

# Tuesday Afternoon, October 21, 2008

## Graphene Topical Conference

Room: 306 - Session GR+TF+NC-TuA

### Graphene: Characterization, Properties, and Application

Moderator: Y.J. Chabal, University of Texas at Dallas

1:40pm **GR+TF+NC-TuA1 Computational Modeling of Graphene.** **K.J. Cho, G. Lee,** University of Texas at Dallas **INVITED**

Using the ab initio density functional theory (DFT), tight-binding (TB), and non-equilibrium Green's function (NEGF) methods, we have studied the electronic properties of graphene oxides (GOs) and graphene nanoribbons (GNRs). Dry oxidation of graphene induces epoxide groups on the basal plane, and the corresponding electronic structures of GOs show directional band gap opening. We found that GOs have small energy gaps due to the lattice distortion at low oxygen coverage  $\theta_0$ , and that they become semiconductors for  $\theta_0 \geq 1/2$  with the larger gap at the higher  $\theta_0$  ( $E_g = 3.3$  eV at  $\theta_0 = 1$ ). However, for intermediate coverage, GOs become metallic along one zigzag direction while opening directional energy gaps along other zigzag directions depending on O adsorption patterns. We apply the percolation theory and NEGF method to explain the electron transport behavior of GOs. The insulating property of GOs is used to explain the inactive edge width of GNRs which are observed in GNR experimental studies. Electronic properties of GNRs are shown to have strong dependence on the edge chemistry indicating a practical challenge in graphene nanoelectronics using GNRs as channel materials.

2:20pm **GR+TF+NC-TuA3 Control of Conductivity in Graphene by Formation of Defects.** **S.H.M. Jafri, T. Blom, E. Widenqvist, K. Carva, B. Sanyal, O. Eriksson, H. Grennberg, U. Jansson,** Uppsala University, Sweden, **R.A. Quinlan,** College of William and Mary, **B.C. Holloway,** Luna Innovations Incorporated, **A. Surpi, K. Leifer,** Uppsala University, Sweden

Due to their large surface areas, the conductivity of graphene and carbon nano-sheets depends strongly on their chemical environment. This is the base for future environmental sensors containing graphene sheets. Here, ab-initio calculations propose a possibility of conductivity increase. In the experiment, a 1-2 orders of magnitude increase of the conductivity is observed experimentally on sub-nanometre carbon nano-sheets by using an in-situ nano-manipulation set-up. The conductivity of the graphene sheets was assessed from first-principle simulations. Insertion of defects in the graphene sheets can lead to a strong increase of the conductivity of single graphene sheets. To study this result experimentally, we carried out conductivity measurements on sub-nanometre graphene nano-sheets that are deposited on W-substrates by radio-frequency plasma-enhanced chemical vapour deposition. This deposition process creates free-standing micrometer-sized carbon nano-sheets with sub-nanometre thickness. These nano-sheets were exposed to an acid treatment. It has been shown recently that such acid treatment creates defects in these sheets. Using a nano-manipulator inside a scanning electron microscope, we individually contacted the nano-sheets and measured their resistance as a function of their functionalization. From more than 1000 measurements we obtain a 1-2 order of magnitude increase of conductivity in the functionalised carbon nano-sheets as compared to just water treated or untreated carbon nano-sheets. This result corresponds well to the conductivity change obtained from theory. This study makes it possible to create environmental sensors based on graphene like carbon nano-sheets.

2:40pm **GR+TF+NC-TuA4 Graphene on Graphite.** **J.W. Choi,** Kyung Hee University, South Korea

Topmost graphine layer of graphite is investigated using scanning tunneling microscopy and spectroscopy. Tunneling gap-distance, gap-voltage and bias polarity play an important role in the atomic image contrast and site-dependent tunneling spectra. The study revealed that the coupling and decoupling of the topmost graphene layer to the underlying graphite is occurred because of the weak physical interaction between graphen layers, the electronically active and mechanically soft beta-carbon atoms of graphite and the strong tip-sample interaction.

3:00pm **GR+TF+NC-TuA5 Using Templates to Assemble Graphite Oxide (GO) and Graphene Nanostructures.** **P.E. Sheehan, Z. Wei, J.T. Robinson, D.E. Barlow, E.S. Snow,** Naval Research Laboratory

Graphene and graphite oxide (GO) are new nanoscale building blocks that have generated widespread interest in both basic and applied research. The rapid, inexpensive, and reproducible generation of graphene and GO samples would expedite this work. To this end, we have directed the assembly of single-layered GO sheets using chemical templates patterned

via micro contact printing.<sup>1</sup> Single-layer GO was inexpensively produced using the Hummer method and redispersed in water. Templates of 11-Amino-1-undecanethiol SAMS were created using microcontact printing. Unlike prior work in fullerene templating, the GO sheets could be captured electrostatically without the aid of surfactants. This process yields isolated, single-layer graphene sheets that are arbitrarily located on a patterned substrate. The electrostatic capture mechanism was verified by varying the pH to turn capture on and off. We will discuss the parameters (pH, time, etc.) that affect GO adsorption as well as the surprising resistance of the unpassivated Au substrate to adsorption of the GO sheets. Finally, the adsorbed GO and graphene were electronically and spectroscopically characterized to determine the effect of capture on the reduction process.

