Graphene and Related Materials Focus Topic
Room: 208 - Session GR-WeA

Graphene Characterization including Microscopy and Spectroscopy
Moderator: J.T. Robinson, Naval Research Laboratory

2:00pm **GR-WeA1 Scanning Probe and Optical Microscopy and Spectroscopy of Graphenes on (sub-) Molecular Layers on Atomically Flat Substrates**, ***J. Rabe***, *N. Severin, P. Lange, M. Dorn, S. Eilers*, Humboldt University Berlin, Germany **INVITED**

Graphenes were used to cover solid substrates, including silicon wafers and atomically flat mica, pre-coated with molecularly thin liquids as well as single macromolecules. Optical reflection microscopy was employed to identify single graphenes on optically transparent substrates in optical reflection microscopy with a contrast of more than 12% [1]. A combined fluorescence and scanning force microscopy study revealed that that graphene is not only a highly conductive and transparent electrode, but also a most effective barrier to protect conjugated polymers against degradation through water and oxygen [2]. Time resolved pump-probe spectroscopy revealed ultrafast nonequilibrium carrier dynamics [3]. Finally, scanning force and electrostatic force microscopy, and also STM/STS were used to characterize structure and electronic properties of single graphenes with molecules either on top or below the graphene, revealing a remarkable stability of the elctronic properties of these hybrid systems.

[1] M. Dorn, P. Lange, A. Chekushin, N. Severin, J.P. Rabe, *J. Appl. Phys.* 108 (2010) 106101.

[2] P. Lange, M. Dorn, N. Severin, D. Vanden Bout, J.P. Rabe, *Verhandlungen DPG Regensburg* 2010.

[3] M. Breusing, S. Kuehn, T. Winzer, E. Malic, F. Milde, N. Severin, J.P. Rabe, C. Ropers, A. Knorr, T. Elsaesser, Phys. Rev. B (2011) 153410.

2:40pm **GR-WeA3 Scanning Tunneling Microscopy and Spectroscopy of Suspended Graphene Membranes**, ***N.N. Klimov***, PML/CNST/NIST and Maryland NanoCenter UMD, *S. Jung,* CNST/NIST and Maryland NanoCenter UMD, *N.B. Zhitenev,* CNST/NIST, *D.B. Newell,* PML/NIST, *J.A. Stroscio*, CNST/NIST

The discovery of graphene, a unique two-dimensional electron system with extraordinary physical properties, has ignited tremendous research activity in both science and technology. Graphene interactions with a substrate such as, for example, SiO_2/Si are known to strongly limit the electrical performance of graphene devices. Suspended graphene devices, where the interaction with substrates can be strongly reduced, have been studied by macroscopic transport measurements and shown to have a 10-fold increase in mobility. However, a detailed investigation of electronic properties of suspended graphene on a microscopic scale is still missing. In this talk we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of free-standing graphene membranes. The device was fabricated from a graphene flake exfoliated over an array of 1 μm holes etched in SiO_2/Si substrate. Electronic spectra of both suspended and supported regions of single-layer graphene can be probed using STM/STS in a perpendicular magnetic field with varying back gate voltages applied to the Si substrate. We found that both the scanning probe tip and applied back gate voltage induce mechanical deformations in the suspended graphene membrane, which, in turn, influences the graphene electronic spectrum. The significant differences found in the electronic spectra of suspended and non-suspended graphene will be discussed.

