt atoms incoming from the

step edges. Also, we show that magnetic anisotropy energy is strongly affected in that case. The spin-dynamics is investigated by means of kinetic Monte Carlo method based on transition-state theory. This work was supported by the RFBR grant RFBR N13-02-01322.

[1] P. Gambardella et al. Nature (London) 416, 301 (2002).

O 36.84 Tue 18:30 P1

FeNi nanoparticle deposition on a W(110) surface — ●MATTHIAS WERNER, HENDRIK BETTERMANN, and MATHIAS GETZLAFF — Institute of Applied Physics, University of Duesseldorf

By a continuously working arc cluster ion source (ACIS), nanoparticles consisting of Fe and Ni with equal amount are prepared and deposited under UHV and soft-landing conditions on a W(110) surface. The composition is defined by the alloy of the anode in the cluster source, in our case it is Fe₅₀Ni₅₀. Using this preparation procedure the nanoparticles are charged which allows a mass separation by an electrostatic field unit. Our experimental setup enables us to generate particles with diameters from 4 nm to about 15 nm. Size and shape of the deposited nanoparticles are determined by STM as these properties are expected to be mainly responsible for their electronic and magnetic behaviour.

O 36.85 Tue 18:30 P1

Preparation of 3d nanoparticles by magnetron sputtering and deposition on a W(110) surface — ●MAREK WILHELM, HENDRIK BETTERMANN, and MATHIAS GETZLAFF — Institute of Applied Physics, University of Duesseldorf

The scientific research of nanoparticles is a broad interdisciplinary area of research, development and industrial activity. Our work is focused on the electronic and the magnetic behaviour which depends on the size and structure of particles. This contribution has an emphasis on FeNi alloy nanoparticles deposited on a W(110) surface. The particles are generated by a magnetron sputter source and subsequently mass selected in a quadrupole. Magnetron sputtering is possible due to thin sputter targets. Scanning Tunneling Microscopy (STM) is the main method to study these objects. The whole measurement system works in an ultra high vacuum environment in the order of $5 \cdot 10^{-10}$ mbar. We will report on our first results of this setup concerning size and structural properties of FeNi nanoparticles with diameters up to 5 nm.

O 36.86 Tue 18:30 P1

Inelastic electron-phonon interaction: towards first principle calculations — ●FLORIAN RITTWEGER¹, NICKI F. HINSCHKE², and INGRID MERTIG^{1,2} — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, DE-06120 Halle — ²Martin-Luther-Universität, Institut für Physik, Von-Seckendorff-Platz 1, DE-06120 Halle

The many-body effect of the electron-phonon interaction is under investigation for a long time due to its basic influence on the phenomena of superconductivity.

While experimental access is given by ARPES measurements, the theoretical studies are related to the computation of the complex electron-phonon self-energy. Within this approach the renormalization of the electronic band structure and the finite lifetime τ of the states can be determined and the electron-phonon coupling strength λ can be obtained. Usually the calculations of τ , λ , etc. are done assuming a quasi-elastic scattering process, i.e. only states on the Fermi surface are considered. Within this conventional approach, phenomena like the phonon drag contribution to thermopower, can not be reproduced by first principle calculations.

Going beyond the quasi-elastic assumption we investigate the inelastic electron-phonon interaction using linear response density functional perturbation theory to study the impact on τ , λ and transport properties like the electrical conductivity, thermal conductivity and the thermopower. First results and discussions involving simple metals, i.e. Al and Cu, will be presented.

O 36.87 Tue 18:30 P1

Electron-phonon self-energy in the KKR formalism — ●CARSTEN EBERHARD MAHR, MARCEL GIAR, and CHRISTIAN HEILIGER — Justus-Liebig-Universität, 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 Korringa-Kohn-Rostocker (KKR) Green's function formalism code.

Instead of including the electron-phonon coupling in the Kohn-Sham

Hamiltonian via an adjusted effective potential V_{eff} , we calculate the Green's function of the 'free' system (i.e., free of electron-phonon coupling) and employ Dyson's equation $G = G_{\text{free}} + G_{\text{free}} \Sigma_{\text{e-ph}} G$ to obtain the dressed Green's function.

