

TT 100: Graphene: Adsorption, Intercalation, Doping (organized by O)

Time: Thursday 16:00–18:45

Location: WIL C107

TT 100.1 Thu 16:00 WIL C107

Covalent binding of single iron phthalocyanine molecules to graphene on Ir(111) — ●SIMON J. ALTENBURG¹, SHIRI R. BUREMA², BIN WANG³, RICHARD BERNDT¹, and MARIE-LAURE BOCQUET^{2,4} — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — ²Université de Lyon, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, CNRS, F69007 Lyon, France — ³Department of Physics & Astronomy, Vanderbilt University, Nashville, TN 37235 — ⁴Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Single iron phthalocyanine (FePc) molecules on graphene on Ir(111) are studied by low temperature scanning tunneling microscopy. The molecules are either unperturbed and weakly coupled to the substrate or bound to graphene by a lobe in a specific region of the moiré unit cell. Concomitant density functional calculations reveal that the binding between the FePc lobe and graphene is the result of a new kind of cyclization reaction. This reaction is activated in certain regions of the moiré unit cell by the presence of the iridium substrate.

TT 100.2 Thu 16:15 WIL C107

Adsorption of Pentacene on Epitaxial Graphene and BN — ●ALEXEI NEFEDOV¹, WENUA ZHANG^{1,2}, HIKMET SEZEN¹, ALEXANDR FEDOROV³, NIKOLAY VERBITSKIY⁴, ALEXANDER GRÜNEIS^{3,4}, and CHRISTOPH WOELL¹ — ¹Institute of Functional Interfaces, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — ²NSRL, Hefei, China — ³IFW, Dresden, Germany — ⁴University of Vienna, Vienna, Austria

Smooth interfaces are a prerequisite for future high-performance and low-cost organic electronic devices based on small conjugated molecules. Since all important charge transport processes are confined to the first several monolayers, the quality of the first layer plays a key role on device performance. Pentacene stands out as a model molecule among organic semiconductors due to its ability to form well-ordered films showing a high field effect mobility. Moreover, the morphology of the first layer of a thin Pn film is known to be strongly influenced by the substrate termination, which further decisively affects the interfacial charge transport properties. Thus, information on the molecular orientation of pentacene in a case of (sub)monolayer coverages can provide a key information on improvement of device performance. In this study the adsorption of pentacene on a single layer of graphene or boron nitride (BN) has been investigated by means of XPS and NEXAFS spectroscopy. The experiments were performed on the HESGM beamline at BESSY II in Berlin. It was found that pentacene molecules demonstrate a dependence of their orientation and electronic structure on the coverage.

TT 100.3 Thu 16:30 WIL C107

Wetting properties of para-hexaphenyl on exfoliated graphene — ●MARKUS KRATZER¹, STEFAN KLIMA¹, BORISLAV VASIĆ¹, ALEKSANDAR MATKOVIĆ², MARIJANA MILIĆEVIĆ², RADOS GAJIĆ², and CHRISTIAN TEICHERT¹ — ¹Institute of Physics, Montanuniversität Leoben, Franz Josef Straße 18, 8700 Leoben, Austria — ²Institute of Physics, University of Belgrade, Pregrevica 118 P.O. Box 68, 11080 Belgrade, Serbia

Graphene (Gr) bears potential to serve as transparent and flexible electrode material in organic electronics. Therefore, understanding of the growth of organic thin films on it is essential. Here, we investigated the growth morphology of films formed by the rodlike para-hexaphenyl (6P) molecule on Gr as a model system. As substrates exfoliated graphene transferred onto a silicon oxide support were used. Submonolayer amounts of 6P were deposited by means of hot-wall epitaxy between 333 K and 393K. The evolving film morphologies, investigated by atomic-force microscopy (AFM), exhibited a strong dependence on temperature and number of supporting Gr layers. At 333 K, needle like structures - which are known to be composed of flat lying molecules [1]- and islands composed of upright standing molecules coexist on the Gr. For the higher temperatures solely needles, forming networks, are found. The needles forming at 363 K exhibit an increasing dewetting with increasing number of Gr layers which is attributed to Gr layer dependent changes in surface energy, diffusion properties and preferential adsorption sites.

[1] C. Teichert et al. Appl. Phys. A 82 (2006) 665.

TT 100.4 Thu 16:45 WIL C107

H-adsorption and H₂-splitting on graphene/SiC(0001) — ●GABRIELE SCLAUZERO and ALFREDO PASQUARELLO — École Polytechnique Fédérale de Lausanne (EPFL), Lausanne (Switzerland)

High-quality graphene grown epitaxially on SiC(0001) can be regarded as a convenient template for the realization of graphene-based electronics. However, the presence of a carbon “buffer” layer buried at the interface between the SiC surface and the epitaxial graphene is detrimental to the electronic transport properties of graphene. Hydrogen intercalation at high temperatures can be used to convert the buffer layer into a quasi-free standing graphene lying directly above a H-saturated SiC(0001) surface, which provides a much more effective decoupling from the substrate.

