

Thursday Morning, October 21, 2010

Graphene Focus Topic

Room: Brazos - Session GR+AS+TF-ThM

Graphene Synthesis on Metals

Moderator: A.W. Ghosh, University of Virginia

8:00am **GR+AS+TF-ThM1 Contrast Behavior of Carbon Adatom Diffusion and Nucleation in the Initial Stage of Graphene Epitaxial Growth on Stepped Metal Surfaces**, *H. Chen, W. Zhu*, University of Tennessee at Knoxville; Oak Ridge National Laboratory, *Z. Zhang*, Oak Ridge National Laboratory; University of Tennessee at Knoxville

Using first-principles calculations within density functional theory, we study the energetics and kinetics of carbon adatom diffusion and nucleation on three stepped metal surfaces: Ir(111), Ru(0001) and Cu(111). We find that on the flat surfaces, two carbon atoms repel each other on Ir(111) and Ru(0001), while they prefer to form a dimer on Cu(111). Moreover, the step edges on Ir and Ru surfaces cannot effectively trap single carbon adatoms either, whereas it is strongly favorable to form carbon dimers at the step edges. The different behaviors are attributed to the competition between C-C bonding and different types of C-metal bonding, and the picture is generalized to other C-on-metal systems with predicted results. These findings provide an insight into the understanding of experimentally observed carbon nucleation in the initial stage of graphene epitaxial growth on metal surfaces.

8:20am **GR+AS+TF-ThM2 Density and Height Distribution of Ru and Bimetallic Pt/Ru Nanoclusters Self-Assembled on Ru(0001) Supported Monolayer Graphene**, *A.K. Engstfeld, S. Beckord, H.E. Hoster, R.J. Behm*, Ulm University, Germany

The Moiré-type nm-scale patterns of graphene monolayers on metal single crystals were recently shown to allow facile fabrication of ordered arrays of virtually monodisperse metal nanoclusters by simple metal vapour deposition in UHV [1-3]. In view of a potential utilization as model systems in electrocatalysis, we have tested the possibility of preparing Ru and bimetallic PtRu clusters by an analogous procedure. This included an extended study on the growth behaviour of the pure Ru clusters. Statistically evaluated STM images indicate that density and height distribution of Ru clusters are largely independent from the evaporation rate at room temperature. Lower/higher cluster densities along with larger/smaller cluster sizes were only achieved by higher/lower substrate temperatures during evaporation. For a given temperature, the lateral density of Ru clusters is higher than that of Pt clusters. Hence, the fabrication of bimetallic clusters can be performed more reliably when Ru is deposited first. We discuss in how far the found growth behaviour can be understood using classic nucleation theory.

8:40am **GR+AS+TF-ThM3 From Perfect Graphene to Cluster Superlattices**, *T. Michely*, University of Cologne, Germany **INVITED**

Through pyrolysis of hydrocarbons on noble metal surfaces monolayer graphite – graphene – is readily formed. Using scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM) we investigate the temperature dependent growth and the nature of point and line defects in the graphene layer on Ir(111). We identify heptagon-pentagon pairs of carbon atom rings to accommodate for slight misalignments of graphene domains, and wrinkles in the graphene layer for the mismatch in thermal expansion of graphene and Ir. After a systematic optimization of the growth procedure we obtain a single sheet of well oriented graphene on Ir(111) with a minimum of point and line defects.

Angle resolved photo emission finds graphene on Ir(111) to be only marginally doped and to display the characteristic Dirac cone at the K-point of the graphene Brillouin zone. The absence of hybridization of Ir and graphene states is consistent with the weak graphene - Ir interaction, as inferred from the large graphene - substrate separation as measured by the X-ray standing wave method and calculated by density functional theory including van der Waals interactions. The moiré resulting from the incommensurate epitaxy of graphene on Ir(111) gives rise to a large graphene supercell. In the graphene electronic structure it is reflected by the opening of minigaps at the boundaries of the induced mini-Brillouin zone.

The graphene moiré with Ir(111) is an active template allowing one to grow superlattices of metal clusters (Ir, Pt, Au, W, Fe, Re, Co, etc), spatially and thermally stable below 450 K. The graphene moiré enables also patterned adsorption of molecules and the template effect is not limited to the Ir(111) substrate. Based on STM and XPS measurements as well as density functional theory calculations it is proposed that at geometrically defined locations within the supercell and if sandwiched between substrate and

cluster metal the graphene rehybridizes from sp^2 graphitelike to sp^3 diamondlike bonding, resulting in strong covalent bonds between metal and graphene. The relevance of the graphene template effect for nanocatalysis, nanomagnetism and electrochemistry will be outlined.