The self-energy $\Sigma_{\text{e-ph}}$ is calculated using Keldysh NEGF formalism, which lends itself to a perturbative diagrammatic approach. Within this method it can be shown – ignoring any terms represented by disconnected Feynman diagrams – that at least so-called First Born Approximation is recovered.

O 36.88 Tue 18:30 P1

Energy level alignment and quantum conductance of functionalized metal-molecule junctions: Density functional theory versus GW calculations — ●CHENGJUN JIN¹, MIKKEL STRANGE², TROELS MARKUSSEN¹, GEMMA SOLOMON², and KRISTIAN THYGESEN¹ — ¹Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark — ²Nano-Science Center and Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

We study the effect of functional groups (CH₃*4, OCH₃, CH₃, Cl, CN, F*4) on the electronic transport properties of 1,4-benzenediamine molecular junctions using the non-equilibrium Green function method. Exchange and correlation effects are included at various levels of theory, namely density functional theory (DFT), energy level-corrected DFT (DFT+ Σ), Hartree-Fock and the many-body GW approximation. All methods reproduce the expected trends for the energy of the frontier orbitals according to the electron donating or withdrawing character of the substituent group. However, only the GW method predicts the correct ordering of the conductance amongst the molecules. The absolute GW (DFT) conductance is within a factor of two (three) of the experimental values. Correcting the DFT orbital energies by a simple physically motivated scissors operator, Σ , can bring the DFT conductances close to experiments, but does not improve on the relative ordering. We ascribe this to a too strong pinning of the molecular energy levels to the metal Fermi level by DFT which suppresses the variation in orbital energy with functional group.

O 36.89 Tue 18:30 P1

Convergence of different gradient corrected functionals towards accurate prediction of formation energy of solids using experimental database — ●MOHNISH PANDEY and KARSTEN WEDEL JACOBSEN — Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, Denmark

In the work by Lany (Phys. Rev. B 78, 245207 (2008)), GGA(+U) has been used to accurately predict the formation energies of solids using experimental enthalpies by fitting the reference energies of elements. In this work we show that different functionals predict similar formation energies which is close to the experimental values as long as the reference energies are recalculated by fitting the DFT formation energies to the standard experimental enthalpies which shows the general applicability of the fitting scheme. We use PBE, RPBE and PBE+U gradient corrected methods for calculations. Different training and test sets have been used to validate the predictability of the method.

O 36.90 Tue 18:30 P1

Forces in the FLAPW method revisited — ●AARON KLÜPPELBERG, MARKUS BETZINGER, and STEFAN BLÜGEL — Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Density functional theory (DFT) is nowadays the workhorse for simulating the electronic and geometric structure of real materials. Forces, i.e., the derivatives of the DFT total energy with respect to atomic positions, are indispensable for any structural optimization. Accurate forces, moreover, enable the calculation of phonon spectra using the finite displacement method and of subsequent quantities such as electron- and magnon-phonon interaction.

We analyze the accuracy of the force computed within the all-electron full-potential linearized augmented plane-wave (FLAPW) method as realized in the FLEUR code [1] according to the formalism of Yu *et al.* [2]. As one criterion for the accuracy we employ the drift-force, i.e., the sum of all atomic forces in the unit cell, which should strictly vanish. Another criterion is the quality of the symmetry of the force-constant matrix. We show that both criteria can be fulfilled to an accuracy of $1\mu\text{Htr}/a_0$ only if (a) the core-electron tails are properly taken into account and (b) a large angular momentum cut-off is applied. We propose a refined formulation of the force that cures the aforementioned demands on the LAPW setup to a great extent. As an example, we

present results for MgO and EuTiO₃.

[1] www.flapw.de

[2] R. Yu, D. Singh, and H. Krakauer, *Phys. Rev. B* **43**, 6411 (1991).

