

Wednesday Afternoon, November 11, 2009

Graphene Topical Conference

Room: C3 - Session GR+AS-WeA

Graphene: Surface Characterization

Moderator: P. Sheehan, Naval Research Laboratory

2:00pm GR+AS-WeA1 Tuning the Properties of Dirac Fermions in Graphene, A. Lanzara, University of California, Berkeley INVITED

Graphene, a one atom thick layer of carbon, the supposedly ideal Dirac material, has been under the radar of theorists and experimentalist for many decades. Although novel physical properties were envisioned, graphene, as any other 2D material, was presumed not to exist in its free state because of long wavelength fluctuations will easily destroy purely 2D membranes. The recent success in isolating a single sheet of graphene has certainly challenged this view. In this talk I will present our experimental work in this field using a combination of spectroscopic and microscopy tools. I'll present experimental evidence of what drives the stability of a graphene membrane and show comparison between exfoliated and epitaxial graphene. I will then discuss the nature of fermions in graphene sheets and how their peculiar electronic structure can be tuned by engineering small terraces of graphene down to nm size, where the physics gets dominated by quantum confinement. The implications of our study on the properties of Dirac materials and their potential role for applications are discussed

2:40pm GR+AS-WeA3 Growth of Semiconducting Graphene on Pd(111), S. Kodambaka*, S.-Y. Kwon, University of California, Los Angeles, C.V. Ciobanu, Colorado School of Mines, V. Petrova, J. Barenco, University of Illinois, V.B. Shenoy, Brown University, V. Gambin, Northrop Grumman Space and Technology, I. Petrov, University of Illinois INVITED

We report *in situ* variable-temperature scanning tunneling microscopy studies of graphene growth on Pd(111) during ethylene deposition at temperatures between 723 and 1023 K. We observe the formation of monolayer graphene islands, 200-2000 Å in size, bounded by Pd surface steps. Surprisingly, the topographic image contrast from graphene islands reverses with tunneling bias, suggestive of a semiconducting behavior. Scanning tunneling spectroscopy measurements confirm that the graphene islands are semiconducting, with a bandgap of 0.3 ± 0.1 eV. Using density functional theory calculations, we attribute this phenomenon to the breaking of hexagonal symmetry due to a strong interaction between graphene and the nearly commensurate Pd substrate. Our findings suggest the possibility of preparing semiconducting graphene layers for future carbon-based nanoelectronic devices via direct deposition onto strongly interacting substrates.

4:00pm GR+AS-WeA7 Electronic Corrugation of Rippled Graphene Grown on Ru(0001), B. Borca, S. Barja, Universidad Autonoma de Madrid, Spain, M. Garnica, IMDEA Nanociencia, Spain, J.J. Hinarejos, Universidad Autonoma de Madrid, Spain, A.L. Vazquez de Parga, R. Miranda, UAM & IMDEA Nanociencia, Spain

By means of Scanning Tunneling Microscopy/Spectroscopy (STM/STS) we investigate the electronic and structural modulation of epitaxial graphene grown on Ru(0001). The difference in lattice parameter between graphene and Ru(0001) induces in the graphene overlayer a Moiré pattern with hexagonal order and a lateral periodicity of around 3nm. The bonding with the substrate occurs through the hybridization of C *p*-states with Ru *d* states. Photoelectron spectroscopy shows that the bonding between the graphene and the metallic substrate is not carbidic and the graphene is doped with electrons from the substrate [1].

The hybridization between the carbon and ruthenium atoms changes inside the unit cell [2]. Measuring dI/dV maps we observe inhomogeneities in the charge distribution, i.e., electron pockets, in some areas of the ripples. This inhomogeneity can be understood with the help of a tight-binding model which incorporates a periodic potential associated with the structural ripples that induces a shift of the electronic levels and a corresponding charge transfer from conduction to valence bands for some atoms and the opposite in the others [3].

The influence of the modulated electronic structure in the STM images is quite strong. Large differences in corrugation values were measured in the STM images taken exactly in the same spot and changing the bias voltage applied between tip and sample. A compilation of data measured with different tips and different samples show that the apparent corrugation of the Moiré superstructure is essentially constant (0.1 nm) in the interval from

-3V to -1V and diminish as the voltage goes from -1V up to +2V (0.03 nm). For a bias voltage higher than +2.5V, the contrast of the Moiré is inverted. By means of STS we measured, spatially resolved, the surface unoccupied density of states. The dI/dV spectra show that the contrast inversion is due to the presence of a strong peak at 3V above the Fermi level in the lower areas of the Moiré structure.

These results demonstrate that the electronic effects in this system are strong enough to overcome the actual geometric corrugation of the graphene layer.

[1] F. J. Himpsel *et al.*, Surf. Sci. Lett. **115**, L159 (1982)

[2] A.B. Preobrajenski *et al.*, Phys. Rev. B **78**, 073401 (2008)

[3] A. L. Vázquez de Parga *et al.*, Phys. Rev. Lett. **100**, 05680 (2008)

4:20pm GR+AS-WeA8 Mapping the Geometric and Electronic Structures of Epitaxial Graphene, B. Wang, M. Caffio, R. Schaub, University of St Andrews, UK

A single layer of graphite is known as graphene [1]. It is acknowledged that graphene is a candidate for future electronic devices when supported. Hence a detailed understanding of its geometric and electronic properties is essential. Many studies have in common the observation of moiré superstructures with parameters depending on the mismatch between graphene and substrate [2]. However, an in-depth characterization of the monolayer and its interaction with the support has so far been hampered by experimental limitations, and is strongly debated. We report on a low temperature STM study of graphene grown by low-pressure CVD of ethylene on Rh(111).

