

Tuesday Afternoon, October 19, 2010

Graphene Focus Topic

Room: Brazos - Session GR+TF-TuA

Graphene and 2D Nanostructures

Moderator: Y. Chen, Purdue University

2:00pm **GR+TF-TuA1 Graphene and Its Progeny: from Fundamental Material Properties to Device Applications**, *A.W. Ghosh*, University of Virginia **INVITED**

The incredible material properties of graphene have spurred intense interest among chemists, physicists and engineers towards potentially exciting electronic applications. Much like nanotubes, graphene electrons have high mobilities due to the sharp curvature of their bands at the Gamma point that reduces their effective masses, as well as long scattering lengths due to symmetry selection rules among their pseudospin separated bands. However, a potential problem with graphene is its metallicity, which makes its ON-OFF ratio unacceptable for digital logic. Effort is under way to mitigate this by opening bandgaps through various chemical and electrostatic means. I will argue that any such band-gap opening leads to an inevitable reduction in mobility *even if we manage to do so without affecting its scattering length*. The trade-off arises from a fundamental asymptotic constraint on all graphitic materials (epitaxial graphene, strained graphene, nanoribbons, nanotubes, and bilayer graphene) that pins the high energy electrons away from the Gamma point to an ultimately linear dispersion. However, opening a bandgap by width confinement, e.g. in a nanoribbons, can provide distinct electrostatic if not material advantages. The presence of diffuse boundary conditions at the edges, along with strain and edge roughness, systematically erases any signs of chirality and metallicity in GNRs, making their widths the single arbiter of metallicity. This allows us to envisage wide-narrow-wide (WNW) nanoribbons monolithically patterned out of a single template into both switches and interconnects. The 2-D electrostatics of the source-drain contact edge capacitances improves the gate control, allowing the current to show a highly desirable saturation characteristic. Furthermore, the presence of C-C bonds at the channel-contact interface makes metal induced gap states relatively ineffective in pinning the bands, promoting Ohmic behavior. I will quantify the advantages and disadvantages of WNW devices, and compare with alternate GNR switches, such as utilizing electron focusing in p-n junctions.

2:40pm **GR+TF-TuA3 Electronic Structure of Graphene/BN Heterojunctions formed by Graphene CVD: Doped Graphene**, *C. Bjelkevig, Z. Mi*, University of North Texas, *J. Xiao, P.A. Dowben*, Nebraska Center for Nanostructures and Materials, *S. Gaddam, S. Pokharel, J.A. Kelber*, University of North Texas

Graphene has been grown by chemical vapor deposition of C_2H_4 on a monolayer of h-BN(0001) formed by atomic layer deposition (BCl_3 , NH_3) on Ru(0001). AES, STM and LEED confirm a graphene-like overlayer, with near-zero DOS near the Fermi level, in registry with a BN $R30(\sqrt{3}\times\sqrt{3})$ substrate. Raman spectra reveal graphene "G" and "2D" features with relative intensities indicative of single layer graphene. A large (350 cm^{-1}) redshift in the 2D feature relative to HOPG indicates significant BN-to-graphene charge transfer. The charge transfer is confirmed by photoemission/angle-resolved inverse photoemission spectroscopies (PES/ARIPES), that demonstrate filling of the lowest unoccupied graphene state (π^*) near the Brillouin zone center. These results are in direct contrast to PES/ARIPES results for graphene/Cu, and reported results for graphene/SiC(0001), that show empty graphene π^* states. The data show that the BN layer acts as an n-type dopant for graphene. For the graphene/BN heterojunctions, the ARIPES-determined dispersion of the unoccupied graphene $\sigma^*(\Gamma_1+)$ state yields an effective mass of $0.05 m_e$, in excellent agreement with reported transport measurements on graphene sheets, and indicating that BN doping does not fundamentally alter the graphene electronic structure. The direct growth of graphene on dielectric substrates, and the controlled exploitation of graphene/substrate heterojunction properties, are critical issues for practical device fabrication. The implications of direct CVD of undoped graphene and graphene/BN heterojunctions on high dielectric constant substrates for device applications will be discussed in light of recent results in our laboratories for graphene thermal and free radical-assisted CVD on OH-terminated MgO(111).

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07-1-0008), and the NSF "QSPINS" MRSEC (DRM-0820521) at UNL. The authors also thank Luigi Colombo and Adam Pirkle for acquisition of the Raman spectra.

