

# Wednesday Afternoon, October 31, 2012

## Graphene and Related Materials Focus Topic

Room: 13 - Session GR+AS+EM+NS+SS-WeA

### Dopants and Defects in Graphene; Graphene Interfaces with Other Materials

Moderator: D. Gunlycke, Naval Research Laboratory

2:00pm **GR+AS+EM+NS+SS-WeA1 Increasing Interface Bonding and Tuning Doping Behavior at Metal-Graphene-Metal Sandwich Contact.** C. Gong, R.M. Wallace, K.J. Cho, Y.J. Chabal, The University of Texas at Dallas

Two types of interfaces can be formed between metals and graphene depending on the strength of the metal-graphene interaction: weak (metal physisorption) and strong (metal chemisorption) interfaces. "Physisorption" interfaces (e.g., with Al, Ag, Cu, Ir, Pt and Au) are characterized by a larger metal-carbon distance ( $>3 \text{ \AA}$ ) with some charge transfer between metal and graphene (i.e. doping of graphene) that maintains its overall  $\pi$ -band dispersion. "Chemisorption" interfaces (e.g. with Ni, Co, Pd, and Ti) are characterized by a smaller metal-carbon distance ( $<2.5 \text{ \AA}$ ) and strong orbital hybridization between metal- $d$  and carbon- $p_z$  orbitals, resulting in the destruction of the graphene's  $\pi$ -band dispersion around the Dirac point. Till now, only a small fraction of all available metals has been used as electrode materials for carbon-based devices due to metal-graphene interface debonding problems. The issue therefore is to keep graphene's intrinsic  $\pi$  bandstructure by using weakly interacting metals while enhancing the interface stability.

We report an enhancement of the bonding energy of weakly interacting metals by using a metal-graphene-metal sandwich geometry, without sacrificing the intrinsic  $\pi$ -electron dispersions of graphene that is usually undermined by strong metal-graphene interface hybridization. This sandwich structure further makes it possible to effectively tune the doping of graphene with an appropriate selection of metals. Density functional theory calculations reveal that the strengthening of the interface interaction is ascribed to an enhancement of interface dipole-dipole interactions. Raman scattering studies of metal-graphene-copper sandwiches are used to validate the theoretically predicted tuning of graphene doping through sandwich structures.

2:20pm **GR+AS+EM+NS+SS-WeA2 Defects in Two-Dimensional Materials and their Heterostructures.** L. Adamska, I.I. Oleynik, University of South Florida

Recent developments in graphene electronics have stimulated an interest in other two dimensional materials such as hexagonal boron nitride (BN) and molybdenum disulfide ( $\text{MoS}_2$ ). In contrast to graphene, BN and  $\text{MoS}_2$  possess appreciable band gap and may form good interfaces with graphene, which opens up exciting opportunities for development of novel nanoelectronic devices. For practical applications, it is important to understand the effect of defects, which appear during growth and processing, on resulting electronic properties. The defects in graphene, BN,  $\text{MoS}_2$  and their heterostructures have been investigated by first-principles density functional theory. Their effect on electronic properties including density of states and simulated STM images will be discussed.

4:00pm **GR+AS+EM+NS+SS-WeA7 Metal Oxide Growth and Characterization on CVD Graphene.** A. Matsubayashi, College of Nanoscale Science and Engineering, University at Albany

Thin metal oxide layers deposited on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel. This is important for graphene based spintronic devices as dielectric layers between the ferromagnetic electrode and graphene have been shown to increase the spin relaxation time measured utilizing non-local detection and spin precession measurements<sup>[1]</sup>. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier<sup>[2]</sup>. In addition it is important to understand the stoichiometry of the resulting film. We will present a systematic study of aluminum oxide layers grown on CVD (chemical vapor deposition) graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS (X-ray photoelectron spectroscopy) will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium.

