

O 61: Graphene II: Adsorption, Intercalation and Doping

Time: Wednesday 15:00–18:00

Location: S053

O 61.1 Wed 15:00 S053

H atom scattering from epitaxial graphene on Pt(111) — ●HONGYAN JIANG¹, YVONNE DORENKAMP¹, ALEC WODTKE^{1,2,3}, and OLIVER BUENERMANN^{1,2,3} — ¹Institute for Physical Chemistry, Georg-August University of Goettingen, Goettingen, Germany — ²Department of Dynamics at Surfaces, Max Planck Institute for Biophysical Chemistry, Goettingen, Germany — ³International Center for Advanced Studies of Energy Conversion, Georg-August University of Goettingen, Goettingen, Germany

Adsorption of hydrogen atoms on graphene is playing an important role in hydrogen storage, graphene based electronics, nuclear fusion and interstellar chemistry. The interaction of hydrogen atoms with graphene is studied in a newly built atom-surface scattering machine. A nearly mono-energetic hydrogen atom beam is formed by laser photolysis. The hydrogen atoms are scattered from a well-defined sample held in UHV. The scattered hydrogen atoms are detected using Rydberg-atom neutral time-of-flight. This technique allows us to record angle resolved, high resolution energy loss spectra of scattered hydrogen atoms. Scattering of hydrogen atoms from epitaxial graphene on Pt(111) shows a very different behavior than scattering from clean Pt(111). For low incidence kinetic energy, graphene acts like an atomic mirror. We observe narrow scattering angle and kinetic energy distribution and small translational energy loss. For high incidence kinetic energy, broad distribution and large translational energy loss is observed. The process obeys normal energy scaling. We speculate that this behavior is connected to the barrier of hydrogen atom adsorption on graphene.

O 61.2 Wed 15:15 S053

A nanodiamond superlattice on graphene/Ir(111) — ●CHARLOTTE HERBIG¹, PHILIPP VALERIUS¹, TIMO KNISPEL¹, SABINA SIMON^{1,2}, ULRIKE A. SCHRÖDER¹, ANTONIO J. MARTÍNEZ-GALERA¹, MOHAMMAD A. ARMAN³, CHRISTIAN TEICHERT^{1,4}, JAN KNUDSEN^{3,5}, ARKADY V. KRASHENINNIKOV^{6,7}, and THOMAS MICHELY¹ — ¹II. Physikalisches Institut, Universität zu Köln, Germany — ²Department of Physics, University of Konstanz, Germany — ³Division of Synchrotron Radiation Research, Lund University, Sweden — ⁴Institute of Physics, Montanuniversität Leoben, Austria — ⁵MAX IV Laboratory, Lund, Sweden — ⁶Department of Applied Physics, Aalto University, Finland — ⁷Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Germany

Atomic C deposition onto the graphene moiré with Ir(111) leads in a broad temperature range from 130 K to 550 K to the formation of a nanodiamond superlattice with one C cluster per moiré unit cell. The size of the C clusters is tunable between about 20 and 150 C atoms. For deposited amounts exceeding about 200 C atoms per moiré unit cell the ordering is lost, but still nanodiamond structures remain. The nanodiamond superlattice is thermally stable up to 800 K. Annealing to higher temperatures results in C intercalation and eventually bilayer graphene formation. On the basis of scanning tunneling microscopy, X-ray photoelectron spectroscopy, and density functional theory a model for C cluster formation, structure, stability, and decay is developed. Based on the generality of our model, we speculate that nanodiamonds may form on other moirés of 2D materials with their substrate.

O 61.3 Wed 15:30 S053

Core level shifts of doped graphene — ●ULRIKE A. SCHRÖDER¹, MARIN PETROVIĆ², TIMM GERBER¹, ELIN GRÄNÄS³, ANTONIO J. MARTÍNEZ-GALERA¹, MOHAMMAD A. ARMAN³, CHARLOTTE HERBIG¹, JOACHIM SCHNADT³, MARKO KRALJ², JAN KNUDSEN^{3,4}, and THOMAS MICHELY¹ — ¹II. Physikalisches Institut, Universität zu Köln, Germany — ²Institut za fiziku, Zagreb, Croatia — ³Division of Synchrotron Radiation Research, Lund University, Sweden — ⁴MAX IV Laboratory, Lund, Sweden