3:00pm **GR-WeA4 Moiré Twist and Absence of Chirality in Graphene on Ru(0001)**, *K.L. Man,* ***M.S. Altman***, Hong Kong University of Science and Technology, China

The strength of the interaction between graphene and a supporting metal substrate is revealed in its influence on electronic structure and properties. Knowledge of structure is of elementary importance for understanding the nature of this interaction. The structure of a single layer of graphene (g) on the Ru(0001) surface has been controversial, beginning with the elementary matter of its lateral periodicity. It was eventually shown using surface x-ray diffraction (SXRD) that a superstructure forms from the moiré-like superposition of (25x25) graphene on (23x23) Ru units [1]. Although corrugation was detected within the supercell, the predominant origin of corrugation in this system, whether physical or electronic, has been disputed. Intriguing evidence from SXRD was also put forth that g/Ru(0001) exhibits chirality, whereby the weakly bound, protruding regions of a physically corrugated graphene layer are rotated in-plane by up to two degrees [2]. We have investigated single layer g/Ru(0001) using low energy electron microscopy (LEEM) and micro-low energy electron diffraction (μLEED) in order to verify the existence of chirality. Chirality should give rise to differences between the intensities of diffraction spots mirrored across the high symmetry directions. However, this broken mirror symmetry will be very difficult to detect using laterally averaging techniques such as SXRD because of the presence of two chiral enantiomers and two terminations of the hcp substrate. Using LEEM and μLEED we have successfully obtained diffraction information from an area with a diameter of 250 nm within a single surface termination. While no evidence is found with such high spatial resolution diffraction measurements that confirms chiral features within the unit cell, we do in fact observe rotation or twist of the moiré-like superposition over long length scales. Moiré twist causes the entire ensemble of satellite diffraction spots around each integer order spot to rotate as a group about their respective stationary foci. When the μLEED beam is scanned across the surface, the rotation angle undulates randomly. The data also suggest that the ground state configuration comprises a graphene layer that is slightly rotated with respect to the underlying substrate surface. Conceivably, the orientational variations that are observed here over sub-micron length scales might produce a signature in laterally averaging measurements that could be construed as evidence of chiral features on the short length scale within the unit cell.

[1] D. Martoccia *et al.*, Phys. Rev. Lett. **101**, 126102 (2008).

[2] D. Martoccia *et al*., New J. Phys. **12**, 043028 (2010)

4:00pm **GR-WeA7 Scanning Tunneling Microscopy Study on a Graphene Layer Grown on a Single-crystal Cu(111) Surface by Using Chemical Vapor Deposition**, ***W. Kim***, Korea Research Institute of Standards and Science, Republic of Korea, *K.-E. Yang,* KRISS and Chunnam National Univ., Republic of Korea, *K. You, S.J. Kim, E.K. Seo, C. Hwang*, Korea Research Institute of Standards and Science, Republic of Korea

We investigated the surface atomic structure of a graphene layer grown on a single-crystal Cu(111) surface by using a chemical vapor deposition method. The low-energy electron diffraction pattern shows a clear ring structure, which indicates the existence of multiple domains with different in-plane orientations. In the scanning tunneling microscopy(STM) experiment, two domains showing different Moiré patterns and a domain boundary between them are observed. The misorientation angle between the domains was estimated from the quantum interference pattern around the domain boundary and the atom-resolved image of each domain. In the STM images of the domain boundary, the chain of protrusions was observed, which indicates the existence of localized electronic states originated from the pentagon or heptagon structures at the boundary.

4:20pm **GR-WeA8 Interface Structure of Graphene on SiC(000-1)**, ***N. Srivastava***, *G. He, R.M. Feenstra*, Carnegie Mellon University

The graphene/SiC interface structure is quite well understood on the SiC(0001) surface (the *Si-face*) but the situation is less clear on the SiC(000-1) surface (the *C-face*). For the C-face some groups report a 3×3 and/or 2×2 interface structure with weak interaction with the underlying substrate.[1] A single study however found an interface layer that was strongly bonded to the SiC.[2] We demonstrate that the interface layer on the C-face depends on the means of graphene formation. For graphitization in vacuum we observe a 3×3 interface in agreement with other groups. However for graphitization in a Si-rich environment we observe a new interface indicative of a buffer layer similar to that seen on the Si-face.

