

O 27: Graphene II

Time: Tuesday 10:30–13:00

Location: MA 041

O 27.1 Tue 10:30 MA 041

How clusters bind to the graphene moiré on Ir(111) - XPS compared to DFT — ●TIMM GERBER¹, JAN KNUDSEN², PETER J. FEIBELMAN³, ELIN GRÄNÄS², KARINA SCHULTE⁴, PATRICK STRATMANN¹, JESPER N. ANDERSEN², and THOMAS MICHELY¹ — ¹II. Physikalisches Institut, Universität zu Köln — ²Division of Synchrotron Radiation Research, Lund University — ³Sandia National Laboratories, Albuquerque, New Mexico — ⁴MAX-lab, Lund University

Our understanding of metal-atom cluster adsorption on graphene on Ir(111) is based on elementary chemical ideas, rehybridization and buckling, supported by density functional theory (DFT) calculations. We have tested the DFT picture by comparing calculated core level spectra to X-ray photoemission spectroscopy (XPS) measurements. For pristine graphene, which forms a gently undulating moiré on Ir(111), DFT predicts a 140 meV modulation of C 1s core level shifts (CLS), consistent with the measured spectrum. With Pt clusters adsorbed, measured Pt 4f CLS of the adsorbed clusters also support the calculations. The modulation of the C 1s spectrum is strengthened with clusters adsorbed, and C-atom ionization potentials under and in the vicinity of the Pt clusters are shifted enough to be experimentally distinguished as a broad shoulder of positive C 1s CLS. Further, DFT calculations imply that sp^2 to sp^3 rehybridization of C-atoms below the Pt cluster induce a 1.1 eV CLS-splitting between Pt and Ir bonded C atoms; this prediction is also consistent with the XPS data.

O 27.2 Tue 10:45 MA 041

The stretching vibration of hydrogen adsorbed on epitaxial graphene — HYUNIL KIM, ●THORSTEN BALGAR, and ECKART HASELBRINK — Universität Duisburg-Essen, Fakultät für Chemie, Essen, Germany

The adsorption of hydrogen is one favorable approach for opening a bandgap in the bandstructure of graphene[1]. However, the binding geometry is still a matter of debate. Vibrational spectroscopy is a powerful tool which provides insight into the binding situation of adsorbates. We use IR/Vis sum-frequency generation (SFG) spectroscopy to study the stretching vibration of hydrogen chemically bound to a graphene sheet epitaxially grown on an Ir(111) crystal surface. The assignment of the observed resonances to C-H (C-D) stretching vibrations is discussed in view of the propensity for local cluster formation[2,3].

[1] Balog et al., Nat. Mater. (2010) 9 (4) pp. 315-319

[2] Kim et al., Chem. Phys. Lett. (2011) 508 (1-3) pp. 1-5

[3] Ng et al., J. Phys. Chem. C (2010) 114 (43) pp. 18559-18565

O 27.3 Tue 11:00 MA 041

Phase Coexistence of Clusters and Islands: Europium on Graphene — DANIEL F. FÖRSTER¹, TIM O. WEHLING², ●STEFAN SCHUMACHER¹, ACHIM ROSCH³, and THOMAS MICHELY¹ — ¹II. Physikalisches Institut, Universität zu Köln, D-50937 Köln — ²1. Institut für Theoretische Physik, Universität Hamburg, D-20355 Hamburg — ³Institut für Theoretische Physik, Universität zu Köln, D-50937 Köln

The adsorption and equilibrium surface phases of Eu on graphene on Ir(111) are investigated in the temperature range from 35 K to 400 K and for coverages ranging from a small fraction of a saturated monolayer to the second layer by scanning tunnelling microscopy (STM). Using density functional theory (DFT) including the 4f-shell Coulomb interactions and modelling of the electronic interactions, excellent agreement with the experimental results for the equilibrium adsorbate phase, adsorbate diffusion and work function is obtained. Most remarkable, at 300 K in an intermediate coverage range a phase of uniformly distributed Eu clusters (size 10–20 atoms) coexists in two dimensional equilibrium with large Eu-islands in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. We argue that the formation of the cluster phase is driven by the interplay of three effects: First, the metallic Eu-Eu binding leads to the local stability of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures. Second, electrons lower their kinetic energy by leaving the Eu clusters, thereby doping graphene. Third, the Coulomb energy penalty associated with the charge transfer from Eu to graphene is strongly reduced for smaller clusters.