References:

(1) E. I. Rashba, Phys. Rev. B, **62**, 16267 (2000)

(2) W. Han *et al*, Phys. Rev. Lett., **105**, 167202 (2010)

4:20pm **GR+AS+EM+NS+SS-WeA8 Bi-layer Graphene Growth on Ni(111): The Role of Monolayer Graphene Rotation.** A. Dahal, A. Rafik, University of South Florida, P.W. Sutter, Brookhaven National Laboratory, M. Batzill, University of South Florida

Bi-layer graphene synthesis by chemical vapor deposition is of importance for field effect devices because the band gap can be tuned in bi-layer graphene by an applied electric field. Here, we demonstrate that bi-layer graphene can be synthesized above  $650^\circ\text{C}$  by chemical vapor deposition on thin Ni(111) films grown on YSZ(111) substrates in ultra high vacuum (UHV). We characterize the bi-layer graphene growth by low energy electron microscopy (LEEM), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Below  $600^\circ\text{C}$  graphene grows in registry with the Ni(111) lattice and no second layer graphene is formed upon cooling. At  $650^\circ\text{C}$  rotationally misaligned graphene domains are formed on Ni(111) and we observe second layer graphene to grow by carbon-segregation under those rotated monolayer graphene domains. The difference in second layer graphene nucleation and growth is explained by the graphene-Ni interaction, which is much stronger for graphene in registry with the substrate than for rotated graphene. The segregated second layer graphene sheet is in registry with the Ni(111) substrate and this suppresses further carbon-segregation, effectively self limiting graphene formation to two layers.

4:40pm **GR+AS+EM+NS+SS-WeA9 Energetic and Kinetic Factors of Graphene Nucleation on Cu.** N. Safron, M.S. Arnold, University of Wisconsin-Madison

Chemical Vapor Deposition (CVD) of graphene on Cu substrates uniquely allows for growth of uniform monolayer graphene and is a promising route for its scalable production for many industrial applications due to low cost. The growth is a purely surface driven process, due to carbon's low solubility in the Cu substrate, and relies on the Cu surface catalytically decomposing a carbon precursor (methane). As the growth of graphene proceeds across the surface, the reactivity of the Cu is passivated by the graphene, making the growth self-limiting to monolayer coverage. Research interest on the control of nucleation is intensifying, as the polycrystalline character of the graphene films can limit mobility, thermal conduction, and mechanical strength via grain boundaries.

In this paper, we study the nucleation dependencies of graphene at ambient pressure CVD in the context of surface nucleation theory. At low methane partial pressures, the concentration of carbon on the surface on the copper is low and carbon clusters cannot grow to a critical size for nucleation. As the partial pressure is increased, the methane partial pressure reaches a critical value and nucleation occurs. Tracking the critical pressure as a function of temperature from  $880$  to  $1075^\circ\text{C}$ , we have determined the formation energy of the critical graphene nucleus to be  $\sim 1.5 \text{ eV/carbon atom}$ , via the relation  $c_{\text{muc}} \sim \exp(-E_{\text{form}}/k_{\text{B}}T)$ . Additionally, we have found that the nucleation density of the graphene varies by 5 orders of magnitude over this temperature range at the critical methane concentration. The results are described under the desorption controlled regime of surface cluster nucleation.

Growths near the critical methane concentration yield hexagonal growing graphene domains characteristic of attachment limited kinetics, while at higher rates yield other growth shapes. Characterization by Raman Spectroscopy has been used to identify defects in the graphene layers. We find that the Raman defect band (D-Band) scales with the root of the nucleation density, indicating the majority of defects are located at the domain boundaries and the D-band intensity scales with the distance between them. Electrical mobility measurements show nearly constant values in samples across the range of temperatures indicating other limiting factors besides internal defects. Growths at  $900^\circ\text{C}$  yield  $\mu > 1000 \text{ cm}^2/\text{Vs}$ , ON/OFF ratio  $\sim 10$ , and Raman D/G ratio  $< 1$ , demonstrating high quality of growth even at relatively low temperatures.

5:00pm **GR+AS+EM+NS+SS-WeA10 Magnetic Spin Reorientation Transition in Graphene Covered Cobalt on Iridium(111).** A.T. N'Diaye, Lawrence Berkeley National Laboratory, J. Coraux, N. Rougemaille, C. Vo-Van, O. Fruchart, Institut NÉEL, CNRS & Université Joseph Fourier, France, A.K. Schmid, Lawrence Berkeley National Laboratory

One of graphene's promises is to be material for spintronic applications. While the influence of a magnet on graphene is under intense investigation by many groups little attention is given to the influence of graphene on a magnet.

With spin polarized low energy electron microscopy (SPLEEM) we studied thickness dependent spin reorientation transition on this system and

compare with Co/Ir(111) without graphene. Monitoring the spin orientation in three dimensions while increasing the film thickness by one ML at a time, we find that the presence of graphene on the film at least doubles the thickness at which the spin reorientation from out-of-plane to in-plane occurs from 6ML Co to transition to 12ML-13ML at 300°C and to between 14ML and 20ML at room temperature.