<sup>1</sup> submitted to Nano Letters.

4:00pm **GR+TF+NC-TuA8 Studies of Graphene Oxidation and Graphene Oxide Reduction by In-Situ FTIR.** **L. Goux, R. Guzman, J.-F. Veyan, Y.J. Chabal,** University of Texas at Dallas

Graphene oxide (GO) is being investigated by the graphene community because it represents one of the most promising ways to produce graphene single sheets on a large scale.<sup>1,2</sup> Indeed graphene oxidation followed by exfoliation and reduction has been recently demonstrated to give single graphene layers in solution<sup>3</sup>. In addition, in any practical electronic device systems, electron transporting materials need to be controlled by insulating materials which can function as gate dielectrics or separator between device structures. Thus, the role of GO in graphene-based nanoelectronics may be comparable to that of SiO<sub>2</sub> in silicon-based microelectronics. We have therefore developed in-situ IR characterization to monitor graphene oxidation and GO reduction, in order to facilitate the development of graphene-based nanoelectronics. Graphene oxidation is being achieved using a remote oxygen plasma generator. We have designed a vacuum IR-cell (10<sup>-7</sup> Torr base pressure), connected to the oxygen plasma and a Nicolet 6700 FT-IR spectrometer. Preliminary experiments have been carried out using HOPG. The GO reduction is performed in-situ by high temperature annealing in a Specac high temperature cell. In-situ FTIR studies of GO upon thermal reduction have shown a production of CO<sub>2</sub> gas concomitant with the disappearance of the vibrations associated to carboxyl, hydroxyl and peroxide groups in the 120°C-230°C temperature range. Interestingly the vibrational lineshape suggests that CO<sub>2</sub> is incorporated in GO. Around 290°C, there is a strong increase of the absorbance associated with structure changes of GO, resulting from an increase in scattering due to a higher refractive index. The change of refractive index most likely arises from an increase of electrical conductivity after reduction of GO.

<sup>1</sup>Stankovich, S. et al. Carbon 45, 1558-1565 (2007).

<sup>2</sup>Stankovich, S. et al. J. Mater. Chem. 16, 155-158 (2006).

<sup>3</sup>Li, D. et al. Nature Nanotechnology 3, 101 - 105 (2007).

4:20pm **GR+TF+NC-TuA9 Growth of Few Layer Graphene by Microwave Plasma Enhanced CVD.** **R.G. Vitchev, A. Malesevic, A. Vanhulsel, R. Kemps, M. Mertens,** Flemish Institute for Technological Research (VITO), Belgium, **G. Van Tendeloo,** University of Antwerp, Belgium, **C. Van Haesendonck,** Catholic University of Leuven, Belgium, **R. Persoons,** Flemish Institute for Technological Research (VITO), Belgium

Graphene has recently attracted considerable attention as a potential material for nanoelectronic devices. A promising method for its mass production is microwave plasma enhanced chemical vapour deposition (MW PECVD). The main advantage of this technique is that few layer graphene (FLG) can be grown without the need of a catalyst on different substrates that can withstand high temperature (up to 700°C). However, the growth mechanism of PECVD synthesized graphene is not well understood. The aim of this work was to investigate the growth process of FLG deposited by MW PECVD on several substrates (quartz, silicon, platinum). The resulting thin films were characterized by X-ray diffraction, scanning and transmission electron microscopy, Raman spectroscopy and angle resolved X-ray photoelectron spectroscopy (ARXPS). Three stages of film growth on silicon were identified by ARXPS: formation of a carbide layer on the substrate, deposition of an amorphous carbon layer and finally formation of a graphitic layer parallel to the substrate surface. It was established that crack edges in this graphitic layer serve as nucleation sites from which FLG flakes, only four to six atomic layers thin, grow perpendicular to the surface. This growth mechanism appears to be substrate dependent since no intermediate carbide layer was formed on both quartz and platinum surfaces. Furthermore, no amorphous carbon layer was detected on the platinum substrates, even for the shortest deposition time intervals.

4:40pm **GR+TF+NC-TuA10 Uniform Transparent and Conducting Solution Processed Graphene Thin Films for Large Area Electronics, M. Chhowalla, Rutgers University** **INVITED**

The integration of novel materials such as single walled carbon nanotubes and nanowires into devices has been challenging. Similarly, although fundamental research on graphene has been prolific since its discovery, reports on making it technologically feasible for integration into devices have only recently appeared. In this presentation, a solution based method which allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. The opto-electronic properties can thus be tuned over several orders of magnitude, making them useful for flexible and transparent semiconductors or semi-metals. The thinnest films exhibit graphene-like ambipolar transistor characteristics while thicker films behave as graphite-like semi-metals. Controllable p-type doping via exposure to SOCl<sub>2</sub> vapor is also demonstrated. Cl doping leads to breakup of symmetry in ambipolar field effect characteristics, providing a route for unipolar devices. In addition, composite graphene/polymer thin film devices exhibiting on/off ratios >10 will also be reported. Collectively, our deposition method could represent a route for translating the interesting fundamental properties of graphene into technologically viable devices.