3:00pm **GR+TF-TuA4 Electrical Transport in Graphenoid and Graphene Nanomembranes from Pyrolyzed Self-Assembled Monolayers**, *A. Turchanin*, Univ. of Bielefeld, Germany, *D.H. Weber*, National Metrology Inst., Germany, *M. Bünenfeld*, Univ. of Bielefeld, Germany, *J. Mayer*, Ernst Ruska-Centre for Microscopy, Germany, *C. Kisielowski*, National Center for Electron Microscopy, *T. Weimann*, National Metrology Inst., Germany, *A. Götzhäuser*, Univ. of Bielefeld, Germany

Ultrathin carbon nanomembranes have recently attracted enormous interest. We report a molecular route to the fabrication of a monolayer or few layers of free-standing graphenoid and graphene nanomembranes based on molecular self-assembly, electron processing and pyrolysis. Aromatic biphenyl self-assembled monolayers (SAMs) are cross-linked by electron irradiation. The cross-linking results in mechanically stable graphenoid sheets with the thickness of a single molecule ($\sim 1\text{ nm}$) and arbitrary sized. The graphenoid sheets can be lifted from their surface and transferred to another solid substrate or holey structures, where they become free-standing nanomembranes. Upon annealing (pyrolysis) up to 1300 K the molecular sheets transform into nanocrystalline graphene phase. This transformation is accompanied by a drop of the sheet resistivity from $\sim 10^8$ to ~ 10 k Ω /sq and a 2D insulator to metal transition. We characterize the insulator to metal transition by electrical transport measurements as well as by complementary spectroscopic and microscopic techniques. A plethora of applications of the suggested molecular route to free-standing ultrathin carbon materials is feasible that take advantage from the fact that the large scale fabrication, control over the thickness and nanostructuring are easily controlled.

[1] A. Turchanin, A. Beyer, C. T. Nottbohm, X. H. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, and A. Götzhäuser: One Nanometer Thin Carbon Nanosheets with Tunable Conductivity and Stiffness, *Adv. Mater.* 21, 1233-1237 (2009)

[2] A. Turchanin, D. Käfer, M. El-Desawy, C. Wöll, G. Witte, and A. Götzhäuser: Molecular Mechanisms of Electron-Induced Cross-Linking in Aromatic SAMs, *Langmuir* 25, 7342-7352 (2009).

[3] C. T. Nottbohm, A. Turchanin, A. Beyer, A. Götzhäuser: Direct e-beam writing of 1 nm thin carbon nanoribbons, *J. Vac. Sci. Technol. B* 27, 3059-3062 (2009).

4:00pm **GR+TF-TuA7 From 2D to 1D - Supramolecular Architectures on Rippled Graphen**, *M. Roos, H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded 2D networks on solid surfaces.¹⁻⁴ The preferred hydrogen bond configurations and thus the resulting structures are steered via the positions of the nitrogen atoms within the BTP molecules. Elaborate synthesis procedures allow varying these positions without altering the footprint shape of the molecules.¹ On smooth surfaces like graphite or metal single crystals, the molecule-substrate interactions play a secondary role for the structures, mainly by determining the orientations of the molecules and thus of the ordered networks.²⁻⁴ In this contribution, we will demonstrate that more pronounced template effects arise for substrates where the molecule-substrate interaction laterally varies at nm-scales. As an example, we will show the ordering behaviour of two different types of BTP molecules on Graphene monolayers grown on Ru(0001). The moiré-type pattern of these surfaces has a periodicity of 3 nm, i.e., in the order of the BTP dimensions and the network meshes they usually form. Submolecularly resolved STM images show that the BTP molecules are confined to the valleys of the graphene ripple structure. We will compare the resulting supramolecular 1D and 2D assemblies to the ordered 2D networks formed by the same molecules on smooth substrates, and we will discuss in how far the template effect can be quantitatively explained by a lateral modulation of the van der Waals interactions due to the height corrugation of the Graphene sheet.⁵

1 C. Meier et al., *J Phys Chem B* 109 (2005) 21015.

2 M. Roos et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5672.

3 H. E. Hoster et al., *Langmuir* 23 (2007) 11570.

4 T. Waldmann et al., *ChemPhysChem* 11 (2010) 1513.5 W. Moritz et al., *Phys. Rev. Lett.* 104 (2010) 136102.

4:20pm **GR+TF-TuA8 Understanding the Functionalization of Graphene by Electron-Beam Generated Plasmas**, *M. Baraket, S.G. Walton, E.H. Lock, J.A. Robinson, F.K. Perkins*, Naval Research Laboratory

4:40pm **GR+TF-TuA9 Chemically Tailoring Graphene via Organic Self-Assembled Monolayers**, *M.C. Hersam*, Northwestern University **INVITED**

Chemically functionalized semiconductor surfaces have been widely explored due to their potential for enabling molecular electronic and sensing devices that are compatible with conventional microelectronic technology [1]. Thus far, the vast majority of work in this field has focused on established semiconductors including silicon, germanium, and gallium arsenide. Meanwhile, the condensed matter physics community has diverted substantial experimental and theoretical effort to graphene, an emerging electronic material with superlative carrier mobility and exotic charge transport phenomena such as the quantum Hall effect.