O 36.91 Tue 18:30 P1

RPA correlation energy calculated within the FLAPW method — ●MARKUS BETZINGER, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

According to the adiabatic-connection fluctuation dissipation theorem the exchange-correlation energy of Kohn-Sham density-functional theory (KS DFT) is expressed in terms of the many-electron density response function. Approximating the latter by the random-phase approximation (RPA) leads to the RPA correlation energy of KS DFT. It has been demonstrated that the RPA describes covalent, ionic, and vdW bonded systems equally well. The main obstacle in calculating the RPA correlation energy is the slow convergence of the KS response function in terms of the orbital basis set and the number of unoccupied states. We present an extension of the recently developed incomplete-basis-set correction (IBC) [1] to the frequency domain, which enables to compute the RPA response function accurately. The IBC, which is based on the FLAPW method, comprises a basis response term that lies in part outside the Hilbert space spanned by the original basis. The convergence of the RPA response function in terms of basis-set size and number of unoccupied states is considerably accelerated by the IBC. We show first results for RPA lattice constants and bulk moduli calculated for a set of prototype materials.

This work is supported by the Helmholtz Postdoc Programme.

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O 36.92 Tue 18:30 P1

Efficient Path-Integral Molecular Dynamics with High-Order Decomposition of the Boltzmann Operator — ●IGOR POLTAVSKY¹, KIM KWANG², and ALEXANDRE TKATCHENKO¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Center for Superfunctional Materials, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea

Recently it has become possible to reach the so-called "chemical accuracy" of 1 kcal/mol for the binding energies of small molecules and supramolecular systems, which is an essential prerequisite for predictive first-principles modeling. However, at this level of accuracy another serious issue arises, namely the need to accurately account for the quantum nature of (light) nuclei that plays a vital role in the structure, stability, and dynamical properties of many systems, including water, ice, as well as most biological molecules.

The most widely used tool to study quantum nuclear effects is the imaginary-time path integral (PI) approach which can be easily incorporated into *ab initio* calculations. Here we propose efficient PI molecular dynamics (MD) methods based on third and fourth order decompositions of the Boltzmann operator. These methods decrease the required number of replicas by more than a factor of two comparing to the standard second-order PIMD simulations, while at the same time visibly increasing the accuracy for a wide range of temperatures. Results are shown for model systems and an accurate quantum-mechanical model of the water molecule.

O 36.93 Tue 18:30 P1

Modified Mott-Wannier Model for Excitons in Atomically Thin Semiconductors — ●SIMONE LATINI, THOMAS OLSEN, and KRISTIAN S. THYGESEN — Department of Physics Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Despite the numerous extraordinary properties of pristine graphene, its application to (opto)-electronics is problematic due to the lack of a band gap. This issue inevitably requires the systematic research for new materials which combine a strong 2D nature and a semiconducting behaviour. As soon as a band gap is opened, excitonic effects start to play a fundamental role on the optical properties determining, for example, the onset of the optical transitions. The Bethe-Salpeter Equation (BSE) is nowadays the most refined method to quantitatively describe excitons but its applicability is limited to relatively simple systems because of its computational complexity. Here we propose a simple method to estimate the energy of the lowest bound exciton based on a modified Mott-Wannier model. For 2D semiconductors the dielectric function turns out to be strongly dependent on the wave vector and therefore the definition of the value for the dielectric con-

stant to plug into the hydrogenic model has to be revised. This is done accounting for a quasi-2D picture of the exciton. The validity of the method is checked thoroughly benchmarking the binding energies and exciton radii for a large variety of 2D materials against the values obtained from the solution of the BSE. Our method has the merit to both keep the computational cost low and to provide a straightforward physical intuition on excitonic effects.

O 36.94 Tue 18:30 P1

Effective interactions in the constrained random phase approximation — ●MERZUK KALTAK, MARTIJN MARSMAN, and GEORG KRESSE — University of Vienna, Computational Material Physics

We compare different approaches to the determination of the effective interaction parameters of Hubbard Hamiltonians within the constrained random phase approximation (CRPA) from *ab-initio* calculations. In addition, we investigate the dependence of the interaction parameters on the choice of the local bases, such as maximally localized Wannier functions (MLWF) and linear combination of atomic orbitals (LCAO).

