Wednesday Afternoon, October 30, 2013

Graphene and Other 2D Materials Focus Topic
Room: 104 B - Session GR+AS+EM+NS+SS-WeA

Dopants, Defects and Interfaces in 2D Materials
Moderator: B.J. LeRoy, University of Arizona, A. Sinitskii, University of Nebraska-Lincoln

2:00pm **GR+AS+EM+NS+SS-WeA1 Atomic Force Acoustic Microscopy Detecting Defects in Graphene-Substrate Interface**, ***Q. Tu***, *Z. Parlak, R. Ferris, S. Zauscher*, Duke University

Graphene has extraordinary mechanical and electrical properties and has been demonstrated wide applications in flexible electronics and sensors. Most of the graphene-based devices functionalizes with graphene on a substrate. The conformation of graphene to the substrate and the bonding between graphene and substrate[1] will influence the electronic properties of graphene[2] and the stress transferred from the substrate to graphene, which is a big issue of device stability. Herein we show that the defects in graphene-substrate interface could be nondestructively detected by atomic force acoustic microscopy (AFAM), which is a dynamic AFM technique sensitive to the tip-sample contact stiffness. The contact stiffness mapping indicates that the graphene covered silicon was softer than uncovered area, which contradicts that graphene is the stiffest material ever known. This is due to the cavity and water molecules present in the graphene-substrate interface. With the topography data, a layered structure model is built up and the simulated contact stiffness mapping matches the experiment well. In addition, graphene was transferred to a substrate with patterened surface chemistry and the contact stiffness in hydrophobic area is higher than that in hydrophilic area, which indicates that reducing water molecules in the interface would increase the graphene-substrate contact.

[1] L. H. Liu and M. D. Yan, "Simple Method for the Covalent Immobilization of Graphene," vol. 9, pp. 3375-3378, Sep 2009.

[2] M. Lafkioti, B. Krauss, T. Lohmann, U. Zschieschang, H. Klauk, K. von Klitzing, and J. H. Smet, "Graphene on a Hydrophobic Substrate: Doping Reduction and Hysteresis Suppression under Ambient Conditions," vol. 10, pp. 1149-1153, Apr 2010.

2:20pm **GR+AS+EM+NS+SS-WeA2 Polarization Induced p-type Doping in the H-intercalated Epitaxial Graphene on SiC(0001)**, ***S. Rajput***, *M. Chen, Y.Y. Li, M. Weinert, L. Li*, University of Wisconsin Milwaukee

Hydrogen intercalation at the epitaxial graphene/SiC(0001) interface was achieved by annealing in hydrogen atmosphere at 800 ^{o}C. Raman spectroscopy, scanning tunneling microscopy and spectroscopy measurements were performed to determine the electronic and structural properties of the H-intercalated graphene. We find that while the as-grown graphene is n-type with the Dirac point at -0.35 eV below Fermi level, the H-intercalated graphene is p-type with a Dirac point +0.2 eV above the Fermi level. These results are explained by density functional theory calculations, which indicate that the carrier type and concentration in H-intercalated graphene/SiC are determined by the spontaneous polarization of the hexagonal SiCsubstrate.

2:40pm **GR+AS+EM+NS+SS-WeA3 Engineering Chemical Dopants in Monolayer Graphene**, ***A. Pasupathy***, Columbia University **INVITED**

Chemical doping is a promising route to achieve control over the carrier concentration in graphene. I will describe recent experiments on the growth of graphene that is chemically doped using nitrogen and boron atoms. Using a combination of scanning tunneling microscopy, Raman and x-ray spectroscopies, we are able to obtain a picture of the chemical and electronic structure of doped graphene from the atomic to the macroscale. At the atomic scale, I will describe the local bonding of nitrogen and boron dopants and their effect on free carrier concentration in the graphene sheet. At larger length scales, I will show that nitrogen dopants avoid edges and grain boundaries of the graphene film over length scales that can be as large as a micron. I will also discuss dopant clustering and show that nitrogen and boron behave very differently in this respect. Understanding these various effects requires us to consider both the mechanism by which graphene grows by chemical vapor deposition, and the interaction between the dopant atoms and the underlying substrate during growth.

4:00pm **GR+AS+EM+NS+SS-WeA7 Water-Induced Splitting of Epitaxial Graphene and Resulting Graphene Flake**, ***X. Feng****, *M.B. Salmeron*, Lawrence Berkeley National Laboratory

Epitaxial graphene on metal substrates has been demonstrated to be a promising route for graphene synthesis. The produced graphene is however typically polycrystalline, with defects that can affect its properties. The impact of defects might be critical when graphene interacts with gas molecules due to their enhanced reactivity, so there is a need to understand the adsorption of environmentally abundant molecules (such as water and oxygen). Here we report a study of water adsorption on epitaxial graphene on Ru and Cu substrates using scanning tunneling microscopy (STM). We found that on Ru(0001), graphene line defects are extremely fragile towards chemical attack by water, which splits the graphene into numerous fragments at temperatures as low as 90 K, followed by water intercalation under the graphene [1]. On Cu(111) water can also split graphene but far less effectively, indicating that the chemical nature of the substrate strongly affects the reactivity of C-C bonds in epitaxial graphene.