9:20am **GR+AS+TF-ThM5 Graphene on Pd(111): In situ Low-Energy Electron Microscopy Studies of Growth Kinetics and Structure – Work Function Relationship**, *S. Kodambaka, Y. Murata*, University of California Los Angeles, *E. Starodub, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

Using *in situ* low-energy electron microscopy, we investigate the dynamics of graphene layer formation and the relationship between domain structure and its work function on Pd(111). We observe, in real time, the nucleation and growth of graphene islands during cooling via surface segregation of C atoms from the Pd bulk. Interestingly, we observe rapid motion of Pd substrate surface steps during graphene growth. Using low-energy electron diffraction, we identify at least five different orientations (domains) of monolayer graphene islands on the surface. We determine their relative orientations with respect to the substrate as approximately 2° , 6° , 11° , 19° , and 26° . We measured electron reflectivity (image intensity) values for each of the domains as a function of incident electron energy. From this data, we extracted the work functions of graphene domains which are found to vary with the domain orientation. Our results suggest that the substrate-graphene interactions influence the growth kinetics as well as the electronic structure of graphene.

9:40am **GR+AS+TF-ThM6 Second-Layer Graphene on Ir(111) – Relating Growth Mechanism to Physical and Electronic Structure**, *S. Nie*, Sandia National Labs, *A.L. Walter*, Lawrence Berkeley National Lab and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Starodub, K.F. McCarty, K. Thürmer*, Sandia National Labs, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, Lawrence Berkeley National Lab, *N.C. Bartelt*, Sandia National Labs, *E. Rotenberg*, Lawrence Berkeley National Lab

An interesting question is how the second layer of graphene grows on transition-metal substrates. First-layer graphene on Ir(111) [1] exists with four discrete in-plane orientations relative to substrate directions [2]. Thus, this system offers potential to better understand the relationship between second-layer growth and first-layer structure. We use low-energy electron microscope (LEEM) to characterize where the second-layer graphene forms on Ir(111) covered by domains of differently oriented first-layer graphene. We find that the second layer does not grow easily where the lattice of the first-layer graphene is aligned with the lattice of the substrate. Instead the second-layer graphene forms most easily where the first-layer graphene is rotated, by 30° , for example. Angle-resolved photoemission spectroscopy (ARPES) confirms this strong preference. So how does the orientation of the first layer control the growth of the second layer? ARPES and Raman spectroscopy provide insight, revealing that the rotated variants of first-layer graphene are even less strongly bound to the substrate than the more abundant, non-rotated variant [3]. This information suggests the following growth mechanism. Carbon atoms segregating from the substrate build up in concentration under the first layer. The second layer nucleates and grows where it is easier to debond the first layer from the substrate, that is, under the rotated first-layer domains. Electron diffraction also reveals that the second graphene layers are usually but not always aligned with the first-formed layer. Finally, we will discuss the doping of the different types of second-layer graphene, as revealed by ARPES.

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[1] A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse, and T. Michely, *New J. Phys.* 10, 16 (2008).

[2] E. Loginova, S. Nie, K. Thürmer, K., N. C. Bartelt, and K. F. McCarty, *Phys. Rev. B* 80, 085430 (2009).

[3] I. Pletikoscic, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N'Diaye, C. Busse, and T. Michely, *Phys. Rev. Lett.* 102, 056808 (2009).

10:40am **GR+AS+TF-ThM9 Graphene on Transition Metals – Growth and Interfacial Processing**, *P. Sutter, E. Sutter*, Brookhaven National Laboratory **INVITED**

Graphene has been used to explore the fascinating properties of two-dimensional sp^2 bonded carbon, and shows great promise for applications. A key bottleneck lies in synthesizing the required starting material: structurally perfect, macroscopically large graphene sheets with uniform thickness, into which active device structures can be patterned.

Epitaxial growth on transition metals has recently become one of the most promising methods for large-scale graphene synthesis. Here we discuss the fundamental mechanisms of graphene growth on ruthenium [1] and platinum [2], both single crystals and polycrystalline thin films, studied by a combination of *in-situ* surface microscopy methods. Real-time observations by low-energy electron microscopy (LEEM) show that epitaxy on Ru(0001) produces arrays of macroscopic monolayer graphene domains, whose coalescence is followed by the formation of large bilayer areas in a controlled layer-by-layer fashion. LEEM imaging together with diffraction, selected-area angle resolved photoemission spectroscopy (micro-ARPES), and scanning tunneling microscopy provide unique insight into the interaction between graphene and transition metal substrates, key to the synthesis of high-quality graphene [2, 3].

