

TT 9: Graphene I: Structure and Growth (joint session O/TT)

Time: Monday 10:30–13:00

Location: H24

Invited Talk

TT 9.1 Mon 10:30 H24

Real-time imaging of adatom-promoted graphene growth on nickel — ●LAERTE L. PATERA — Department of Physics, University of Trieste, 34127 Trieste, Italy — IOM-CNR - TASC Laboratory, Basovizza, 34149 Trieste, Italy — Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany

Single adatoms are expected to participate in many processes and chemical reactions occurring at solid surfaces. We demonstrate, both experimentally and theoretically, the catalytic role played by single metal adatoms during the graphene growth on Ni(111). The catalytic action of individual Ni atoms at the edges of a growing graphene flake was directly captured by scanning tunneling microscopy imaging at video-rate, allowing the precise determination of the atomic structure of reaction intermediates in the ms time-scale. Force field molecular dynamics and density functional theory calculations rationalize the experimental observations. Our results unveil the mechanism governing the activity of a single-atom catalyst at work [1].

[1] L. L. Patera et al., *Science* 359, 1243-1246 (2018)

TT 9.2 Mon 11:00 H24

Adsorption Heights and Coupling Strength at Graphene/Ni(111) and h-BN/Ni(111) interfaces —

●CHRISTINA SCHOTT¹, JOHANNES SEIDEL¹, MARKUS FRANKE², ANJA HAAGS², YOU-RON LIN², MARTIN AESCHLIMANN¹, CHRISTIAN KUMPF², and BENJAMIN STADTMÜLLER¹ — ¹Department of Physics and Research Center OPTIMAS, TU Kaiserslautern, 67663 Kaiserslautern, Germany — ²Peter Grünberg Institut, Functional Nanostructures at Surfaces, 52425 Jülich, Germany

From a technological point of view, 2D material stacks consisting of light elements grown on ferromagnetic surfaces are highly promising for spintronic applications due to their low spin-orbit coupling and the large charge and spin carrier velocity. However, utilizing the exotic properties requires a minimization of the chemical interaction between the 2D layers and the ferromagnet. Therefore, we have investigated the interlayer interaction strength and coupling mechanisms in bilayer films of prototypical 2D materials on the ferromagnetic surface Ni(111) by using the NIXSW technique. The small vertical bonding distance between graphene or the nano-graphene molecule coronene and the Ni(111) surface suggests a strong chemical interaction across the interface. To achieve a decoupling of coronene from Ni, we used one layer of h-BN as a buffer layer between one the coronene layer and the Ni substrate. Here, we will discuss the modifications of the vertical adsorption height of gr and coronene upon the passivation of the Ni surface and correlate our findings to the chemical interaction and the vertical distortions of these 2D layers.

TT 9.3 Mon 11:15 H24

Thermodynamically Stable Small-Angle Twisted Domains in Graphene on Iridium (111) — ●KARIM M. OMAMBAC¹,

CHRISTIAN BRAND¹, HICHEM HATTAB¹, LAURENZ KREMEYER¹, GIRIRAJ JNAWALI¹, ALPHA T. N'DIAYE², JOHANN CORAUX², RAOUL VAN GASTEL³, BENE POELSEMA³, THOMAS MICHELY², FRANK-JÖRG MEYER ZU HERINGDORF¹, and MICHAEL HORN-VON HOEGEN¹ — ¹Universität Duisburg-Essen, Germany — ²Universität zu Köln, Germany — ³University of Twente, The Netherlands

Lattice rotations or twists is one to the characteristics in the catalytic growth of monolayer graphene on a hot metallic surface. In particular, these small-angle twists have not yet been found experimentally but have been predicted partly through density functional theory calculations [1]. In this low energy electron diffraction study we evaluated the distribution of twisted domains of the epitaxially grown graphene on Ir(111) through spot profile analysis of the moiré spots. We find a new class of small-angle twisted domains with clear and distinct twist angles of 1.7°, 1.1° and 0.6° at growth temperatures of 1255 K, 1350 K, and 1460 K, respectively. To further analyze, we performed a simple two-dimensional in-plane coincidence site lattice analysis taking only into account the thermal expansion coefficients between the substrate and the epitaxially grown graphene. The results show a very good agreement with the experimental findings suggesting the origin of these small-angle twisted domains is strongly dependent on the variation of the lattice mismatch between graphene and Ir(111) substrate during growth. [1] *J. Phys.: Condens. Matter* **24**, 314214 (2012)

TT 9.4 Mon 11:30 H24

Buckling of graphene on Ir(111) by the intercalation of cobalt — ●DAVID A DUNCAN¹, NICOLAE ATODIRESEI², SIMONE LISI³,

