

TT 117: Graphene: Intercalation (jointly with O, HL)

Time: Friday 10:30–12:45

Location: MA 041

TT 117.1 Fri 10:30 MA 041

Keeping Argon under a Graphene Lid - Argon intercalation between Graphene and Ni(111) — ●FLORIAN SPÄTH, KARIN GOTTERBARM, CHRISTOPH GLEICHWEIT, MAX AMENDE, UDO BAUER, OLIVER HÖFERT, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Graphene with its thickness of only one single atomic layer can be considered as the thinnest membrane or gas barrier. We present a spectroscopic investigation of related properties under well-defined ultra-high vacuum conditions in a surface science experiment: We implant argon into a Ni(111) crystal by sputtering prior to the growth of graphene. Subsequently, when growing graphene on Ni(111), argon diffuses out of the bulk and is caught underneath graphene. We investigate the system with high-resolution in-situ X-ray photoelectron spectroscopy. From the growth behavior of these intercalated argon bubbles during graphene preparation and from temperature programmed XP spectra we are able to deduce a model of the intercalation system (G/Ar/Ni) and estimate the pressure for argon under graphene. Furthermore, we find an increased thermal stability of graphene due to a decoupling of graphene from the Ni(111) substrate. This work was supported by SFB 953 "Synthetic Carbon Allotropes"

TT 117.2 Fri 10:45 MA 041

Intercalation of Gadolinium underneath graphene on SiC(0001) — ●STEFAN LINK, STIVEN FORTI, ALEXANDER STÖHR, and ULRICH STARKE — Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Investigating the properties of graphene in a highly doped state, such that the Fermi level reaches a saddle point of its electronic bands is an on-going field. Superconductivity could be one potential effect in this regime. Functionalization with highly reactive species such as alkali and/or earth alkali atoms has been pursued for strong doping effects. However, such systems are prone to fast degradation by environmental influences which needs to be circumvented for any kind of application.

Here, we present a method of doping graphene to such levels and simultaneously making the system stable to temperatures higher than 1000°C as well as to air exposure. This was achieved by the intercalation of Gadolinium atoms underneath the so-called buffer layer on SiC(0001), i.e., the carbon rich $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction of this surface. Significant hybridization effects of the graphene π -bands with the adatom states are observed in the ARPES data. In addition, evidence for strong electron-phonon scattering is visible. Spectroscopic weight appears in the measurements completely interlinking two Dirac cones through the \bar{M} -point, thus indicating the presence of an electronic topological transition (ETT).

TT 117.3 Fri 11:00 MA 041

Nitrogen Intercalation and Nitrogen-based Molecular Doping of Epitaxial Graphene on 6H-SiC(0001) — ●NUALA MAI CAFFREY, RICKARD ARMIENTO, ROSITSA YAKIMOVA, and IGOR ABRIKOSOV — Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden

The thermal decomposition of silicon carbide (SiC) is one of the most promising methods to produce high-quality epitaxial graphene on a wafer scale. Sufficient control has even been achieved to selectively grow monolayer, bilayer and few-layer graphene, rendering it a indispensable technique for the manufacture of graphene-based electronics. A disadvantage of this method is that the first carbon layer is covalently bonded to the surface Si atoms, with only subsequent layers displaying the characteristic electronic features of graphene. Several methods have been proposed to electronically decouple this buffer layer, as well as to reduce the high substrate-induced doping, including intercalation and chemical doping. Understanding such chemical functionalizations is a fundamental first step towards engineering the properties of graphene on SiC. It is clear that the graphene layer, as well as the interface between it and the SiC surface, can be significantly influenced by the growth environment. We consider how common environmental dopants can affect the electronic structure of mono- and bilayer graphene grown on a 6H-SiC(0001) substrate. We show, using first-principles calculations, how nitrogen intercalation and nitrogen-based molecular dopants, such as NO₂ and NH₃, present a promising route

to tailor the properties of this system.

