Graphene and Related Materials Focus Topic
Room: 208 - Session GR+TF+NS-ThA

Graphene Nanoribbons and Related Structures
Moderator: Y.J. Chabal, University of Texas at Dallas

2:00pm **GR+TF+NS-ThA1 Rationally Patterned Large-Area Semiconducting Graphene Materials from the Top-Down and the Bottom-Up**, *N. Safron, M. Kim, P. Gopalan,* ***M. Arnold***, University of Wisconsin-Madison **INVITED**

We are experimentally investigating self-assembling lithography (e.g. block co-polymer and nanosphere lithography) to create nanostructured graphene materials with feature sizes below what is easily achieved using optical and electron-beam lithography (< 20 nm), with the motivation of opening up a technologically relevant band gap in graphene. We are particularly interested in a novel form of semiconducting graphene that we call nanoperforated graphene, which consists of graphene perforated by regular hexagonal arrays of nanoscale holes. Unlike nanoribbons, nanoperforated graphene advantageously retains a large-area two-dimensional form factor. In this talk, we will discuss the inter-relationship between the physical structure of nanoperforated graphene and its electronic properties, with specific emphasis on how its band gap experimentally varies with feature size and how charge transport is affected by structure (including the role of edge defects and the observation of single-electron charging effects). We will also report on efforts in our group to realize nanostructured graphene materials with well controlled edge structure and superior properties via scalable and rationally controlled bottom-up growth that avoids top-down etching without sacrificing arbitrary pattern forming ability.

2:40pm **GR+TF+NS-ThA3 Quantum Pumping in Graphene Nanoribbons**, ***T. Kaur***, Ohio University, *L. Arrachea,* Universidad de Buenos Aires, Argentina, *N. Sandler,* Ohio University

The interest in the development of devices at the nanoscale has intensified the search for mechanisms that provide tailored control of transport properties while reducing effects of heat dissipation and contact resistance. For instance, *charge pumping* is one of the current generating methods that allows for minimizing the effects of contact resistance. *Charge pumping* is the mechanism used to generate DC currents in open-quantum systems by applying local de-phased time-dependent potentials.

We analyze the properties of non-equilibrium zero-bias current through nano-ribbons using tight-binding Hamiltonians and the *Keldysh formalism*. This theoretical treatment, based on non-equilibrium Green's function techniques, is the most appropriate one to address questions for systems in non-linear, out of equilibrium conditions. We develop a numerical implementation for the models described below in a wide range of non-equilibrium regimes.

After reviewing results for quantum pumping in a one-dimensional chain attached to two reservoirs, with two local single-harmonic potentials oscillating in time, we study finite-width ribbons of square and graphene lattices. The transmission function reveals the value of the *resonant frequency* and explains how the quantum charge pumping works. We analyze the dependence of the *DC current* as a function of different parameters such as chemical potential, pumping amplitude, frequency, etc. In addition, the role of reservoirs is fully described. Pumped currents can also be generated by application of laser fields. We present the comparison between these two pumping methods. Possible extensions for disordered systems will be discussed.

3:00pm **GR+TF+NS-ThA4 First-principles Study of Field Emission from Graphene Nanoribbons**, ***J. Driscoll***, *K. Varga,* Vanderbilt University

A real-space, real-time implementation of time-dependent density functional theory [1,2,3] is used to study electron field emission from graphene nanoribbons. The structures are shown to be good field emitters with spatial variation of the emission current influenced by the presence of passivating hydrogen. The nanoribbons are seen to produce slightly lower currents than nanotubes formed from the ribbons. Spin-polarized field emission from carbon nanotubes has been calculated with and without Fe adsorbates (atoms and clusters). It was observed that various adsorbates cause the separation of density into spin-polarized regions. The calculations predict that carbon nanotubes with various adsorbates can be used as spin-polarized current sources. The spin-polarized results for nanotubes will be compared to similar

calculations for graphene nanoribbons.

References

[1] J.A. Driscoll and K.Varga, Phys. Rev. B 80, 245431 (2009).

[2] J.A. Driscoll, S. Bubin, W. French, and K. Varga (submitted).

[3] J.A. Driscoll, B. Cook, S. Bubin, and K. Varga (submitted).

Acknowledgments

This work is supported by NSF grant CMMI0927345.