PHIL J BLOWEY^{1,4}, VASILE CACIUC², JAMES LAWRENCE⁴, TIEN-LIN LEE¹, MARIA GRAZIA BETTI⁵, PARDEEP THAKUR KUMAR¹, ADA DELLA PIA⁵, GIOVANNI COSTANTINI⁴, and D. PHIL WOODRUFF⁴ — ¹Diamond Light Source, Didcot, UK — ²Forschungszentrum Jülich, Jülich, Germany — ³Institut Néel, Grenoble, France — ⁴University of Warwick, Coventry, UK — ⁵University Sapienza of Rome, Rome, Italy

The intercalation of Co between graphene and Ir(111) results in a corrugated network of strongly and weakly bound carbon [1]. Utilising the X-ray standing wave method to monitor the chemical-state resolved C 1s photoemission components [2], we determine that the strongly bound C atoms adsorb with a mean adsorption height, above the Co layer, of 2.06(3) Å, almost 0.75 Å lower than that of the weakly bound C atoms (2.76(5) Å). DFT calculations using DFT-D2 and vdW-DF corrections predict a subtle difference corrugation structure, with DFT-D2 predicting a local maximum where the vdW-DF predicts a global minimum. The DFT-D2 calculations result in a structural model that more closely matches the experimental results, with the vdW-DF calculations predicting mean adsorption heights for the strongly and weakly bound C atoms that are 0.10 Å and 0.37 Å closer to the Co intercalant, respectively, than measured experimentally. Despite this difference, both functionals predict a covalent like interaction between the Co and the C, resulting in a weak nearest-neighbour C-C buckling.

[1] PRB 87 (2013), 041403; [2] PRB, 90 (2014), 195446

TT 9.5 Mon 11:45 H24

Understanding the first steps of graphene growth: a study of small carbon clusters on Cu surfaces — ●JUAN SANTIAGO CINGOLANI, MIE ANDERSEN, and KARSTEN REUTER — Chair of Theoretical Chemistry, Technical University of Munich, Germany

It has been shown that high quality single layer graphene can be obtained through chemical vapor deposition on liquid Cu [1]. The role of the liquid surface in carbon nucleation as well as in defect healing is not yet well understood. While a comprehensive description of the growth mechanism would require molecular dynamics (MD) simulations, a first step is to study the precursors for graphene growth and the influence of the surface on them.

We performed a series of density-functional theory (DFT) calculations of carbon clusters of different sizes adsorbed to different Cu facets aiming to shed some light on the effects of the surface on relative stabilities, as well as on experimentally accessible properties such as vibrational frequencies. We also take advantage of the data generated to fit the parameters of density-functional tight binding, a semi-empirical method, which in turn allows us to carry out MD simulations for longer timescales and in larger systems than otherwise accessible through *ab initio* methods. We then simulate graphene flakes on liquid Cu at different levels of theory to get a clearer picture of what the Cu surface might look like under growth conditions.

[1] L. Tan, M. Zeng, T. Zhang, L. Fu, *Nanoscale* 7, 9105 (2015).

TT 9.6 Mon 12:00 H24

Aperiodically ordered nano-graphene — ●MAHALINGAM

MANIRAJ¹, LU LYU¹, SEBASTIAN BECKER^{1,2}, DOMINIK JUNGKERN¹, SEBASTIAN EMMERICH¹, SINA MOUSAVION¹, D L SCHLAGEL³, T A LOGRASSO³, SUDIPTA ROY BARMAN⁴, STEFAN MATHIAS⁵, BENJAMIN STADTMULLER¹, and MARTIN AESCHLIMANN¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Germany — ²Department of Chemistry, TU Kaiserslautern, Germany — ³Division of Materials Sciences and Engineering, Ames Laboratory, USA — ⁴UGC-DAE Consortium for Scientific Research, Indore (M.P.), India — ⁵I. Physikalisches Institut, Georg-August-Universität Göttingen, Göttingen, Germany

We demonstrate that the quasiperiodic order of surfaces can be transferred to 2D adsorbate systems by investigating the self-assembly of the nano graphene molecule coronene on the icosahedral(i)-Al-Pd-Mn quasicrystalline surfaces using multiple surface sensitive techniques. We find a quasiperiodic ordering of coronene on the i-Al-Pd-Mn surface which can be explained qualitatively by the P1 Penrose tiling. Using angle resolved photoemission spectroscopy, we observe a 5-fold sym-

metric modulation of the photoemission intensity distribution in the k_x - k_y -plane with a clear band dispersion along the high symmetry axis in momentum space. The latter suggests a direct correlation between the energy and momenta of the electrons in the quasicrystal and the rotational symmetry of the system. Moreover, the pseudogap of the bare Al-Pd-Mn persists even after the adsorption of the aperiodically ordered coronene confirming the quasiperiodic nature of the interface.