In X-ray photoemission spectroscopy, core level shifts of the carbon 1s photoelectrons are frequently monitored to investigate adsorption and intercalation on and underneath graphene. An understanding of their origin and magnitude are thus desirable both from a scientific and an applicational point of view. Through intercalation of metals and gases, the Dirac cone of graphene on Ir(111) can be shifted with respect to the Fermi level without becoming destroyed through strong hybridization. Upon such chemical doping with Cs, Eu, H, O, and Li, the carbon

1s core level shift displays a functional dependence on the graphene doping level. Of specific interest is the case of doping by Li, since for Li no phase separation takes place upon intercalation. Thereby, this core level shift can be monitored as a function of the intercalated amount. To first approximation, the core level shift may be described as a superposition of a rigid band shift, which is counteracted by a shift proportional to the transferred charge.

O 61.4 Wed 15:45 S053

Structural phases of Au-intercalated graphene on Ni(111) — ●MAXIM KRIVENKOV^{1,2}, EVANGELOS GOLIAS¹, DMITRY MARCHENKO¹, JAIME SÁNCHEZ-BARRIGA¹, GUSTAV BIHLMAYER³, OLIVER RADER¹, and ANDREI VARYKHALOV¹ — ¹Helmholtz-Zentrum Berlin, BESSY-II, 12489, Berlin, Germany — ²Department of Physics, Potsdam University, Am Neuen Palais 10, D-14415, Potsdam, Germany — ³Forschungszentrum Jülich and JARA, 52425, Jülich, Germany

Graphene grown epitaxially on Ni(111) and intercalated with Au is a remarkable system revealing a giant (~ 100 meV) spin-orbit splitting of Dirac cone in spin-resolved photoemission experiments [1]. In present study we investigate structural origin of this giant Rashba effect. We report extensive microscopic study of Au-intercalated graphene and discover versatile structural phases of Au locally coexisting at graphene-Ni interface. Besides a continuous monolayer phase giving rise to a pronounced moiré pattern identified as (9.7×9.7) misfit dislocation loop structure [2], we observe various well periodic arrays of nanoparticles trapped under graphene. Overall arrangement of such Au nanoclusters is laterally coherent to the principle moiré pattern of Au monolayer. We test whether these nanoparticles can be a source of giant spin-orbit splitting in graphene by performing DFT study of structural and electronic properties of the system.

[1] D. Marchenko, A. Varykhalov, M. R. Scholz, G. Bihlmayer, E. I. Rashba, A. Rybkin, A. M. Shikin, O. Rader, *Nature Commun.* **3**, 1232 (2012); [2] J. Jakobsen *et al.*, *Phys. Rev. Lett.* **75**, 489 (1995).

O 61.5 Wed 16:00 S053

How to manipulate the dispersion interaction at organic-graphene interfaces — ●VASILE CACIUC¹, FELIX HUTTMANN², NICOLAE ATODIRESEI¹, THOMAS MICHELY², and STEFAN BLÜGEL¹ — ¹Peter Grünberg Institut (PGI-1) and Institute for Advanced Simulation (IAS-1), Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — ²II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany

In this contribution we will explore how to rationally engineer the strength of the van der Waals (vdW) interactions present in a molecule-surface physisorbed system. More specifically, we investigated by means of *ab initio* density functional theory (DFT) simulations using a non-local correlation vdW functional [1] the adsorption of a π -conjugated organic molecule such as naphthalene ($C_{10}H_8$) on the graphene/Ir(111) surface [2]. To tailor the magnitude of the naphthalene-graphene dispersion interaction, the key ingredient is to modify the spatial extent of the charge distribution in graphene by doping it via intercalated electropositive and electronegative atoms at its backside to Ir(111) [3]. Finally, the comparison of the predicted adsorption energies and those obtained by thermal desorption measurements is also discussed [4].

- [1] M. Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004).
 [2] C. Busse *et al.*, *Phys. Rev. Lett.* **107**, 036101 (2011).
 [3] S. Schumacher *et al.*, *Nano Lett.* **13**, 5013 (2013).
 [4] F. Huttman *et al.*, *Phys. Rev. Lett.*, accepted.