O 36.95 Tue 18:30 P1

Ab-initio calculation of Hubbard U parameter for solids — ●ERSOY SASIOGLU, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The problem of calculating Hubbard U parameter for solids from first-principles has been addressed by several authors and a number of different approaches have been proposed. Among them, the constrained random-phase approximation (cRPA) has recently become the most popular [1]. The basic idea of the cRPA is to define an effective Coulomb interaction U between the localized d (f) electrons by restricting the screening processes to those that are not explicitly treated in the effective model Hamiltonian. Using Wannier functions within the FLAPW method [2] we have developed a parameter-free realization of the cRPA method [3]. Employing the cRPA method we have calculated the Hubbard U parameter for different classes of materials such as transition metals [3], half-metallic magnets [4], carbon-based systems [5], and surfaces of metals and insulators [6]. This work has been supported in part by DFG-FOR-1346.

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O 36.96 Tue 18:30 P1

Electronic communication through molecular bridges — ●JONNY PROPPE and CARMEN HERRMANN — Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Various areas of scientific research focus on the concept of electronic communication through molecular bridges as it plays a major role in potentially innovative future devices and as an academic challenge due to its diverse manifestations, in particular exchange coupling between spin centers and macroscopic electrodes connected by single molecules. Recent results suggest a correlation between both mechanisms of communication in certain cases, which is supported by molecular orbital arguments [1,2]. While Ref. [1] provides a first overview, we systematically compare trends and aim at deriving rules to identify instances in which it is possible to transfer knowledge between the areas of molecular magnetism and molecular electronics. For this purpose, we study the influence of chemical modification on the electronic communication of organic diradicals and dithiols. We find that the energy gap between magnetic orbitals in diradicals correlates with the HOMO/LUMO energy gap in dithiols, both affecting the mechanisms of electronic communication. Thus, for certain bridges the kind of exchange spin coupling (either ferromagnetic or anti-ferromagnetic) may determine the conductance for a given molecular structure and *vice versa*.

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O 36.97 Tue 18:30 P1

Bandgap engineering in two-dimensional heterostructures — ●FILIP ANSELM RASMUSSEN and KRISTIAN SOMMER THYGESEN — De-

partment of Physics, Technical University of Denmark, Kongens Lyngby, Denmark

Since the discovery of single layer graphene the search for other two-dimensional materials that might have equally interesting properties has begun. Contrary to graphene these materials may be anything from metals to large-gap insulators. Especially the possibility of combining materials with different band gaps may be useful for some applications like field-effect transistors and solar cells. Previously it has been shown that when a molecule comes in close proximity of a metal its energy levels shift due to increased screening from the metal. To investigate if such an effect is also present in extended two-dimensional systems we have performed first principles calculations on heterostructures consisting of metal-2D insulator-2D semiconductor layers, to estimate the effect of screening from the metal on the semiconductor band gap. To include the effect of the long-range Coulomb interaction we have calculated the quasiparticle energies using the non-self-consistent G_0W_0 approximation and we find that the semiconductor band gap decreases from its vacuum value when brought in close proximity of a metal. This shows that it is possible to engineer the band gap of the 2D semiconductor by varying the number of insulating spacer layers.

O 36.98 Tue 18:30 P1

Intrinsic LiNbO₃ point defects from total-energy difference and Slater-Janak transition state calculations — ●YANLU LI, SIMONE SANNA, and WOLF GERO SCHMIDT — Lehrstuhl für Theoretische Physik, Universität Paderborn, Paderborn, Germany

The formation energies and charge transition levels of the most relevant LiNbO₃ point defects, i.e. Nb antisites and Li as well as Nb vacancies are studied within density functional theory (DFT). In particular the effects of cell symmetry and the finite size error in calculations using periodic boundary conditions are examined. It is found that in particular the Nb vacancy causes a long-range strain field and requires large supercells for its adequate modeling. The extrapolation to infinitely large supercells decreases the relative stability of the Nb antisite and increases the relative stability of the Nb vacancy with respect to the Li vacancy, indicating the stability of VNb-5 in the wide range of Fermi level positions close to the conduction band minimum.