Here, the processes of H-adsorption and H₂-splitting at the graphene/SiC(0001) interface is addressed through first-principles atomistic simulations based on realistic interface models, including the experimentally observed $6\sqrt{3}\times 6\sqrt{3}$ R30° reconstruction. Our main finding is a great enhancement of the chemical reactivity of the carbon buffer layer with respect to pristine graphene, as a result of the partial sp^2 to sp^3 rehybridization of the C atoms in the buffer. H-binding energies on threefold-coordinated C atoms of the buffer are three-to-four times larger than on graphene and H₂-splitting becomes an exothermic process, with activation barriers that can be up to four times smaller than on graphene. On favorable sites, energy barriers can become as low as 1 eV and are in agreement with the observation of atomic-H intercalation also when H₂ is used as hydrogen source.

TT 100.5 Thu 17:00 WIL C107

Deuterium adsorption on (and desorption from) SiC(0001)-(3x3), (R3xR3)R30°, (6R3x6R3)R30° and quasi-free-standing graphene obtained by hydrogen intercalation — ●BOCQUET F.C.¹, BISSON R.², THEMLIN J.-M.³, LAYET J.-M.², and ANGOT T.² — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich - 52425 Jülich, Germany — ²Aix-Marseille Université, PIIM, CNRS, UMR 7345, 13013 Marseille, France — ³Aix-Marseille Université, IM2NP, 13397, Marseille, France and CNRS, UMR 7334, 13397, Marseille - Toulon, France

I present a comparative High-Resolution Electron Energy-Loss Spectroscopy (HREELS) study on the interaction of atomic hydrogen and deuterium with various reconstructions of SiC(0001). We show that deuterium passivation of the (3x3) is only reversible when exposed to atomic deuterium at a surface temperature of 700 K since tri- and dideuterides, necessary precursors for silicon etching, are not stable at this temperature. On the other hand, we show that the deuteration of the (R3xR3)R30° is always reversible because precursors to silicon etching are scarce on the surface [1]. Further, the comparison of the deuterium binding in the intercalation layer of quasi-free-standing graphene with the deuterated (R3xR3)R30° surface provides some indication on the bonding structure at the substrate intercalation layer [1,2].

[1] F.C. Bocquet et al. J. Phys. D: Appl. Phys. (2014) in press

[2] F.C. Bocquet et al. Phys. Rev. B. 85 (2012) 201401

TT 100.6 Thu 17:15 WIL C107

Charge doping induced phase transitions in hydrogenated and fluorinated graphene — ●TIM WEHLING^{1,2}, BERNHARD GRUNDKÖTTER-STOCK², BÁLINT ARADI², THOMAS NIEHAUS³, and THOMAS FRAUENHEIM² — ¹Institute for Theoretical Physics, Universität Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany — ²Bremen Center for Computational Material Science, Universität Bremen, Am Fallturm 1, 28359 Bremen, Germany — ³Department of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany

We show that charge doping can induce transitions between three distinct adsorbate phases in hydrogenated and fluorinated graphene. By combining *ab initio*, approximate density functional theory and tight binding calculations we identify a transition from islands of C₈H₂ and C₈F₂ to random adsorbate distributions around a doping level of ± 0.05 e/C-atom. Furthermore, in situations with random adsorbate coverage, charge doping is shown to trigger an ordering transition

where the sublattice symmetry is spontaneously broken when the doping level exceeds the adsorbate concentration. Rehybridization and lattice distortion energies make graphene which is covalently functionalized from one side only most susceptible to these two kinds of phase transitions. The energy gains associated with the clustering and ordering transitions exceed room temperature thermal energies.

TT 100.7 Thu 17:30 WIL C107

Graphene Oxide Formation by Adsorption and Photolysis of NO₂ and SO₂ on Graphene/Ir(111) — ●STEFAN BÖTTCHER, HENDRIK VITA, and KARSTEN HORN — Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Graphene oxide is a widely discussed precursor for the technological application of graphene-based systems; for example, its controlled reduction into graphene may lead to a tunable band gap. We report on the formation of oxidized graphene layers on Ir(111) by adsorption and photodissociation of NO₂ and SO₂ at low temperatures. Both adsorbates induce atomic oxygen on the surface when irradiated with intense UV light, leading to an oxidation of the graphene layer. The method presented here is expected to be less intrusive compared for example to oxygen bombardment methods. We also believe the photon induced oxidation to be more selective compared to other physical or wet chemical methods. A band gap opening at room temperature is observed, showing that the graphene oxide phase is also stable above 100 K. High quality graphene can be recovered after annealing, judged by the reappearance of its core and valence level spectral features. Apart from the selective formation of the epoxidic phase, the reaction can also be driven towards a metastable oxide phase from NO₂ using low photon flux. SO₂ on the other hand produces fragments upon dissociation, which have a strong influence on the hybridization state of the graphene backbone.