3:40pm **GR+TF+NS-ThA6 Quantum Transport Properties of Modified Graphene Nanoribbons with Boron Nitride Domains at the Nanoscale**, ***A. Lopez-Bezanilla***, Oak Ridge National Laboratory

Carbon-based systems are being widely investigated as potential candidates for nanoelectronic interconnects and transistors. The control of electric current is, therefore, an important challenge in nanostructures engineering. The possibility of creating hybrid one-atom thick layers containing C, B and N atoms have attracted much attention as they can provide an efficient way to create new materials with properties complementary to those of graphene and h-BN.

Here we present a theoretical methodology and study of charge transport through GNRs with BN domains randomly distributed along the ribbon surface. We resort to both first principles calculations, to obtain a suitable parametrization of the electronic structure, and a transport approach based on the ab initio results to explore conduction regimes through large and disordered systems. The quantum transport modeling is based on the Green's function formalism, combining an iterative scheme for the calculation of transmission coefficients with the Landauer's formula for the coherent conductance.

Our results describe how the conductance of the hybrid systems is altered as a function of incident electron energy and BN domain density. We explore the transport regimes comparing different degrees of BN doping and BN domain size for ribbons of various widths and lengths on the order of the micrometer. A comparison with other types of defects such as atoms in epoxy configuration and functional groups covalently attached to the ribbon surface will be also discussed.

4:00pm **GR+TF+NS-ThA7 Simple and Scalable Route for the 'Bottom-Up' Synthesis of Few-Layer Graphene Platelets and Thin Films**, ***K. Coleman***, University of Durham, UK

Graphene has generated much interest owing to its exceptional electronic properties and high mechanical strength. This has enabled new types of electronic devices and composite materials to be envisaged. The main problem is the availability of the material and the difficulties associated with its synthesis. Here we present a simple, convenient and scalable chemical vapour deposition method involving metal alkoxides in ethanol to produce few-layer graphene platelets. The graphene platelets have been fully characterised using TEM, SEM, AFM, XPS and XRD. The methodology used has the added flexibility in that it can be used to grow conducting transparent thin films on inert substrates such as silicon wafer and quartz glass. Importantly, no heavy metal catalysts were required to produce the few-layer graphene platelets or graphene films and all non-carbon by-products are soluble in water.

4:20pm **GR+TF+NS-ThA8 Approaching the Intrinsic Bandgap in Suspended High-Mobility Graphene Nanoribbons**, *M.-W. Lin, C. Ling,* Wayne State University, *L.A. Agapito, N. Kioussis,* California State University Northridge, *Y. Zhang, M.-C. Cheng,* Wayne State University, *W.L. Wang, E. Kaxiras,* Harvard University, ***Z.X. Zhou***, Wayne State University

We report the first variable-temperature electrical-transport study of suspended ultra-low-disorder GNRs with nearly atomically smooth edges. Suspension of the GNRs not only removes the substrate influence but also allows a thorough removal of impurities, including those trapped at the interface between the GNR and the substrate, leading to a substantial increase of the carrier mobility. We observe high mobility values over 3000 $cm^2 V^{-1} s^{-1}$ in GNRs that are ~ 20 nm wide, the highest reported to date on GNRs of similar dimensions. Furthermore, we demonstrate that the activation gap extracted from the simple activation behavior of the minimum conductance and residual carrier density at the charge neutrality point approaches the intrinsic bandgap in ultra-low-disorder GNRs. Comparison of the bandgap values of multiple samples shows that the bandgap in our ultra-low-disorder samples is approximately inversely proportional to the ribbon width, consistent with theoretical predictions. On the other hand, non-negligible disorder in GNRs obscures the observation of the intrinsic bandgap in transport measurements. In addition, the size of the bandgap derived from the transport measurements is in *quantitative* agreement with the results of our complementary tight-binding calculations

for a wide range of chiral angles characterizing the GNR structure, suggesting that the underlying electronic origin of bandgap enhancement is the magnetism of the zigzag edges.

4:40pm **GR+TF+NS-ThA9 Fabrication of Polymer-Protected Graphene Nanoribbons by Thermal Dip-Pen Nanolithography (tDPN)**, ***W.K. Lee***, *J.T. Robinson, R. Stine, A.R. Laracuente,* Naval Research Laboratory, *W.P. King,* University of Illinois at Urbana Champaign, *P.E. Sheehan,* Naval Research Laboratory