O 36.99 Tue 18:30 P1

Semiclassics for matrix Hamiltonians and semiclassical perturbation theory and its use for graphene physics — ●MICHAEL VOGL, SAM SHALLCROSS, and OLEG PANKRATOV — Lehrstuhl für Theoretische Festkörperphysik Staudtstr. 7-B2 91058 Erlangen

Electrons in graphene based systems are for low energies often described very well by first quantized matrix Hamiltonians, such as the Dirac-Weyl Hamiltonian in the case of single layer graphene. Nevertheless, such Hamiltonians remain, especially for the more complex graphene multilayer systems such as the twist graphene bilayer, very difficult to solve. Semi-classical methods often give great insight into the underlying structure of such complex systems; in particular in terms of semi-classical orbits and 2-forms such as the Berry phase. Following Bolte and Keppeler [1] we derive a general semi-classical method for treating the matrix Hamiltonians that arise in graphene based systems. This is based on an ansatz for the time-dependent Greens function that allows one to effectively bypass the problems of solution matching that, in other approaches, severely curtails the efficiency of the semi-classical approach. This leads, for a $n \times n$ Hamiltonian, to n Hamilton-Jacobi equations, and n transport equations. From the latter arises a term that can be separated into a term resembling the Berry phase and a term arising from the coupling between the n classical systems. We implement this scheme for the Bernal bilayer modeled by the full 4×4 Hamiltonian, as well as exploring how the theory may be implemented for the more complex case of the graphene twist bilayer. [1]J. Bolte & S. Keppeler Phys. Rev. Lett. 81 (1998) 1987-1991

O 36.100 Tue 18:30 P1

Structure formation on prepatterned surfaces — ●OLEG BULLER and ANDREAS HEUER — Institut für Physikalische Chemie, WWU, Münster

The main focus of our investigations is the analysis of structure formation on prepatterned surfaces of deposited molecules. The resulting self-organisation strongly depends on the chosen conditions such as substrate temperature, flux, concentration or surface geometry. Here we study the structure formation on prepatterned stripes as well as on a prepatterned grid. We use discrete kinetic Monte Carlo simula-

tions. It turns out that in particular the length of the aging period after the deposition process as well as the chosen particle concentration strongly influences the characteristics of the resulting structure. In contrast, the flux is much less relevant since the final structures mainly form during the aging period. We also characterize the stability of the structures. The simulation results are finally compared with corresponding experiments where organic molecules are deposited on prepatterned surfaces.

O 36.101 Tue 18:30 P1

Catalytic oxidation of HCl over CeO₂ within kinetic Monte Carlo simulations — ●STEFANO MATTIELLO¹, STEFAN KOLLING¹, CHRISTIAN HEILIGER² und HERBERT OVER³ — ¹Institut für Mechanik und Materialforschung, Technische Hochschule Mittelhessen, Gießen, Germany — ²I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Germany — ³Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Germany

Understanding of catalytic oxidation of HCl over CeO₂ is a challenging task for theoretical as well as experimental solid state physics. In particular, the role of the elementary reaction steps in the entire process is not yet completely understood. Within kinetic Monte Carlo simulations the different reaction steps can be investigated. In order to achieve *ab initio* calculations the input for the simulations, i.e. energy barriers for the microscopic reactions, have to be determined by density functional theory (DFT). For the time being we focus on the oxygen sub-lattice. We investigated the possibility of ad- and desorption of oxygen on the ceria (111)-surface as well as the diffusion of the oxygen vacancies on the surface and in the bulk. In particular the agglomeration of vacancies on the surface has been considered. The competition between the different elementary reactions was also investigated in detail.