O 27.4 Tue 11:15 MA 041

Adsorption of beryllium atoms, dimers and clusters on graphene and in graphite investigated by DFT — ●YVES FERRO¹, ALAIN ALLOUCHE¹, and CHRISTIAN LINSMEIER² — ¹Laboratoire de Physique des Interactions Ioniques et Moléculaires, Aix-Marseille Université /CNRS - UMR 6633, Campus de Saint Jérôme, Service 252, 13397 Marseille Cedex 20, France — ²Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstrasse 2, 85748 Garching b. München, Germany

We here investigate the interaction of beryllium with graphene and a bilayer of graphite by means of periodic DFT calculations. While non-magnetic, graphene and beryllium dimer can yield to an interacting structure in a magnetic electronic configuration; the magnetization is $1\mu\text{B}$ in the unit-cell. Another non-magnetic interacting structure has been found, but is not the electronic ground state. In all cases, we found the beryllium atoms and dimers to be more weakly bonded on graphene than in the bilayer, which is supported by the two following findings: (i) a Be atom is physisorbed on graphene while it is chemically bonded in the bilayer with an energy of about 1eV, (ii) the magnetic and non-magnetic beryllium dimers are adsorbed on graphene with energies of about one electron-Volt (1.3eV and 0.8 eV, respectively), while Be₂ is bonded into the bilayer with an energy of 2.1eV. We eventually found the stability of Be clusters to increase with the size of the beryllium clusters in the bulk of graphite. We also found a charge transfer to occur from beryllium to graphite.

O 27.5 Tue 11:30 MA 041

Electronic properties of Ni adatoms on graphene — ●MIKE GYAMFI¹, THOMAS EELBO¹, MARTA WAŚNIEWSKA¹, TIM O. WEHLING², STIVEN FORTI³, ULRICH STARKE³, ALEXANDER I. LICHTENSTEIN², MIKHAIL I. KATSNELSON⁴, and ROLAND WIESENDANGER¹ — ¹Institute of Applied Physics, University of Hamburg, Hamburg, Germany — ²1st Institute of Theoretical Physics, University of Hamburg, Hamburg, Germany — ³Max Planck Institute for Solid State Research, Stuttgart, Germany — ⁴Institute for Molecules and Materials, Radboud University of Nijmegen, Nijmegen, The Netherlands

We investigated Ni adatoms adsorbed on epitaxial monolayer graphene grown on the silicon terminated SiC(0001) surface by means of scanning tunneling microscopy (STM) and spectroscopy (STS).

The experiments were performed at 5 K and Ni was evaporated on the sample at 12 K which results in the adsorption of well isolated monomers. STM images with atomic resolution of the graphene lattice reveal all Ni atoms being located on the same adsorption site, i.e. on the center of a carbon hexagon. The electronic structure of the monomers is characterized by pronounced peaks below the Fermi energy which are related to Ni *d*-states. Due to the interaction with the substrate the electronic configuration of the Ni atoms is predominantly d^{10} and consequently the monomers are nonmagnetic. Furthermore, we observed an orbital selective coupling between the Ni adatoms and the Dirac electrons of graphene. The experimental results are compared to theoretical calculations.

O 27.6 Tue 11:45 MA 041

Role of electron correlations in cobalt adsorption on graphene: A quantum chemical perspective — ●ALEXANDER RUDENKO and FRERICH KEIL — Hamburg University of Technology, Chemical Reaction Engineering, Eißendorfer Str. 38, D-21073 Hamburg, Germany

Correct theoretical description of transition metal (TM) complexes represents a challenging task due to the presence of strong electron correlations. Commonly used theoretical concepts, such as DFT or single-determinant (HF-based) approaches are often unreliable even in terms of qualitative description of these systems. In the present work we investigate the adsorption of a single cobalt atom on graphene within the finite cluster approach by means of the complete active space SCF approach (CASSCF), additionally corrected by the second-order perturbation theory. We construct the active space by considering 3*d*, 4*s*, and 4*p* cobalt orbitals as well as two pairs of the most relevant π and π^* surface orbitals. In contrast to standard DFT studies, we find that the Co adatom *physisorbs* on graphene without formation of any chemical bonds. As a result, the spin state of adsorbed Co remains to be the same as for the free cobalt atom, i.e., $S=3/2$. The ground

orbital configuration changes, however, from $3d^7 4s^2$ to $3d^8 4s^1$ as Co approaches the surface. These results are in qualitative agreement with the LDA+ U and hybrid-functional calculations, which really indicate an important role of the Coulomb repulsion in the bonding and electronic properties of Co on graphene. In addition, we analyze the obtained CASSCF results in terms of a simple model Hamiltonian.