O 61.6 Wed 16:15 S053

Coverage dependent evolution of electronic states of tetraphenyldibenzoperiflanthene (DBP) on HOPG and graphite — ●TOBIAS HUEMPFNER¹, TINO KIRCHHUEBEL¹, ROMAN FORKER¹, NORIAKI KAWAKITA², TAKASHI YAMADA², TOSHIKI MUNAKATA², and TORSTEN FRITZ^{1,2} — ¹Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany — ²Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka 560-0043, Osaka, Japan

We report on a combined study of the dye molecule tetraphenyldibenzoperiflanthene (DBP) deposited on HOPG and single crystalline

graphite surfaces. The film growth is successively traced in situ via differential reflectance spectroscopy (DRS). This data is compared to ultraviolet photoelectron spectroscopy (UPS) as well as two photon photoemission (2PPE) measurements recorded at various coverages. All methods applied show that there are two different species of the DBP molecule that appear at certain film thicknesses. For low coverages, namely up to one monolayer (ML), the absorption gap of the molecules is smaller (low energy - LE) compared to coverages slightly above 1 ML (high energy - HE). For thicker films up to 10 ML the LE species is formed again and the film composition shifts continuously in favor of this species with increasing coverage. This study is assisted by structural data gained from low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) that depicts a highly ordered first ML.

O 61.7 Wed 16:30 S053

Supramolecular nanopatterns of organic molecules on graphite — ●STEFAN-SVEN JESTER — Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn

The self-assembly of organic molecules at the solid/liquid interface provides an approach towards defined 2D architectures. However, predicting how a specific molecule renders into a supramolecular 2D crystal is still a challenge. A promising approach relies on the transfer of concepts from discrete geometry (e.g. Archimedean surface tiling) to supramolecular chemistry: Arylene-alkynylene macrocycles of distinct symmetries and sizes that carry flexible alkyl/alkoxy side chains can be viewed as molecular polygons that form supramolecular patterns of specific symmetries and lattice constants. E.g., the cocrystal of molecular triangles and hexagons has increased lattice constants as compared to the individual compounds. We describe a concentration-driven alteration between porous and dense packings of hexagons with reduced symmetry and alike unit cell parameters for rings with different interiors. In addition, we discuss mono- and multilayer growth of molecular spoked wheels on graphite. In all cases, scanning tunneling microscopy provides a submolecularly resolved insight into the molecular structures that can be utilized for chemical compound analysis.

O 61.8 Wed 16:45 S053

Molecular friction and proton dynamics in sulfuric acid intercalated graphite from ab-initio MD simulations — ●STEFFEN SEILER and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg
Wet-chemical exfoliation of graphite via Hummers' method [1,2] is a promising route for large-scale graphene production. In this solution-based process first graphite is intercalated by concentrated sulfuric acid, then the graphite intercalation compound (GIC) is oxidized, graphene oxide (GO) layers are separated in solution by hydrolysis reactions, and finally the GO layers are reduced to graphene [3]. We performed Car-Parrinello molecular dynamics (CP-MD) simulations to study the dynamic properties of the liquid sulfuric acid within the confined space between the graphene layers. The friction coefficient, proton-transfer barriers and electron distributions have been analyzed, and we will show how these properties are affected by the oxidation and the stacking sequence of the graphene sheets. Finally, consequences for the mechanism of GIC formation and oxidation will be discussed.

[1] W. S. Hummers, *J. Am. Chem. Soc.* **80**, 1339 (1958).

[2] D. C. Marcano et al., *ACS Nano* **4**, 4806 (2010).

[3] A. M. Dimiev and J. M. Tour, *ACS Nano* **8**, 3060 (2014).

O 61.9 Wed 17:00 S053

Surface mediated oxidation of supported coronene molecules — ●WEIPPERT JÜRGEN¹, GEWIESE VINCENT¹, BÖTTCHER ARTUR¹, and KAPPES MANFRED M.^{1,2} — ¹Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

We have explored surface-mediated oxidation of coronene (C₂₄H₁₂) molecules as a route to prepare molecular equivalents of graphene oxides (GOs). We found that exposure of C₂₄H₁₂/HOPG to a flux of atomic oxygen leads to oxidation of both the substrate and the coronene molecules adsorbed thereon (O/HOPG and C₂₄H₁₂O_n). We did not observe molecular fragments indicative of epoxy-species induced unzipping and scission of the adsorbed coronene. Instead des-

orption mass spectra were dominated by Coronene molecules deriving from electron impact ionization of the intact parent species, two oxidic species and an unusual coronene fragment, C₂₁H₉⁺. These observations suggest that sample heating activates the surface diffusion of preformed epoxy species and that subsequently pronounced fragmentation of the oxidized molecular periphery is induced either by further on-surface heating or by ionization. The reaction path results in the emission of coronene oxides with a mean yield of 0.07. Systematic measurements (TDS, UPS and XPS) reveal further details of the reaction chain associated with efficient thermal desorption of coronene oxides - a process analogous to the exfoliation of graphene oxide.

