

## HL 32: Graphene: Growth &amp; intercalation (O with HL/TT)

Time: Tuesday 10:30–13:00

Location: MA 041

HL 32.1 Tue 10:30 MA 041

**First-principles Study of the Origin of a Rippled Graphene Phase on Ir(001)** — ●MIGHFAR IMAM<sup>1</sup>, NATASA STOJIC<sup>1,2</sup>, and NADIA BINGGELI<sup>1,2</sup> — <sup>1</sup>The Abdus Salam International Centre for Theoretical Physics Strada Costiera 11, 34151 Trieste, Italy — <sup>2</sup>IOM-CNR Democritos, Trieste, I-34151, Italy

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

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

HL 32.2 Tue 10:45 MA 041

**Graphene induced faceting of Ir(557)** — CHRISTIAN WITT, MICHAEL HORN-VON HOEGEN, and ●FRANK-J. MEYER ZU HERINGDORF — University Duisburg-Essen, Faculty for Physics and CENIDE, Lotharstrasse 1, 47057 Duisburg

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

HL 32.3 Tue 11:00 MA 041

**Comparing graphene growth on Cu(111) vs. oxidized Cu(111)** — STEFANO GOTTARDI<sup>1</sup>, KATHRIN MÜLLER<sup>1</sup>, LUCA BIGNARDI<sup>1</sup>, JUAN CARLOS MORENO LOPEZ<sup>1</sup>, TUAN ANH PHAM<sup>1</sup>, ALEXEI BARINOV<sup>2</sup>, JONAS BJÖRK<sup>3</sup>, PETRA RUDOLF<sup>1</sup>, and ●MEIKE STÖHR<sup>1</sup> — <sup>1</sup>University of Groningen — <sup>2</sup>Sincrotrone Trieste — <sup>3</sup>Linköping University

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

HL 32.4 Tue 11:15 MA 041

**Ir(111) surface state stability against Li adsorption: role of graphene** — ●PETAR PERVAN<sup>1</sup>, IVO PLETIKOSIĆ<sup>2</sup>, MARIN PETROVIĆ<sup>1</sup>, IVA ŠRUT RAKIĆ<sup>1</sup>, MARKO KRALJ<sup>1</sup>, MILORAD MILUN<sup>1</sup>, TONICA VALLA<sup>2</sup>, and PREDRAG LAZIĆ<sup>3</sup> — <sup>1</sup>Institut za fiziku, Bijenička 46, 10000 Zagreb, Croatia — <sup>2</sup>Department of Condensed Matter Physics & Materials Science, Brookhaven National Lab, Upton — <sup>3</sup>Institut Rudjer Bošković, Bijenička 54, 10000 Zagreb, Croatia

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

HL 32.5 Tue 11:30 MA 041

**Chemical Functionalization of Graphene via Hyperthermal Molecular Reaction** — GIRJESH DUBEY<sup>1</sup>, ROBERTO URCUYO<sup>1</sup>, SABINE ABB<sup>1</sup>, GORDON RINKE<sup>1</sup>, MARKO BURGHARD<sup>1</sup>, ●STEPHAN RAUSCHENBACH<sup>1</sup>, and KLAUS KERN<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institute for Solid State Research, Stuttgart, Germany — <sup>2</sup>Institut de Physique de la Matière Condensée, EPFL, Lausanne, Switzerland

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

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

HL 32.6 Tue 11:45 MA 041

**Quantum interference on the doped graphene/SiC systems** — ●MYKOLA TELYCHKO<sup>1</sup>, PABLO MERINO<sup>2</sup>, PINGO MUTOMBO<sup>1</sup>, MARTIN ONDRAČEK<sup>1</sup>, PROKOP HAPALA<sup>1</sup>, OLEKSANDR STETSOVYCH<sup>1</sup>, MARTIN ŠVEC<sup>1</sup>, and PAVEL JELÍNEK<sup>1</sup> — <sup>1</sup>Institute of Physics ASCR, Cukrovarnická 10, Praha, Czech Republic — <sup>2</sup>Max Planck Institute for Solid State Research, Heisenberg Strasse 1, 70569 Stuttgart

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

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

clear chemical discrimination between the N and B atoms.

HL 32.7 Tue 12:00 MA 041

**Scanning Tunneling Microscopy of epitaxial Graphene with single ion-implanted Boron, Nitrogen and Carbon atoms** — ●PHILIP WILLKE<sup>1</sup>, ANNA SINTERHAUF<sup>1</sup>, JULIAN AMANI<sup>2</sup>, SANGEETA THAKUR<sup>3</sup>, THOMAS KOTZOTT<sup>1</sup>, STEFFEN WEIKERT<sup>2</sup>, KALOBARAN MAITI<sup>3</sup>, HANS HOFSSÄSS<sup>2</sup>, and MARTIN WENDEROTH<sup>1</sup> — <sup>1</sup>IV. Physikalisches Institut, Universität Göttingen, Germany — <sup>2</sup>II. Physikalisches Institut, Universität Göttingen, Germany — <sup>3</sup>Department of Condensed Matter Physics and Materials' Science, TIFR, Mumbai, India

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

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

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

HL 32.8 Tue 12:15 MA 041

**Reversible Hydrogenation of Graphene on Ni(111) - Synthesis of 'Graphone'** — ●JULIAN GEBHARDT<sup>1</sup>, WEI ZHAO<sup>2</sup>, FLORIAN SPÄTH<sup>2</sup>, KARIN GOTTERBARM<sup>2</sup>, CHRISTOPH GLEICHWEIT<sup>2</sup>, HANS-PETER STEINRÜCK<sup>2</sup>, and ANDREAS GÖRLING<sup>1</sup> — <sup>1</sup>Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — <sup>2</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Understanding the adsorption and reaction between hydrogen and graphene is of fundamental importance for developing graphene-based concepts for hydrogen storage and for the chemical functionalization of graphene by hydrogenation. Recently, theoretical studies of single-sided hydrogenated graphene, so called graphone, predicted it to be a promising semiconductor for applications in graphene-based electronics. Here, we report on the synthesis of graphone bound to a Ni(111) surface. We investigate the formation process by X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and density-functional theory calculations, showing that the hydrogenation of graphene with atomic hydrogen indeed leads to graphone, i.e., a hydrogen coverage of 1 ML (4.2 wt%). In addition, the dehydrogenation of graphone was shown to be possible by XPS and TPD measurements. The complex desorption process was attributed to coverage-dependent changes in the activation energies for the associative desorption of hydrogen as molecular  $\text{H}_2$ .

HL 32.9 Tue 12:30 MA 041

**Towards Understanding the Wetting of Nanostructured Surfaces** — ●MAUSUMI CHATTOPADHYAYA and ALEXANDRE TKATCHENKO — Fritz Haber Institut der MPG, Berlin, Germany

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

HL 32.10 Tue 12:45 MA 041

**Fingerprinting graphene: self-assembly by breaking the rules of surface science** — ●SAMUEL GRANDTHYLL<sup>1</sup>, STEFAN GSELL<sup>2</sup>, MICHAEL WEINL<sup>2</sup>, MATTHIAS SCHRECK<sup>2</sup>, KARIN JACOBS<sup>1</sup>, and FRANK MÜLLER<sup>1</sup> — <sup>1</sup>Saarland University, Experimental Physics, 66041 Saarbrücken, Germany — <sup>2</sup>University of Augsburg, Experimental Physics 4, 86135 Augsburg, Germany

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

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