The graphene splitting produced many graphene flakes that were displaced onto the first graphene layer on Ru. These flakes show very facile translational and rotational motions between commensurate initial and final states at temperatures as low as 5 K. The motion is initiated by a transition of the flakes from a commensurate to an incommensurate registry with the underlying graphene (the superlubric state), followed by a rapid sliding until another commensurate position is reached [2]. We also studied the electronic screening effects in stacked graphene flakes on Ru. The screening affects the apparent STM height of each flake in successive layers reflecting the density of states near the Fermi level and thus the doping level. It is revealed in this way that the strong doping of the first graphene layer on Ru(0001) is attenuated in the second one, and almost eliminated in the third and fourth layer [3].

References:

[1] X. Feng, S. Maier and M. Salmeron. *J. Am. Chem. Soc.***134**, 5662–5668 (2012).

[2] X. Feng, S. Kwon, J. Y. Park and M. Salmeron. *ACS Nano***7**, 1718–1724 (2013).

[3] X. Feng and M. Salmeron. *Appl. Phys. Lett.***102**, 053116 (2013).

4:20pm **GR+AS+EM+NS+SS-WeA8 STS Observation of Landau Levels on the Flat Area of Nitrogen-doped HOPG Surface under the Zero Magnetic Fields**, ***T. Kondo***, *D. Guo, T. Sikano, T. Suzuki, M. Sakurai, J. Nakamura*, University of Tsukuba, Japan

The charge carriers in graphene are known to follow a relativistic Dirac equation and behave as massless Dirac fermions [1]. In a magnetic field, massless Dirac fermions in graphene exhibit a relativistic Landau-level quantization and an anomalous quantum Hall effect [2,3]. The Landau-level energy sequence in graphene (single layer) shows a square-root dependence on both the magnetic field and the Landau index *n*, where a zeroth Landau level appears at the Dirac point. However, we have recently reported based on the scanning tunneling spectroscopy (STS) that the Landau levels of massless Dirac fermions generate in the absence of an external magnetic field on a partially potassium-intercalated highly oriented pyrolytic graphite (K-HOPG) surface [4]. The observation of the Landau levels of massless Dirac fermions indicates appearance of the graphene characters in K-HOPG. The generation of the Landau levels is ascribed to a vector potential induced by the perturbation of nearest-neighbour hopping, which may originate from a strain or a gradient of on-site potentials at the perimeters of potassium-free domains. There are other reports that the strain of graphene induces the Landau levels generation under the zero magnetic fields [5-8]. Here, we report the generation of the Landau levels of massive Dirac fermions on a nitrogen-doped graphite (N-HOPG) surface without strain under the zero magnetic fields. The pseudomagnetic fields are estimated to be as much as 60 T. Landau levels are observed at the flat area of the N-HOPG surface and thus the strain can be excluded as the possible origin of the perturbation of nearest-neighbour hopping. According to XPS, STM, and STS, our N-HOPG sample was found to consist mainly of the graphitic-N species which has a positive charge and modulates a potential on the surface [9]. Therefore, the generation of the Landau levels on N-HOPG is probably originated from a gradient of on-site potentials of carbon across the domain of the equipotential contour induced by the dopant graphitic-N species of N-HOPG.

[2] K.S.Novoselov, *et al.* Nature 438, 197 (2005).

[3] Y. Zhang, et al., Nature **438**, 201 (2005).

*** Morton S. Traum Award Finalist**

[4] D.Guo, T.Kondo, J.Nakamura et al., Nature Communications **3**, 1068 (2012).

[5] N.Levy, *et al.* Science **329**, 544 (2010).

[6] H.Yan, et al., Phys. Rev. B 85, 035422 (2012).

[7] K.K.Gomes, et al., Nature, 483, 306 (2012).

[8] J. Lu, A.H. C. Neto and K.P.Loh, Nature Communications **3**, 823 (2012).

[9] T.Kondo, S.Casolo, J.Nakamura, et al., Phys. Rev. B **86**, 035436 (2012).