TT 9.7 Mon 12:15 H24

The role of the curvature of graphitic materials in the oxygen adoption reaction — JAKOB HAUNS, JULIAN WÜST, JÜRGEN WEIPPERT, REGINA FISCHER, FRANK HENNRICH, DMITRY STRELNİKOV, ●ARTUR BÖTTCHER, and MANFRED M. KAPPES — Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

The capability of graphitic materials to bind atomic oxygen has been studied under ultrahigh vacuum conditions by monitoring the oxygen-induced evolution of the XPS- O_{1s} , - C_{1s} and the valence band states, UPS-VB. Three groups of solid films were investigated: HOPG (planar graphene sheet), felts of metallicity-sorted single walled carbon nanotubes S-, M-SWCNTs and solid C_{60} films. The monodispersed materials chosen here differ by the curvature C of the graphene layers. In order to quantify the role of strained C-C-C bonds in the oxidation pathway exactly the same oxidation procedure has been applied to all graphitic materials. The VB-DOS profiles measured for oxidized films differ clearly by their oxygen-derived bands and the work functions. The evolution of the XPS- O_{1s} and - C_{1s} states indicate that whereas the oxidation of planar graphene sheets proceeds via epoxy species [1], ether functionalities dominate the oxidative scenario of the curved surfaces of SWCNT and C_{60} . The yield for the initial oxygen-adoption reaction for all curved surfaces is significantly higher than that measured for planar graphene sheets. This finding stresses the unique role of the strained -C-C-C- bonds which facilitate the formation of ether functionalities. [1] A. Barinov, et al. J. Phys. Chem. C 2009, 113, 9009.

TT 9.8 Mon 12:30 H24

Thermal reduction of graphene oxide studied by electron spectroscopy — ●GIANLUCA DI FILIPPO¹, ANDREA LISCIO², and ALESSANDRO RUOCCO¹ — ¹Dipartimento di Scienze, Università degli Studi Roma Tre, Rome, Italy — ²Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi, Rome, Italy

Graphene oxide (GO) is a purely 2D material composed of a conductive filter given by sp^2 domains and an insulating matrix containing

sp^3 -carbons, defects, holes and oxygen functional groups. The latter make GO an insulator, but its electronic, optical and structural properties can be tailored via controlled removal of the oxygen groups. This enables reduced graphene oxide (rGO) to be used in many fields such as sensors development and energy storage applications.

In this work, we investigated the thermal reduction of GO in ultra-high-vacuum by combining several electron spectroscopies. Photoemission spectroscopy (XPS and UPS) was used to investigate variations in the chemical and electronic structure of GO reduced in the 150 °C - 750 °C temperature range. The optical properties of rGO were investigated using electron energy loss spectroscopy (EELS). The build-up of the π -plasmon excitation was observed upon reduction at 300 °C, this revealing the formation of ordered graphene-like areas with dimensions around 5 nm. The vibrational spectrum revealed the presence of CH groups on the surface. Most of the hydrogen atoms are bound to sp^3 -carbon and are probably located in oxidized regions in the basal plane of rGO. The sp^3 -CH impurities can be removed upon annealing at 750 °C where only sp^2 CH defects are observed.

TT 9.9 Mon 12:45 H24

Intercalation dynamics of sulfur underneath graphene on Ru(0001) — ●LARS BUSS¹, JENS FALTA^{1,2}, and JAN INGO FLEGE³ — ¹Institute for Solid State Physics, University of Bremen, Germany — ²MAPEX Center for Materials and Processes, University of Bremen, Germany — ³Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

It is known that the binding of epitaxially grown graphene to the substrate has a detrimental effect on its electronic properties. This is especially true for the strong binding to various transition metals and particularly ruthenium. However, via intercalation the interlayer coupling can be lifted and its unique electronic properties can be restored. Therefore, we have investigated the interaction of sulfur with single-layer graphene grown on Ru(0001) via surface segregation and CVD of ethylene under UHV conditions with in situ low-energy electron microscopy (LEEM) and micro-diffraction (μ LEED). At elevated temperature and under dimethyl disulfide background pressure, we observe that sulfur intercalates through the open edges of the graphene islands. Prolonged exposure to sulfur induces wrinkling of the graphene islands, consistent with substantial relief of tensile strain after successful sulfur insertion underneath the graphene. It can be seen that the intercalation dynamics are both dependent on the temperature during intercalation and the preparation method of the graphene sheets. Furthermore, darkfield imaging and μ LEED of the intercalated graphene reveal a graphene induced improved ordering of sulfur underneath.