Topography measurements show that the C-Rh interactions lead to distortions of the ideal, free-standing graphene, resulting into two sets of superstructures: one is characterized by a coincidence lattice expanded to $(12 \times 12)/(11 \times 11)$, while the other is contracted to $(11 \times 11)/(10 \times 10)$. The coexistence of several graphene superstructures on a transition metal substrate is in contrast to previous reports. Both superlattices exhibit remarkable coherence lengths, in excess of 1000 nm. However, high-resolution images allow us to precisely monitor the registry of the C atoms with respect to the underlying substrate, revealing that the atomic arrangements are subject to local distortions. Resonance transmission microscopy and spectroscopy, in combination to DFT calculations, were further used to obtain deeper insight into the altering environment at the graphene/Rh(111) interface. Our results show how variations of the local work function within the overlayer unit cell provide invaluable information on the electronic coupling between graphene and Rh(111) substrate.

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

[2] J. Coraux *et al.*, Nano Letters **8**, 565 (2008)

4:40pm GR+AS-WeA9 Rotational Domains of Graphene on Ir(111), S. Nie, E. Loginova, K. Thürmer, N.C. Bartelt, K.F. McCarty, Sandia National Laboratories

We use scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM) to study four different orientations of single-layer graphene sheets on Ir(111). The most-abundant orientation (R0) has been previously characterized in the literature [1]. While less prevalent than R0, the three additional structures can still occur as relatively large domains, tens of microns in spatial extent. We find that the four types of graphene differ simply in how the graphene sheets are oriented relative to the in-plane directions of the Ir lattice. That is, the four types of graphene are rotational variants, similar to the rotational variants of graphene on Pt(111) [2,3]. Using selective-area LEED, we find the graphene sheets in the other three variants to be rotated by approximately 14°, 18.5° and 30° (R30), respectively. The R30 structure is studied in detail with STM. Compared with the R0 structure, R30 has much less height corrugation. We propose atomic models for the new variants. The moiré structures can be classified using simple geometric rules involving the different periodic and quasiperiodic structural motifs. In addition, LEEM reveals that linear defects form in the graphene sheets during cooling from the synthesis temperature. STM shows that the defects are ridges where the graphene sheets locally delaminate as the Ir substrate contracts. We will describe the factors that control the relative abundance of the different variants.

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

[2] T. A. Land, T. Michely, R. J. Behm, J. C. Hemminger, and G. Comsa, Surf. Sci. **264**, 261 (1992).

[3] M. Sasaki, Y. Yamada, Y. Ogiwara, S. Yagyu, and S. Yamamoto, Phys. Rev. B **61**, 15653 (2000).

* Paul Holloway Award Winner

5:00pm **GR+AS-WeA10 Deposition and Characterization of HfO₂, Al₂O₃ and SiO₂ Dielectrics for Graphene-Based Devices**, *A. Pirkle*, University of Texas at Dallas, *L. Colombo*, Texas Instruments Incorporated, *R.M. Wallace*, University of Texas at Dallas

We present a study of dielectric deposition on graphene and bulk graphite for nanoelectronic device applications. Recent studies have demonstrated that the chemically inert nature of the graphene surface presents challenges to uniform deposition of high quality dielectrics by conventional deposition techniques including ALD. These issues are compounded by the ultrathin nature of graphene, as any covalent bonding that disturbs the underlying graphene lattice is likely to induce scattering and degrade mobility.

In this study, Al, Hf and Si are deposited by electron beam evaporation and subsequently oxidized. We also examine deposition of dielectrics by reactive electron beam evaporation in the presence of a partial pressure of oxygen in the vacuum chamber. Chemical interactions with the substrate are analyzed by means of *in-situ* x-ray photoelectron spectroscopy (XPS) before and after oxidation. Any presence of carbide bonding (AlC, HfC, SiC) is likely to degrade mobility, and we examine the conditions under which carbide bonds are formed. The oxidized films are also characterized by *ex-situ* Raman spectroscopy, particularly with regard to the formation of D-band states that are indicative of damage to the graphene lattice during deposition or oxidation. Surface morphology of the deposited films is studied using atomic force microscopy (AFM), particularly with regard to uniformity as pertinent to thickness scaling.

This work is sponsored by the NRI SWAN center.

5:20pm **GR+AS-WeA11 Large Area Graphene Formed by the Catalytic Exfoliation of Natural Graphite with Invar Alloy**, *J.C. Sung*, KINIK Company, Taiwan, *K. Chang*, *K. Hsu*, National Taipei University of Technology, Taiwan, *M. Sung*, Advanced Diamond Solutions, Inc.

Graphene is the ideal material for many dream applications, such as single electron transistors, field emission sources [1], light through electrodes, clothing solar cells, terra hertz surface acoustic wave (SAW) filters, wall paper displays, UV light emitting diodes, atomic gas sensors, DNA or antigen wafers...etc. However, a practical method to fabricate meter-sized graphene is still beyond imagination. We made use the mechanism of diamond synthesis in liquid phase and produced graphene of several hundreds microns. Such graphene revealed silk-like tenderness with transparent folding lines. This promising process appears scalable for making device-sized graphene in the near future. This paper also presented many intriguing aspects related to the growth of large graphene. We also proposed a new hypothesis of graphene formation by the catalytic exfoliation of graphite in molten iron group alloys.

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