O 27.7 Tue 12:00 MA 041

Visualizing quantum interference nearby individual magnetic impurities on graphene — T. EELBO¹, M. GYAMFI¹, S. FORTI², U. STARKE², M. WAŚNIEWSKA¹, and R. WIESENDANGER¹ — ¹Institute of Applied Physics, University of Hamburg, Jungiusstr. 11, D-20355 Hamburg — ²Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany

The presence of impurities or defects on graphene and their influence on the electronic properties of graphene is an important aspect for next generation electronic devices. On the one hand intrinsic defects on graphene have already been widely studied, on the other hand extrinsic defects, such as adatoms are currently under theoretical and experimental study. We report on the local density of states of graphene in the presence of Co adatoms investigated by scanning tunneling microscopy/spectroscopy. The interaction of an individual Co adatom with graphene modifies the electronic structure over a distance of 1 nm around the adatom, leading to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure in the local density of states. The observed features of this wave pattern are consistent with the electronic intervalley scattering predicted to occur at adatoms' sites.

O 27.8 Tue 12:15 MA 041

Adsorption of polar molecules on graphene Ni(111) by substrate sensitive NEXAFS spectroscopy. — STEFAN BÖTTCHER, MARTIN WESER, HENDRIK VITA, YURIY DEDKOV, and KARSTEN HORN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

On account of its unusual properties, graphene has attracted an enormous interest. However, the interaction of graphene with metals and other adsorbates is still not well understood, for example the strength of its interaction with different metals. Here we investigate the adsorption of water and ammonia molecules on single layer graphene films grown on Ni(111), a lattice matched system. We use NEXAFS at the substrate carbon 1s and the adsorbate N 1s and O 1s absorption edges, and complement these data by angle resolved valence band photoemission. The data are compared with DFT calculations to assign possible adsorption geometries. The unique possibility to study adsorption-induced NEXAFS features *in the substrate* permits an analysis of the adsorbate-substrate interaction mechanism beyond a simple physisorption model.

O 27.9 Tue 12:30 MA 041

Electronic Structure of a Copper Phthalocyanine Mono-

layer on Graphene/Ru(0001) — T. NGUYEN¹, M. SCHOLZ¹, A. SCHOELL^{1,2}, M. MULAZZI¹, D. EHM³, and F. REINERT^{1,2} — ¹Experimentelle Physik VII und Wilhelm Conrad Röntgen Research Center for Complex Material Systems (RCCM), Universität Würzburg, D-97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, D-76021 Karlsruhe — ³Carl Zeiss SMT AG, Rudolf-Eber-Str. 2, 73447 Oberkochen,

We have studied the electronic structure of single layers of copper phthalocyanine (CuPc) on graphene/Ru(0001). The CuPc monolayers were prepared on graphene/Ru(0001) by using organic molecular beam deposition (OMBD). The surface structure of CuPc was characterized by low energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES) was used to investigate the electronic structure and the interaction of the molecules with the substrate. We show that there is a strong coupling between the CuPc molecule and the graphene/Ru(0001) surface. This is reflected by the ARPES data that shows a HOMO peak at a binding energy of 2.1 eV and an additional signal near the Fermi edge at about 0.8 eV. This can be assigned to the former LUMO (F-LUMO) state [1] which is (partly) occupied due to a charge transfer from the graphene/Ru(0001) surface and the CuPc [2].

Reference.

1. Zou, Y., et al., Surface Science, 2006. 600(6): p. 1240-1251.
2. Stadtmüller, B., et al., Physical Review B, 2011. 83(8).

O 27.10 Tue 12:45 MA 041

Ab initio and semi-empirical van der Waals study of graphene-boron nitride interaction at a molecular scale — VASILE CACIUC, NICOLAE ATODIRESEI, MARTIN CALLSEN, and STEFAN BLÜGEL — Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

In the present contribution we report on a theoretical study aimed to investigate the role of the London dispersion effects on the adsorption of a single benzene (C_6H_6), triazine ($C_3N_3H_3$) and borazine ($B_3N_3H_6$) molecule on a freestanding graphene and a single BN sheet. To determine the proper ground-state adsorption geometry, the van der Waals interactions were included in our density functional theory (DFT) calculations by using a semi-empirical [1] and an *ab initio* [2] approach, the latter as implemented in our JuNoLo code [3] recently updated [4] using the scheme proposed by Román-Pérez and Soler [5]. The importance of the non-local *vs.* semi-local correlations on the adsorption energy is also discussed.

- [1] S. Grimme, J. Comput. Chem. **27**, 1787 (2006).
- [2] M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004).
- [3] P. Lazić *et al.*, Comp. Phys. Commun. **181**, 371 (2010).
- [4] M. Callsen, N. Atodiresei, V. Caciuc, and S. Blügel, to be published.
- [5] G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009).