TT 117.4 Fri 11:15 MA 041

Investigation of the electrostatic changes induced by metal islands on graphene/SiC(0001) using field-emission resonance spectroscopy with STM — ●ANASTASIA SOKOLOVA¹, ALEXANDER STÖHR², STIVEN FORTI², ULRICH STARKE^{1,2}, and M.ALEXANDER SCHNEIDER¹ — ¹Solid State Physics, Friedrich-Alexander-University Erlangen-Nuremberg, Germany — ²Max Planck Institute for Solid State Research, Stuttgart, Germany

Using the Scanning Tunneling Microscope in field-emission resonance spectroscopy mode (FRS-STM) it is possible to map changes of the electrostatic potential in front of the graphene surface at the nanoscale [1]. We investigated the properties of 10 nm-sized metal islands on top of epitaxial graphene on SiC(0001) as well as islands intercalated underneath the graphene layer.

For cobalt and palladium islands on top of graphene we observe a spatially localized shift of the 1st field-emission resonance to higher energy strictly occurring at the topographical step. This is consistent with larger work functions of the metals with respect to that of graphene. In the case of intercalated cobalt islands FRS-STM shows a rise of the 1st field-emission resonance energy of only 150 meV and a spatially delocalized transition. Considering the properties of graphene flakes on an extended Co(0001) surface [2] this suggests negative charge of the capping graphene layer and a positive charge on the cobalt island.

[1] S. Bose *et al* 2010 *New Journal of Physics* **12** 023028[2] D. Eom *et al* 2009 *Nano Letters* **9** 2844-2848

TT 117.5 Fri 11:30 MA 041

Oxygen orders differently under graphene: new superstructures on Ir(111) — ●ANTONIO J. MARTÍNEZ-GALERA¹, FELIX HUTTMANN¹, ULRIKE SCHRÖDER¹, FABIAN CRAES¹, CARSTEN BUSSE¹, VASILE CACIUC², NICOLAE ATODIRESEI², STEFAN BLÜGEL², and THOMAS MICHELY¹ — ¹Universität zu Köln, II. Physikalisches Institut, Germany — ²Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich, Germany

Modifying the properties of graphene (Gr) by intercalation of atoms or molecules at the Gr/substrate interface has been proven to be a straightforward and versatile concept. However, the effect of the Gr layer on the ordering of the intercalated material remains much less studied. We present evidence that indeed the Gr cover has a substantial influence on the resulting superstructures of oxygen chemisorbed on Ir(111). As a function of exposure to molecular oxygen and temperature the oxygen adsorbate superstructures on Ir(111) are identified by scanning tunneling microscopy (STM). They are compared to the ones formed by intercalation in between graphene and Ir(111). For bare Ir(111) we observe O-(2x2) and O-(2x1) structures, thereby clarifying a long-standing debate on the existence of these structures and the role of defects for their stability. For Gr/O/Ir(111) with increasing exposure O-(2x2), O-(R3xR3)-R30, O-(2x1) and O-(2R3x2R3)-R30 superstructures referred to Ir(111) are observed. The (R3xR3)-R30 and (2R3x2R3)-R30 structures were not yet reported and they exist only under Gr. Based on density functional theory (DFT) we discuss the origin of the new adsorbate superstructures under graphene.

TT 117.6 Fri 11:45 MA 041

Oxidation of sulfuric acid intercalated graphite: the role of sulfuric acid and permanganate ions — ●STEFFEN SEILER and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Wet-chemical exfoliation of graphite via Hummers' method [1,2] is a promising route for large-scale graphene production. This solution-based process is carried out in concentrated sulfuric acid and involves several steps: first, graphite is converted into a sulfuric acid-graphite intercalation compound (GIC), then the GIC is transformed into oxidized graphite, graphene oxide (GO) layers are separated in solution by hydrolysis reactions, and finally the GO layers are reduced to graphene [3].

To obtain atomistic insights into the mechanisms of the chemical reactions in liquid sulfuric acid within the confined space between graphene layers we performed Car-Parrinello molecular dynamics (CP-MD) sim-

ulations. By changing the coverage of hydroxy and epoxy groups their stabilizing effect on the attack of sulfuric acid (solvent) and KMnO_4 (oxidizing agent) molecules was investigated. Furthermore, different carbon atoms on the partly oxidized graphene sheets were attacked to elucidate the most reactive sites.