In an attempt to unify these two fields, we have been exploring strategies for forming and interrogating organic self-assembled monolayers on graphene surfaces. In particular, we have recently demonstrated that self-assembled monolayers of perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA) can be formed on graphene surfaces via gas-phase deposition in ultra-high vacuum (UHV) environments at room temperature [2]. Molecular-scale resolution scanning tunneling microscopy (STM) images reveal long-range order in the PTCDA monolayers, while scanning tunneling spectroscopy (STS) measurements yield distinct electronic features associated with the PTCDA that are not observed on pristine graphene.

In addition to UHV STM characterization, this talk will summarize our most recent efforts to nanopattern self-assembled monolayers on graphene at the sub-10 nm scale. Nanopatterning chemically functionalized graphene presents opportunities for tailoring the electronic and chemical properties of graphene nanoribbons in addition to providing a molecular-scale resolution template for subsequent materials growth on graphene surfaces.

[1] M. A. Walsh and M. C. Hersam, "Atomic-scale templates patterned by ultrahigh vacuum scanning tunneling microscopy on silicon," *Annual Review of Physical Chemistry*, **60**, 193 (2009).

[2] Q. H. Wang and M. C. Hersam, "Room-temperature molecular-resolution characterization of self-assembled organic monolayers on epitaxial graphene," *Nature Chemistry*, **1**, 206 (2009).

5:20pm **GR+TF-TuA11 Stability of Continuous Graphene Sheet and Graphene Flake on the Si(111) Surface**, *B.B. Kappes, T.E. Davies*, Colorado School of Mines, *S. Jun*, University of Wyoming, *A.C.T. van Duin*, Penn State University, *C.V. Ciobanu*, Colorado School of Mines

While rapid use of carbon nanostructures in the silicon-based nanoelectronics industry will involve the direct integration of graphene with silicon chips, so far graphene has not been grown on pristine silicon surfaces because usual synthesis routes would likely lead to the formation of stable silicon carbide instead of the precipitation of carbon at the surface. Here we show that if graphene can be deposited on pristine Si(111) surfaces, then it forms moiré superstructures and binds strongly to the substrate over a wide range of in-plane orientations. The binding energies depend on the orientation of graphene as well as the strain applied to achieve commensurability with the substrate; the strongest binding estimated from density functional theory calculations is approximately 1.5 eV/carbon atom. Using molecular dynamics simulations based on bond-order and reactive force field interatomic potentials, we present evidence that graphene remains stable and bonded to the substrate for temperatures up to 80% of the substrate melting temperature. Bonding information, study of the local density of states, and simulated scanning tunneling microscopy show graphene on Si(111) is semiconducting, with a sizable number of carbon hybridized sp^3 and a bandgap affected by the orientation of graphene with respect to the substrate.

5:40pm **GR+TF-TuA12 Effect of Point-like Defects on the Atomic Structure and Electronic Properties of Graphene Supported on Amorphous SiO₂**, *K.E. Kweon, G.S. Hwang*, University of Texas at Austin

Graphene supported on the common gate dielectric, SiO₂, has been considered as a highly promising candidate for future electronics. Therefore, it is important to understand the interfacial interaction between graphene and SiO₂. Most of the existing theoretical studies have modeled the underlying SiO₂ surface using defective or H-terminated crystalline structures. However, the gate oxide is amorphous and possibly has a number of point-like defects, yet no detailed study has been undertaken on the defect effect. In this talk, based on first principles calculations we present how the SiO₂-graphene binding and consequent graphene electronic structure are influenced by the presence of point-like defects in not only SiO₂ surface but also graphene

sheet. We considered six different surface defects on SiO₂; silyl radicals [(≡Si-O)-₃Si•], oxy radicals [(≡Si-O)-₃Si-O•], silylene center [(≡Si-O)-₂Si•], silanone [(≡Si-O)-₂Si=O], peroxide radicals [(≡Si-O)-₃Si-O-O•], and dioxasilirane [(≡Si-O)-₂Si <O-sub>2</sub>], along with defective graphene that contains vacancies. This talk will mainly touch on the pathways and energetics of the defect-mediated graphene binding to SiO₂, and how the covalent graphene-SiO₂ binding affects the electronic properties of graphene.

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