The lithographic patterning of graphene nanoribbons (GNRs) to engineer band gaps has gained much attention as one path to realizing graphene-based devices. We employed thermal dip-pen nanolithography (tDPN)[1] to pattern GNRs on CVD single-layer graphene (SLG) that had been transferred onto a SiO_2 substrate. In tDPN, a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. tDPN has been successful at depositing polymers ranging from semiconductors to insulators on a variety of surfaces. To create the nanoribbons, we deposited polystyrene (PS) ribbons via tDPN on a SLG film between the source and drain electrodes. The areas of the graphene not protected by the polymer were then modified to isolate thin graphene nanoribbons. We show that the PS protected ribbon was the only conductive pathway for active device. This method allows a wide range of nanoribbon widths to be created and avoids electron beams which can damage graphene. The impact of the polymer choice on conductivity as well as the choice of isolation will discussed. For instance, we find that the PS ribbon can serve not only as an etch mask to pattern GNRs but also a stable dopant layer. The detailed fabrication and characterization of these structures will be presented.

1. WK Lee, et al. (2010) "Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies using Thermal Nanoprobes", *Nano Letters, 10, 129*

5:00pm **GR+TF+NS-ThA10 Edge Termination of Modified Graphene Oxide during Thermal Exfoliation**, ***M. Acik****, *Y.J. Chabal*, The University of Texas at Dallas

Nanopore formation in carbon materials (e.g. exfoliated nanostacks of graphite) has been widely studied through mechanical exfoliation, intercalation, electrochemical separation, chemical or thermal exfoliation of graphite oxide (GO) via expansion with partial oxygen removal. Amongst all these methods, exfoliation of modified graphene (GO), a solution-processable precursor compound where aromatic and heterocyclic rings with embedded oxygen functionalities exist, by thermal processing still remains elusive for the following reasons: (1) poor control of GO composition (initial oxygen content), (2) poor understanding of the chemical composition, (3) unknown role of oxygen, adjoining oxygen interactions, and edge termination with oxygen. Infrared absorption spectroscopy coupled with *in-situ* thermal annealing process [1] makes it possible to examine the chemical changes taking place during thermal reduction to identify and understand interacting molecular environment and the edge functionalization. To unravel the complex mechanisms leading the removal of oxygen in GO, we have performed *in-situ* transmission infrared absorption spectroscopy (IRAS) measurements of graphene/graphite oxide (GO) thin and bulk films upon thermal annealing (60-850°C) in vacuum (10^{-3}-10^{-4} Torr). Control of the edge geometry of finite-sized modified graphene flakes depends very much on the control of the processing methods. This edge reconstruction further determines electronic, electric, optical and mechanical properties of the exfoliated modified graphene flakes. Therefore, we not only perform studies deriving a thermal reduction mechanism, but also examine the edge reconfiguration with oxygen. We report here the observation of a surprisingly strong IR absorption band that occurs only upon thermal reduction of GO. After annealing at 850°C in vacuum, the strong enhancement of the new IR active absorbance band is observed at ~800 cm^{-1}[2]. The intensity of this band is 10-100 times larger than what is expected for the oxygen content of the reduced GO, namely between 5 and 8 at.%. This band is assigned to a specific oxidation state, involving oxygen located in the basal plane (forming C-O-C bonds) and at *atomically straight* edges of reduced graphene. The large enhancement in IR absorption is attributed to the direct participation of electrons, induced by the asymmetric C-O-C stretch mode displacement. These findings open new possibilities in the field of nanoelectronics for all sensor and energy storage applications. [1] M. Acik, *et al.* J. Am. Chem. Soc. (2011), *in preparation*. [2] M. Acik, *et al.* Nat. Mater. 9, 840-845 (2010).

5:20pm **GR+TF+NS-ThA11 Study of Ridges on Epitaxial Graphene on 6H-SiC(0001)**, ***Y.Y. Li***, *Y. Liu, L. Li*, University of Wisconsin-Milwaukee

The graphitization of hexagonal SiC surfaces provides a viable alternative for the synthesis of wafer-sized graphene for mass device production. During the later stages of growth, ridges are often observed on the graphene layers as a result of bending and buckling to relieve the compressive strain between the graphene and SiC substrate, which also introduce ripples in the otherwise atomically flat graphene sheet. In this work, we show, by atomic resolution STM imaging, that ridges are in fact bulged regions of the graphene layer, forming one-dimentional (nanowire) and zero-dimentional (quantum dot) nanostructures. We further demonstrate that their structures can be manipulated and even new ones created by the pressure exerted by the STM tip during imaging. These results and their impact on the electronic properties of epitaxial graphene on SiC(0001) will be presented at the meeting.

***** Morton S. Traum Award Finalist

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