O 36.102 Tue 18:30 P1

CPMD simulations of liquid Sn anodes for solid oxide fuel cells — ●SEBASTIAN GSÄNGER, JAKUB GOCLON, and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Liquid Sn is a very promising material for anodes in solid oxide fuel cells due to its high robustness toward sulfur contaminations in the gas feed. Very little is known about the bulk and surface chemistry of liquid Sn. Using Car-Parrinello Molecular Dynamics (CPMD) simulations we studied first the structural and dynamic properties of the liquid Sn itself and of dissolved oxygen, sulfur and hydrogen atoms. Subsequently, slabs of liquid Sn were used and the influence of the surfaces on the distribution and diffusion of the impurity atoms was studied. Finally, first molecular dynamics simulations on the interaction of hydrogen and methane gas phase molecules with the liquid Sn surfaces were performed.

O 36.103 Tue 18:30 P1

Electron-hole pair-vibrational coupling during scattering of HCl/Al(111): TDDFT-MD and model study — MICHAEL GROTEMEYER and ●ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Universität Kiel, 24098 Kiel, Germany

Ab initio simulations using time-dependent density functional theory together with Ehrenfest dynamics for the nuclei have revealed a very efficient energy transfer into substrate electron-hole pair excitations in case of highly vibrationally excited HCl-molecules that scatter at an Al(111) surface. The mechanism of vibrational-electron-hole pair coupling has been traced back to the periodic shift of the LUMO eigenenergy as the HCl bond length oscillates. We present an overview over our results for the energy transfer per vibrational period of the molecule as a function of its initial vibrational excitation energy and molecule-surface separation. The results can be qualitatively recovered by a simple tight-binding model. Notably, the energy dissipation rate goes through a maximum at a certain distance above the surface, i.e. not at very close molecule-surface separations. This is different from the steering mechanism suggested by Shenvi *et al.* for NO/Au(111) [1]. The coupling mechanism becomes less efficient for low vibrational excitation energy. We suggest this to explain the in comparison to NO small electronic contribution to the $v = 0 \rightarrow v = 1$ vibrational excitation observed experimentally for HCl-surface scattering [2].

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O 36.104 Tue 18:30 P1

CPMD simulations of oxidized Si clusters — •PAUL SCHWARZ¹, CAROLA KRYSCHI², and BERND MEYER¹ — ¹Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — ²Physical Chemistry, FAU Erlangen-Nürnberg

The oxidation of small Si clusters was studied by Car-Parrinello Molecular Dynamics (CPMD) simulations in order to obtain reasonable structures for oxygen-passivated clusters with a crystalline Si core with size of about 1 nm. The method of simulated annealing was applied to allow for atomic rearrangements and to find favorable low-energy configurations. The clusters were equilibrated at different temperatures, quenched to room temperature and finally relaxed. By increasing stepwise the amount of oxygen, four types of oxidized Si₆₃ clusters with composition of Si₆₃O₂₄, Si₆₃O₃₂, Si₆₃O₄₈, and Si₆₃O₆₈ were obtained.

It is found that at low oxidation clusters with crystalline and amorphous Si core are rather similar in energy. The energy of the clusters is lowered by formation of free-standing SiO₂ groups at the surface, under the condition that the crystalline core is retained during the simulation. These free-standing SiO₂ groups could be precursors for the formation of surface silanone groups. The crystalline core is furthermore stabilized by increasing oxidation. Finally, hydrogen and methyl groups were added at the surface of pure and oxidized Si clusters, with

the aim of finding vibrations that could explain the vibronic structure in the photoluminescence spectra of synthesized Si clusters.

O 36.105 Tue 18:30 P1

Border Search Method - potential energy surface mapping technique alternative to Metadynamics — •PROKOP HAPALA and PAVEL JELINEK — Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague, 16253, Czech Republic

Mapping of Potential Energy Surface (PES), searching for local and global minima of atomistic systems or paths with minimal energy barrier between these local minima is a long term goal of computational chemistry and material science. We propose novel robust method inspired by Meta-Dynamics [1] providing advantages in several aspects: (a) No force evaluation is needed. (b) Positions in configuration space are sampled systematically and homogeneously. (c) Method setup has less parameters and is easier to control (d) Lowest energy barrier is always found (e) Number of PES evaluations required to reliable exploration of lowest energy path to neighboring local minimum is reduced by prohibiting re-examination of the same area.

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