In this work, graphene films are formed by heating the C-face in vacuum or in a disilane environment. It is found that different interface structures occur for the two preparation conditions. In particular, in 5×10^{-5} Torr of disilane we find a graphene-like buffer layer forming at the interface, analogous to the well known behavior of the Si-face. We therefore find that graphene formation on the C-face and Si-face are not so much different (although they appear to be when using vacuum preparation): A buffer layer that acts as a template for graphene formation exists in both cases, so long as equilibrium conditions are employed (i.e. with the disilane environment).

Studies are performed using atomic force microscopy (AFM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM). For graphene prepared in vacuum, LEED patterns show a characteristic 3×3 pattern together with graphene streaks. In contrast, for the graphene produced in 5×10^{-5} Torr of disilane, LEED patterns reveals a complex $\sqrt{43}\times\sqrt{43}$-R±7.6° arrangement. This structure is somewhat similar to the well known $6\sqrt{3}\times6\sqrt{3}$-R30° "buffer layer" of the Si-face, with satellite spots surrounding the primary Si spots, and is interpreted as arising from a C-rich buffer layer with 8x8 graphene unit cells on the SiC (with rotation angle of ±7.6° rather than 30° for the Si-face). After air exposure the $\sqrt{43}\times\sqrt{43}$-

R±7.6° pattern changes, with the intensity of the graphene streaks increasing and the √43×√43 spots themselves disappearing and being replaced by √3×√3-R30° spots. This latter behavior is interpreted as oxidation of the SiC surface beneath the buffer layer,[3] again similar to what occurs on the Si-face. LEEM reflectivity curves on the surface reveal features similar to those for the 6√3×6√3-R30° layer on the Si-face.[4] Importantly, selected area diffraction on those surface areas, after oxidation, reveals a wavevector magnitude precisely equal to that of graphene, thus proving that a decoupled buffer layer does indeed exist on the surface. It is argued that the C-face buffer layer represents the equilibrium structure of the interface, whereas the 3×3 interface forms due to kinetic limitations.

[1] Emtsev et al., Phys. Rev. B **77**, 155303 (2008).

[2] Varchon et al., Phys. Rev. Lett **99**, 126805 (2007).

[3] Oida et al., Phys. Rev. B **82**, 041411 (2010).

[4] Hibino et al., Phys. Rev. B **77**, 075413 (2008).

4:40pm **GR-WeA9 Thermionic Emission of Graphene on Metal Surfaces**, ***E. Starodub***, *N.C. Bartelt, K. McCarty*, Sandia National Laboratories

We employ low-energy electron microscopy (LEEM) to study the thermionic emission of graphene on representative metals, Ru(0001) and Ir(111). In traditional LEEM, an image is produced using low-energy electrons reflected from a surface. The unique capabilities of LEEM allow us to image directly electrons thermionically emitted from graphene at high temperatures, above 1100K, using the same imaging optics. Due to the strong dependence of emission current on temperature, given by the Richardson-Dushman equation, we determine the work function of graphene-covered Ru(0001) and Ir(111) surfaces. The work function of graphene on Ru(0001) is determined to be 3.4 ± 0.1 eV, which is considerably smaller than work function of clean Ru (5.4 eV) and graphene (4.6eV). The obtained value is in good agreement with the result of first principles calculations, 3.6 eV [1], where strong graphene/metal interaction leads to significant film-to-substrate charge transfer and, as a result, reduced work function.

In contrast to the strong interaction with Ru, graphene bounds weakly to the Ir surface reducing the work function. The work functions of graphene on Ir(111) measured for two in-plane orientations on the Ir surface [2], R0 and R30, are 4.5 ± 0.1 eV and 4.7 ± 0.1 eV, respectively. Thus, the in-plane orientation noticeably changes the work function on Ir. It is consistent with our previous observation of the effect of electronic structure on orientation by electron reflectivity [3] and ARPES [4] .

Our finding shows that graphene has another application in addition to be a promising candidate for future electronics. One-monolayer graphene on metals such as Ru and Ir can be used as a chemically inert electron emitter with large surface area and low work function, comparable to lanthanum hexaboride, LaB_6.