TT 100.8 Thu 17:45 WIL C107

Tuning the van der Waals Interaction of Graphene with Molecules by Doping — ●FELIX HUTTMANN¹, ANTONIO JAVIER MARTINEZ-GALERA¹, NICOLAE ATODIRESEI², VASILE CACIUC², STEFAN BLÜGEL², and THOMAS MICHELY¹ — ¹II. Physikalisches Institut, Universität zu Köln, Zùlpicher Straße 77, 50937 Köln, Germany — ²Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jùlich, 52428 Jùlich, Germany

Strong n-doping of graphene on its epitaxial substrate can be introduced via intercalation of highly electropositive elements such as Cs and Eu, and has recently been shown to lead to reduced binding energy for electropositive, ionic adsorbates [1].

Here, we explore tuning of graphene's van der Waals (vdW) interaction with adsorbates via doping. Employing an all in-situ surface science approach, we find by scanning tunneling microscopy and thermal desorption spectroscopy a significantly higher binding energy on n-doped as opposed to undoped graphene for the vdW-bonded molecules benzene and naphthalene. This is just opposite to the case of electropositive, ionic adsorbates. Based on the model character of these simple pi-conjugated molecules [2], we propose that the strength of the van der Waals interaction is modified by doping. The experimental results are compared to density functional calculations, including van der Waals interactions.

References:

[1] S. Schumacher et al., Nano Lett. 13, 5013 (2013)

[2] S. D. Chakarova-Käck et al., Phys. Rev. Lett. 96, 146107 (2006)

TT 100.9 Thu 18:00 WIL C107

Li intercalation at the graphene/Cu interface: An electronic

structure view of synchrotron-based spectroscopy — ●LIANG ZHANG^{1,2}, JINGHUA GUO², and JUNFA ZHU¹ — ¹National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, 230029, China — ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

The synthesis of graphene on metal surfaces (such as Ni, Pd, Ru or Cu) by chemical vapor deposition (CVD) is one of the most promising, inexpensive and readily accessible methods to prepare single-layer graphene, which is a prerequisite for the fabrication of graphene-based electronic devices. In particular, graphene grown on Cu foils over large areas has allowed access to high quality of this material.

In this presentation, we report our recent studies on the electronic structure of graphene/Cu and Li-intercalated graphene/Cu by synchrotron-based spectroscopy. The results indicate a high degree of alignment and a slight corrugation/rippling of the graphene layer on Cu. The deposition of Li atoms on graphene surface under ultrahigh vacuum condition at room temperature results in a charge transfer from the adsorbed Li atoms to graphene. After annealing the as-deposited Li/graphene/Cu sample at 300 °C for 10 min, the Li atoms intercalate into the interface of graphene/Cu. These interfacial Li atoms show a strong passivation from oxidation environment due to the protection of graphene layer.

TT 100.10 Thu 18:15 WIL C107

Progressive nitrogen-doping of graphene on SiC(0001) — ●MYKOLA TELYCHKO, PINGO MUTOMBO, MARTIN ONDRÁČEK, PROKOP HAPALA, JAN BERGER, PAVEL JELINEK, and MARTIN ŠVEC — Institute of Physics ASCR, Cukrovarnická 10, Praha, Czech republic

Doping of epitaxial graphene on SiC substrates was achieved by direct nitrogen ion implantation and stabilization at temperatures above 1300K. Scanning tunneling microscopy reveals very well-defined single substitutional defects on single and bilayer graphene. Repeated nitrogen implantation and stabilization leads to formation of double defects, which comprise of two nitrogen defects in a second-nearest-neighbour (meta) configuration. DFT calculations and scanning tunneling microscopy simulations are used to evaluate the electronic properties and to explain varying contrast of these defects in the atomically-resolved images, depending on the probe type. A mechanism of defect formation is proposed.

TT 100.11 Thu 18:30 WIL C107

Electronic and magnetic properties of cobalt interaction with graphene on Ir(111) — HENDRIK VITA, STEFAN BÖTTCHER, and ●KARSTEN HORN — Fritz-Haber-Institut of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany

The interaction of graphene with transition metal surfaces has attracted much interest because these are ideal templates for the growth of high quality films. Ferromagnetic substrates such as Ni(111) and Co(0001) are interesting since graphene grown on these surfaces can act as a spin filter. We have earlier found that the proximity of graphene to the ferromagnetic Ni(111) substrate induces a sizeable magnetic moment in the carbon π -states as determined from carbon K edge XMCD. Here we study the influence of thin layers of ferromagnetic Co sandwiched between Ir(111) and graphene with consequences for the magnetic properties expected. We find that the cobalt films show ferromagnetic behavior even for very low thicknesses. In order to study the behavior of magnetic heterostructures utilizing graphene as an interlayer we examine sandwich systems consisting of a thin layer of cobalt on top graphene/Ni(111). Using element-specific XMCD and hysteresis measurements it is possible to gain insight into the magnetic coupling across this magnetic heterostructure.