We attribute the significant contribution of the graphene/Cobalt interface to the magnetic anisotropy energy to a strong hybridization of graphene with Cobalt in directional bonds.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, by the French ANR contract ANR-2010-BLAN-1019-NMGEM and by the Alexander von Humboldt Foundation.

5:20pm **GR+AS+EM+NS+SS-WeA11 Nucleation and Growth of Rh and Au Clusters on Graphene Moiré/Ru(0001), B. Habenicht, Oak Ridge National Laboratory, D. Teng, Georgia Institute of Technology, L. Semidey-Flecha, Oak Ridge National Laboratory, D. Sholl, Georgia Institute of Technology, Y. Xu, Oak Ridge National Laboratory**

Nanometer and sub-nanometer sized metal clusters may possess electronic and catalytic properties that differ greatly from those of the corresponding bulk metals. For potential applications, dense arrays of uniform metal clusters are desirable. However, the synthesis of such cluster materials remains a formidable challenge. Moiré superstructures that develop in graphene supported on certain metals have been shown to be viable templates for driving the formation of uniform metal clusters.[1] On graphene moiré (GM) on Ru(0001), dispersed clusters are obtained for Rh whereas Au coalesces into very large 2D islands.[2,3] We carry out a computational study to understand the disparate morphologies of Rh and Au clusters on GM/Ru(0001) via a multi-scale approach. DFT calculations are performed to study the adsorption and diffusion of the adatom and ad-clusters of Rh and Au on GM/Ru(0001) and the bonding mechanism between the metals, graphene, and Ru substrate. The potential energy landscape is then used to perform kinetic Monte Carlo simulations for the diffusion, nucleation, and growth of Rh and Au clusters. This approach allows us to predict the spatial and size distribution of the metal clusters and may be generally applicable to identifying the conditions necessary for obtaining desired cluster morphologies on GM.

(1) N'Diaye, A. T.; Bleikamp, S.; Feibelman, P. J.; Michely, T. *Phys. Rev. Lett.* **2006**, *97*, 215501.

(2) Zhou, Z.; Gao, F.; Goodman, D. W. *Surf. Sci.* **2010**, *604*, L31.

(3) Xu, Y.; Semidey-Flecha, L.; Liu, L.; Zhou, Z.; Goodman, D.W. *Faraday Discuss.*, **2011**, *152*, 267.

5:40pm **GR+AS+EM+NS+SS-WeA12 Graphitic and Pyridinic N Species on N-doped HOPG Studied by STM, STS, PES and DFT, M. Sakurai, T. Shikano, D. Ushigome, T. Suzuki, University of Tsukuba, Japan, Y. Harada, M. Oshima, University of Tokyo, Japan, S. Casolo, University of Milan, Italy, M.I. Trioni, ISTM, Italy, G.F. Tantardini, University of Milan, Italy, T. Kondo, J. Nakamura, University of Tsukuba, Japan**

Nitrogen doped graphene and carbon nanotube have been reported to show superior catalytic activity or superior support effect in the fuel cell. However, effects of the dopant nitrogen on the modification of the electronic structure of such graphite-related materials have not been clarified because a wide variety of defects with different types of C-N bonding configurations can coexist in nitrogen doped graphite.

Here, we report comprehensive atomic-resolution characterization of the defects in a nitrogen-doped graphite surface by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), Photoemission spectroscopy (PES) and first-principles calculations based on the density functional theory (DFT). Nitrogen-doped graphite was produced by nitrogen ion bombardment of the HOPG (highly oriented pyrolytic graphite) followed by thermal annealing at about 900 K.

Two types of nitrogen species were identified at the atomic resolution. One is pyridinic N (N having two C nearest neighbors) with single-atom vacancy. The other is graphitic N (N having three C nearest neighbors). In the case of pyridinic N with single vacancy, the local electronic states of the non-bonding pz orbital of carbon are found to appear at occupied region near the Fermi level at the carbon atoms around pyridinic N. On the other hand, the local electronic states of the non-bonding pz orbital of carbon are found to appear at unoccupied region near the Fermi level at the carbon atoms around graphitic N.

These results indicate that in both cases more than 300 carbon atoms are found to be modified by the dopant N to show the non-bonding pz orbitals. Moreover, these results suggest that the graphitic-N and pyridinic-N as well as their surrounding carbon atoms may act as "acid" and "base", because their non-bonding pz orbitals appear at empty and occupied region, respectively.

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