4:40pm **GR+AS+EM+NS+SS-WeA9 X-ray Photoelectron Spectroscopy Investigation of the Band Alignment at h-BN/Graphene/High-k Dielectric Interfaces**, ***M. Paquette***, *J. Otto*, Univ. of Missouri-Kansas City, *S.W. King*, *J.D. Bielefeld*, *M. Jaehnig*, *M. French*, *B. French*, *M. Kuhn*, Intel Corp., *B. Nordell*, *A.N. Caruso*, Univ. of Missouri-Kansas City, *Y. Song*, MIT, *R. Caudillo*, Intel Corp., *J. Kong*, MIT

Due to a wide band gap (~ 6 eV), close lattice matching (< 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of interest as a potential substrate and gate dielectric in graphene channel transistor devices. A key property for the success of h-BN as a gate dielectric in such devices is its interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and a variety of materials including graphene, Cu, SiO_2, a-SiN_x:H, a-SiC:H, and Si. In combination, we have also investigated the valence band alignment between graphene and various high-k dielectrics including Al_2O_3, HfO_2, ZrO_2, and TiO_2. Combined with reflection electron energy loss spectroscopy measurements of the band gaps for the respective dielectric materials, we have also been able to determine the conduction band offset at these interfaces. We show that in many instances the valence and conduction band offsets are significant (> 2 eV) and favorable for a variety of possible h-BN/graphene transistor devices.

5:00pm **GR+AS+EM+NS+SS-WeA10 Epitaxial Graphene Bands and Adsorption of FePc for Stepped SiC-Si Surfaces**, ***J.E. Rowe***, *D.B. Dougherty*, *A.A. Sandin*, North Carolina State University, *A. Al-Mahboob*, *J.T. Sadowski*, Brookhaven National Laboratory

We have conducted a number of experimental measurements of the adsorption system FePc on stepped and unstepped graphene surfaces which may become important for spin-dependent electronics. Our studies were partially conducted using the PEEM beamline as NSLS, the Brookhaven synchrotron facility and we studied epitaxial graphene grown in UHV on 6H and 4H Si surfaces of SiC. In addition, we have measured changes in graphene bands using local area angle-resolved photoemission spectroscopy (ARPES) and normal emission PES for these surfaces both before and after adsorption of Iron Phthalocyanine (FePc). This is to understand the interactions of the FePc as an alternate approach to spin injection into graphene by the use of planar organic molecules as interfacial layers to enhance spin injection. Since weak intermolecular interactions can be comparable in size to molecule-substrate interactions for planar aromatics on graphene, high quality film growth is more likely. We have studied using PEEM. LEEM and STM the growth of iron phthalocyanine (FePc), a chemically-robust paramagnet, on epitaxial graphene on SiC(0001)-Si for the above mentioned surfaces. Ordered monolayer films are obtained on all surfaces with exposure and post-deposition annealing. Stepped surfaces introduces some preferred orientation domain formation as expected. Details of the PES and ARPES studies are discussed as well as LEEM images that clearly show step-flow growth of graphene.

5:20pm **GR+AS+EM+NS+SS-WeA11 Atomic Collapse in Graphene: Exploring Tunable Charge Impurities at the Nanometer Scale**, ***M.F. Crommie***, *Y. Wang*, *D. Wong*, University of California, Berkeley, *V.W. Brar*, California Institute of Technology, *H.-Z. Tsai*, *S. Choi*, *W. Regan*, University of California, Berkeley, *R. Kawakami*, University of California, Riverside, *A.V. Shytov*, University of Exeter, UK, *A. Zettl*, *S.G. Louie*, University of California, Berkeley, *L.S. Levitov*, Massachusetts Institute of Technology **INVITED**

Graphene has unique electronic properties that arise from its 2D honeycomb structure and which cause novel behavior at the atomic scale. This can be seen in graphene's response to charged impurities, where graphene's ultra-relativistic nature leads to impurity states that are unlike those found in any other material. The physics of Coulomb impurities on graphene is divided into two regimes: subcritical and supercritical. In the subcritical regime no bound states form around the impurity. When the impurity charge exceeds the threshold for supercritical behavior, however, "atomic collapse" states are predicted to emerge. Such states are different from semiconductor impurity states in that their wave functions are composed of a near-field collapsing electron-like component that is coupled via Klein tunneling to a far-field hole-like component that escapes to infinity. We have explored such impurity states across different impurity-charge regimes by building charge centers (i.e., "artificial nuclei") atom-by-atom at the surface of graphene devices and probing them via scanning tunneling microscopy. New results on this topic, including the observation of "atomic collapse" [1], will be discussed.

References:

[1] Y. Wang, D. Wong, A. V. Shytov, V. W. Brar, S. Choi, Q. Wu, H.-Z. Tsai, W. Regan, A. Zettl, R. K. Kawakami, S. G. Louie, L. S. Levitov, M. F. Crommie, " Observing Atomic Collapse Resonances in Artificial Nuclei on Graphene", *Science*, DOI:10.1126, March 7, 2013.

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