Beyond large-scale synthesis, potential applications of graphene will require novel approaches to processing and functionalization. We will highlight experiments by real-time surface microscopy to understand chemical reactions at graphene-metal interfaces, which may become part of novel processing strategies for graphene devices.

Work performed under the auspices of the U.S. Department of Energy under contract No. DE-AC02 98CH1-886.

[1] P. Sutter, J.I. Flege, and E. Sutter, *Nat. Mater.* **7**, 406 (2008).

[2] P. Sutter, J.T. Sadowski, and E. Sutter, *Phys. Rev. B* **80**, 245411 (2009).

[3] P. Sutter, M.S. Hybertsen, J.T. Sadowski, and E. Sutter, *Nano Lett.* **9**, 2654 (2009).

11:20am **GR+AS+TF-ThM11 Real-time Analysis of Graphene Growth on Polycrystalline Copper Foils**, *J.M. Wofford*, University of California at Berkeley and Lawrence Berkeley National Lab, *S. Nie, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories, *O. Dubon*, University of California at Berkeley and Lawrence Berkeley National Lab

Despite the potentially significant technological impact of graphene synthesis on Cu, little is understood about both the growth kinetics of this system and the morphology of the resulting heterostructure. We use low-energy electron microscopy (LEEM) to observe directly the UHV growth of graphene on polycrystalline Cu foils by the electron-beam evaporation of carbon. The temperatures required to synthesize highly ordered graphene simultaneously induce significant Cu sublimation and step flow, leading to a dynamic growth surface. As a result a complex interdependence develops between the graphene growth behavior and Cu surface morphology, with the graphene islands limiting Cu step mobility, and Cu step bunching distorting the propagation of the graphene growth front. This interplay becomes increasingly dramatic over time as the inhomogeneous sublimation of Cu leads to considerable surface roughening. In addition, the graphene islands are not compact in shape. Instead, the islands are ramified, consisting of several distinct lobes extending from a common nucleation site. Diffraction analysis reveals that each constituent lobe has a different in-plane orientation relative to the copper grain below and that the growth velocity of a given lobe depends strongly on its orientation relative to the underlying Cu at the growth front. We will describe the relationship between the orientation-dependent growth velocity and the local atomic geometry at the edge of the graphene sheet. Finally, the implications of this unexpected nucleation and growth mechanism on the formation of high-quality graphene films on Cu foils are evaluated.

Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Work at LBNL was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. JMW acknowledges the support from an NSF fellowship.

11:40am **GR+AS+TF-ThM12 Moiré Superstructures of Graphene on Faceted Nickel Islands**, *Y. Murata*, University of California Los Angeles, *V. Petrova*, University of Illinois at Urbana-Champaign, *B.B. Kappes, A. Ebnommasir*, Colorado School of Mines, *I. Petrov*, University of Illinois at Urbana-Champaign, *Y.-H. Xie*, University of California Los Angeles, *C.V. Ciobanu*, Colorado School of Mines, *S. Kodambaka*, University of California Los Angeles

Using scanning tunneling microscopy and spectroscopy, in combination with density functional theory (DFT), we investigated the morphology and electronic structure of monolayer graphene grown on the (111) and (110) facets of three-dimensional nickel islands on highly oriented pyrolytic graphite substrate. We observed hexagonal and stripe moiré patterns with periodicities of 22 Å and 12 Å, respectively, on (111) and (110) facets of the Ni islands. Graphene domains are also observed to grow, as single crystals, across adjacent facets and over facet boundaries. We suggest that the unexpected observation of moiré patterns of graphene on lattice-matched Ni(111) and the formation of single-crystalline domains across

different surface orientations are a consequence of the kinetic limitations of growth, rather than of the strength of the C-Ni interactions. Scanning tunneling spectroscopy data indicate that the graphene layers are metallic on both Ni(111) and Ni(110), in agreement with the DFT calculations. We attribute this behavior to strong hybridization between the *d*-bands on Ni and the *p* bands of carbon. Our findings point to the possibility of preparing large-area epitaxial graphene layers even on polycrystalline Ni substrates.

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