O 61.10 Wed 17:15 S053

Intercalation of Gadolinium underneath graphene on SiC(0001) — ●STEFAN LINK, STIVEN FORTI, ALEXANDER STÖHR, and ULRICH STARKE — Max-Planck-Institut für Festkörperforschung Stuttgart

Tuning the electronic properties of graphene for potential applications has raised intensive research. Besides spatial confinement for the introduction of a band gap or covalent functionalization, the intercalation of foreign atom species is a promising approach. A highly interesting state of graphene lies in the extreme doping regime, where a van-Hove singularity is reached at the Fermi level. Although this is a rather difficult task, it might pave the way to introduce interesting effects like superconductivity. Gating is illusional for this purpose due to the lack of appropriate dielectrics. Notably, the introduction of dopant adatoms like alkali and/or earth alkali metals onto both sides of the graphene leads to success but on the cost of strongly reduced stability. Here we show in a different approach that such a system can be produced with strong thermal and chemical stability. The system develops by intercalating Gadolinium atoms beneath the so called zerolayer graphene on SiC(0001). We make use of the advanced fabrication of epitaxial graphene on SiC(0001) in our group to achieve homogeneous results on a large scale. This gives the opportunity for exploring graphene's properties in this exotic regime. We show that reaching this regime is accompanied by strong renormalization effects in the electronic band structure, which are partially driven by strong electron-phonon coupling.

O 61.11 Wed 17:30 S053

Transformation of metallic boron into substitutional dopants in graphene on 6H-SiC(0001) — ●JESSICA SFORZINI^{1,2}, MYKOLA TELYCHKO^{3,4}, ONDREJ KREJCIO^{3,4}, MARTIN VONDRACEK⁵, MARTIN SVEC³, FRANCOIS BOCQUET^{1,2}, and STEPHAN TAUTZ^{1,2} — ¹Peter Grunberg Institut (PGI-3), Forschungszentrum Juelich, 52425 Juelich, Germany — ²Juelich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Juelich, Germany — ³Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, CZ-16200 Prague, Czech Republic — ⁴Faculty of Mathematics and Physics, Charles University, V Holesovickach 2, Praha 8, Czech Republic — ⁵Institute of Physics, Academy of Science of the Czech Republic, Na Slovance 2, 10, CZ-18228 Prague, Czech Republic

We investigate the development of the local bonding and chemical state of boron atoms during the growth of B-doped graphene on 6H-SiC(0001). Photoemission experiments reveal the presence of two chemical states, namely boron in the uppermost SiC bilayers and boron substituted in both the graphene and buffer layer lattices. We demonstrate the participation of the dopant in the π^* electron system of graphene by the presence of the π^* resonance in the near edge x-ray adsorption fine structure (NEXAFS) recorded at the B K-edge. The experimental findings are supported by NEXAFS simulations.

O 61.12 Wed 17:45 S053

Chemical modification of bilayer graphene — ●KONSTANTIN WEBER and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Using density functional theory (DFT) together with the empirical Grimme D2 van der Waals correction scheme [1] we studied the energetics, reaction pathway and thermodynamics of the hydroxylation and hydrogenation reaction and subsequent interlayer bond formation in bilayer graphene. Our results show that after the adsorption of two to three adsorbates a critical nucleous size is reached and subsequent adsorption leads to an energy gain for both the adsorption of hydrogen and hydroxyl groups. The covalent adsorption increases the reactivity of bilayer graphene and triggers the formation of interlayer bonds between the graphene sheets. In addition, the reactivity of freestanding

bilayer graphene will be compared to the reactivity of bilayer graphene adsorbed on a Ni(111) substrate. The Ni(111) surface acts as a support and reaction template that facilitates the hydrogenation and hydroxylation reactions, similarly as in the one-sided hydrogenation process

of single-layer graphene supported on Ni(111) [2].

[1] S. Grimme, *J. Comp. Chem.* **27**, 1787 (2006).

[2] W. Zhao et al., *Chem. Eur. J.* **21**, 3347 (2015).