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

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

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

TT 117.7 Fri 12:00 MA 041

Approaching ideal graphene: The structure of hydrogen- and germanium-intercalated graphene on 6H-SiC(0001) — ●F.C. BOCQUET^{1,2}, J. SFORZINI^{1,2}, T. DENIG³, A. STÖHR³, T.-L. LEE⁴, S. SUBACH^{1,2}, U. STARKE³, and F.S. TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany — ³Max Planck Institute for Solid State Research, Heisenbergstraße, 70569 Stuttgart, Germany — ⁴Diamond Light Source Ltd, Didcot, OX110DE, Oxfordshire, United Kingdom

We investigated Quasi-Free-standing Monolayer Graphene epitaxially grown on 6H-SiC(0001) obtained by decoupling the buffer-layer from the Si-terminated surface by hydrogen intercalation (1) or by intercalating one or two monolayers of germanium (2). All three samples show a clear linear dispersion around the K-point, confirming their Quasi-Free-standing character. We used the X-ray standing wave (XSW) technique, combining dynamical diffraction and X-ray photoelectron spectroscopy, to detect the coherent distribution of the chemically different species (Si, C and Ge) at the interface. Based on the lattice parameter of bulk SiC, we accurately determine the vertical height differences between each chemical species. Comparing the overlaps of van der Waals radii between the graphene layer and the topmost intercalating atoms, we conclude on the degree of decoupling of the graphene layers.

TT 117.8 Fri 12:15 MA 041

Bismuth Intercalated Graphene on Iridium Probed by STM and ARPES — ●JONAS WARMUTH¹, MATTEO MICHARDI², TORBEN HÄNKE¹, MARCO BIANCHI², JENS WIEBE¹,

ROLAND WIESENDANGER¹, PHILIP HOFMANN², and ALEXANDER KHAJETOORIANS³ — ¹Department of Applied Physics, University of Hamburg, Germany — ²Department of Physics and Astronomy, University of Aarhus, Denmark — ³Institute for Materials and Molecules, Radboud University, Nijmegen, Netherlands

We report on the investigation of bismuth intercalated graphene grown on Ir(111) by means of STM and ARPES. The STM measurements reveal a complex periodic structure upon Bi intercalation which we attribute to the formation of a $\sqrt{3}$ Bi surface alloy. We characterize the changes to the band structure using ARPES, including the doping effects and the modification to the Dirac dispersion.

TT 117.9 Fri 12:30 MA 041

Enhancement of many-body effects observed on epitaxial monolayer graphene/Au/SiC(0001) — ●STIVEN FORTI¹, STEFAN LINK¹, ALEXANDER STÖHR¹, YURAN NIU², ALEXEI ZAKHAROV², and ULRICH STARKE¹ — ¹Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany — ²Max-Lab, Lund University, Box 118, Lund, S-22100, Sweden

The interaction of graphene with gold atoms has gained high relevance for a series of reasons, from electrical contacts to plasmonics. Here we present the realization of n-type epitaxial monolayer graphene on SiC(0001) via the intercalation of a layer of Au atoms at the heterointerface between the graphene and the SiC substrate. Such a phase exhibits enhanced many-body effects, as observed by ARPES. The plasmaron band is observed and its dispersion is well discernible from the hole-Dirac cone. The effective dielectric constant extracted from the ARPES data is about five times smaller than what is reported in the literature so far. The effectiveness of the intercalation is corroborated by μ LEED measurements, which clearly indicate a suppression of the diffraction spots on the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ grid, except for spots arising from multiple diffraction. CLPES measurements indicate the presence of a single gold component, namely assigned to gold silicides. The quality of the epitaxial graphene grown on SiC(0001) in Ar atmosphere, together with the aforementioned preparation, makes possible to observe bands of unprecedented sharpness for this system. Dispersive states arising from the 5d orbitals of the interfacial gold are observed as well, as predicted by theory.