Acknowledgement: This work is supported by the Office of Basic Energy Science, Division of Materials Sciences and Engineering of the U.S. DOE under Contract No. DE-AC04-94AL85000.

[1] B. Wang, S. Günther, J. Wintterlin and M.–L. Bocquet, New Journal of Physics 12 (2010) 043041

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

[3] S. Nie S, A. L. Walter, N. C. Bartelt, E. Starodub, A. Bostwick, E. Rotenberg, K. F. McCarty, ACS NANO 5 (2011) 2298-2306

[4] E. Starodub, A. Bostwick, L. Moreschini, S. Nie, F. El Gabaly, K. F. McCarty, and E. Rotenberg, PRB 83 (2011) 125428

5:00pm **GR-WeA10 Imaging Epitaxial Graphene on SiC(0001) using STM with Functionalized W Tips**, ***S.H. Rhim***, *Y. Qi, G.F. Sun, Y. Liu, M. Weinert, L. Li*, University of Wisconsin-Milwaukee

Epitaxial graphene on SiC(0001) is studied using scanning tunneling microscopy with W tips functionalized by transition metal (Cr, Fe) coating, which enables the imaging of states within a few meV of the Fermi level that are not accessible with conventional W tips. Modeling of these tips using X/W(110) (X=Cr, Fe, W) by first-principles calculations indicates that states responsible for enhanced tunneling are located 0.4~0.6 eV above and below E_F for Fe/W tips, and 0.3 eV above E_F for Cr/W tips. Further calculations show that the formation of an apex atom is not stable for W/W(110) or Fe/W(110) tips, but is stable for Cr/W(110) tips, resulting in point-like iso-density of states contours that are ideal for the selective imaging of the complex electronic properties of the epitaxial graphene on SiC(0001).

5:20pm **GR-WeA11 Hydrogenation of Epitaxial Graphene on 6H-SiC(0001): The Formation of Hydrogen-Vacancy Complex**, *Y. Liu, M. Weinert,* ***L. Li***, University of Wisconsin-Milwaukee

In this work, we have studied the hydrogenation of epitaxial graphene on 6H-SiC(0001) by Ar/H_2 plasma at room temperature. Two predominant types of defects are observed, and their atomic and electronic structures are studied by scanning tunneling microscopy/spectroscopy (STM/STS) and first principles calculations. The results suggest that vacancies are created with hydrogen atoms trapped nearby between the graphene sheets, forming H-vacancy complexes. In addition, changes in the electronic structures of the defects are also observed during STM imaging, which can be attributed to the dissociation and recombination of these complexes by the electric field of the STM tip. These results and their impact on the gap opening in hydrogenated graphene will be presented at the meeting.

5:40pm **GR-WeA12 Many-Body Interactions in Quasi-Freestanding Graphene**, ***D.A. Siegel****, *C.H. Park,* University of California, Berkeley, *C.G. Hwang,* Lawrence Berkeley National Laboratory, *J. Deslippe,* University of California, Berkeley, *A.V. Fedorov,* Lawrence Berkeley National Laboratory, *S.G. Louie, A. Lanzara*, University of California, Berkeley

Until recently it had been extremely difficult to experimentally address one of the most fundamental questions about graphene: How do the quasiparticles behave in neutral graphene, i.e. when the chemical potential coincides with the Dirac point energy? Here we address this question by investigating graphene on a particularly interesting substrate, the carbon face of SiC, with high-resolution angle-resolved photoemission spectroscopy (ARPES). We present the first direct measurements of the self-energy in graphene near the neutrality point, and show that the many-body physics in graphene differ from those of an ordinary metal. These exciting findings set a new benchmark in our understanding of many-body physics in graphene and a variety of novel materials with Dirac fermions.

***** Morton S. Traum Award Finalist

Authors Index

Bold page numbers indicate the presenter