5:20pm **GR+TF+NC-TuA12 Electronic Manipulation in Graphene Formed by Proton-irradiated Method, C.-H. Chuang, National Taiwan University and National Synchrotron Radiation Research Center, Taiwan, C.-H. Chen, H.-W. Shiu, National Synchrotron Radiation Research Center, Taiwan, X. Gao, M.B.H. Breese, F. Watt, S. Chen, A.T.S. Wee, National University of Singapore, M.-T. Lin, National Taiwan University, Taiwan**

Graphene is referred to the honeycomb lattice of carbon atoms formed as a 2D flat single layer. It is also the building block to construct 0D fullerenes, 1D carbon nanotubes, and 3D graphite in graphitic materials. Similar to carbon-based materials, the strong C-C bonding with sp<sup>2</sup> hybridization is stable and rigid in ambient atmosphere. In this letter, we introduce the simple method to modify its electronic character and use Scanning Photoemission Microscopy (SPEM) to study its electronic structure. The previous reports about ion- or proton-irradiated graphitic materials present the new physical and magnetic property, e.g. induced ferromagnetic behavior. The reasons are mainly related to the disorder lattice, the vacancy density, or hydrogen-absorbed carbon atoms in the graphene network. However, it is necessary to provide the evidence about electronic structure after proton irradiation. SPEM provides the spatial mapping image with different element and the chemical bonding environment of XPS at the individual location. As compared with the graphite, we can know the C 1s state of graphene is similar. After the proton-irradiated impact on the graphene, the irradiated area shows the broad FWHM of C 1s state and chemical shift of 0.4 eV up to the high binding energy. Besides, we find the satellite peak with binding energy 291 eV, related to  $\pi$  to  $\pi^*$  state transition, is decreased after irradiation. The observed result in our irradiation sample may be due to the lattice reconstruction of C-C bond. Our experimental findings open up a new field in electronic manipulation in graphene-based electronics.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Barlow, D.E.: GR+TF+NC-TuA5, 1  
Blom, T.: GR+TF+NC-TuA3, 1  
Breese, M.B.H.: GR+TF+NC-TuA12, 2

## — C —

Carva, K.: GR+TF+NC-TuA3, 1  
Chabal, Y.J.: GR+TF+NC-TuA8, 1  
Chen, C.-H.: GR+TF+NC-TuA12, 2  
Chen, S.: GR+TF+NC-TuA12, 2  
Chhowalla, M.: GR+TF+NC-TuA10, 2  
Cho, K.J.: GR+TF+NC-TuA1, 1  
Choi, J.W.: GR+TF+NC-TuA4, 1  
Chuang, C.-H.: GR+TF+NC-TuA12, 2

## — E —

Eriksson, O.: GR+TF+NC-TuA3, 1

## — G —

Gao, X.: GR+TF+NC-TuA12, 2  
Goux, L.: GR+TF+NC-TuA8, 1  
Grennberg, H.: GR+TF+NC-TuA3, 1  
Guzman, R.: GR+TF+NC-TuA8, 1

## — H —

Holloway, B.C.: GR+TF+NC-TuA3, 1

## — J —

Jafri, S.H.M.: GR+TF+NC-TuA3, 1  
Jansson, U.: GR+TF+NC-TuA3, 1

## — K —

Kemps, R.: GR+TF+NC-TuA9, 1

## — L —

Lee, G.: GR+TF+NC-TuA1, 1  
Leifer, K.: GR+TF+NC-TuA3, 1  
Lin, M.-T.: GR+TF+NC-TuA12, 2

## — M —

Malesevic, A.: GR+TF+NC-TuA9, 1  
Mertens, M.: GR+TF+NC-TuA9, 1

## — P —

Persoons, R.: GR+TF+NC-TuA9, 1

## — Q —

Quinlan, R.A.: GR+TF+NC-TuA3, 1

## — R —

Robinson, J.T.: GR+TF+NC-TuA5, 1

## — S —

Sanyal, B.: GR+TF+NC-TuA3, 1  
Sheehan, P.E.: GR+TF+NC-TuA5, 1  
Shiu, H.-W.: GR+TF+NC-TuA12, 2  
Snow, E.S.: GR+TF+NC-TuA5, 1  
Surpi, A.: GR+TF+NC-TuA3, 1

## — V —

Van Haesendonck, C.: GR+TF+NC-TuA9, 1  
Van Tendeloo, G.: GR+TF+NC-TuA9, 1  
Vanhulsel, A.: GR+TF+NC-TuA9, 1  
Veyan, J.-F.: GR+TF+NC-TuA8, 1  
Vitchev, R.G.: GR+TF+NC-TuA9, 1

## — W —

Watt, F.: GR+TF+NC-TuA12, 2  
Wee, A.T.S.: GR+TF+NC-TuA12, 2  
Wei, Z.: GR+TF+NC-TuA5, 1  
Widenqvist, E.: GR+TF+NC-TuA3, 1