

Thursday Afternoon, October 31, 2013

Graphene and Other 2D Materials Focus Topic

Room: 104 B - Session GR+AS+BI+PS+SS-ThA

Plasma Processing, Surface Chemistry, Functionalization, and Sensor Applications of 2D Materials

Moderator: P.E. Sheehan, Naval Research Laboratory

2:00pm **GR+AS+BI+PS+SS-ThA1 Carbon Monoxide-induced Reduction and Healing of Graphene Oxide, S.L. Weeks, B. Narayanan, B.N. Jariwala, Colorado School of Mines, B. Macco, J.W. Weber, Eindhoven University of Technology, Netherlands, M.C.M. van de Sanden, Eindhoven University of Technology; DIFFER, Netherlands, C.V. Ciobanu, S. Agarwal, Colorado School of Mines**

Reduction of graphene oxide (GO) has recently generated intense research interest due to the possibility of using this method to inexpensively produce large quantities of graphene. Current reductive processes rely on thermal or chemical removal of oxygen functional groups from the surface. While reduction has been demonstrated, a certain fraction of residual oxygen remains after processing with current techniques. Furthermore, the use of high process temperatures in the reduction of GO leads to the generation of defects through the loss of carbon atoms from the basal plane of graphene. The ultimate improvement in the electronic, optical, or mechanical properties of graphene that can be achieved through reduction of GO is limited by defect formation and the residual oxygen remaining after reduction through present reported methods. Here, we report the facile removal of oxygen functional groups from the surface of GO through reduction in a carbon monoxide atmosphere. Common oxygen-containing functional groups on the basal plane of GO (epoxides, hydroxyls, and ketone pairs) are removed from the surface due to the reducing action of CO. First, we have used molecular dynamics simulations and density functional theory calculations to elucidate the mechanisms of removal of these surface species by CO, and show that this reduction process proceeds without degradation of the underlying graphene sheet; CO₂ and H₂O are the only surface reaction products. We also show that the corresponding activation energy barriers for these reactions are easily surmounted at low temperatures. Second, the removal of oxygen-containing functional groups from GO by CO is confirmed experimentally using *in situ* attenuated total reflection Fourier transform infrared spectroscopy, indicating the reduction of the GO surface with CO is consistent with our atomistic-level calculations. Third, through controlled generation of defects into an otherwise pristine graphene sheet, we show that exposure to CO results in near-complete healing of the sheet as demonstrated with *ex situ* Raman spectroscopy. Thus, our results indicate CO induced reduction of GO not only proceeds without damaging the underlying sheet, but also heals defects that are produced in the production of GO via exfoliation of oxidized graphite.

2:20pm **GR+AS+BI+PS+SS-ThA2 Plasma Enhanced ALD of Hafnium Oxide on Graphene Layer with Plasma Pretreatment, T. Kitajima, T. Nakano, National Defense Academy of Japan**

Graphene is the candidate of the future generation semiconductor material due to its high mobility of electrons and ultimately thin feature of the 2D structure. The use of graphene for CMOS technology to replace current silicon devices requires matching of each interface between the substrate, electrodes, channel, and dielectrics. Among these, growth of high dielectric constant film growth over graphene is not successful due to the chemically inert nature of the graphene surface. In order to have reactive chemical bond on graphene surface, there are trials of oxidation with ozone, etc.

Here, the effect of the oxygen plasma pretreatment on the graphene surface is examined in this study.

Graphene layer is prepared by peeling method from HOPG using adhesive tape. The domain size is 1 micron in width. (AFM topograph is shown in Fig.1) The pretreatment of the graphene surface is the exposure of O₂ ICP at 30 Pa for less than 1 min. This atomically modifies the topography (fig. 2), and the chemistry of the surface (fig. 3). The XPS analysis indicates the many of the graphene 2D bonds are replaced by C-O or C-OH bond and the defects are increased.

The growth sequence of Hafnium oxide ALD consists of the exposure of metal precursor (Tetrakis Ethyl Methyl Amino Hafnium : TEMAH) with N₂ buffer flow, N₂ purge, and O₂ ICP at 30 Pa.

The chemical composition from XPS shows the film thickness is specifically controlled by ALD cycle number and it saturates at 4th cycle owing to the limited mean free path of photoelectrons .

The initial growth stage of the film with and without plasma pretreatment is compared for 2nd ALD cycle sample . (AFM in fig. 4 and 5). With pretreatment, the surface consists of 2-5 nm width dispersed nano -islands and 20 nm width HfO₂ mesa (film) of 1nm height. Mesas are separated by base graphene surface by 10 nm pitch. Without pretreatment, the surface is covered by closely packed 5-10nm width nano-islands, around 1nm of height . This comparison indicates the oxygen bonds introduced by O₂ plasma pretreatment contribute to the chemisorption of the precursor and successful 2D growth of HfO₂ in the initial stage. In contrast, inert graphene surface without pretreatment prohibits the interconnection of the physisorbed precursor with the surface and 3D island growth is preferred.

In summary, although the domain size of the HfO₂ is limited to around 20 nm, 2D mode growth is enabled by the introduction of O₂ plasma pretreatment . Further progress is necessary on the increase of the coverage of the film, minimizing the oxidation of the base graphene layer, and reducing nano-sized islands on the film.

2:40pm **GR+AS+BI+PS+SS-ThA3 Detection of Uranium and Plutonium by Graphene-Based Nanosensors, G. Sandi, Argonne National Laboratory, A. Bobadilla, Texas A&M University, A.V. Sumant, L. Ocola, Argonne National Laboratory, J. Seminario, Texas A&M University, C. Mertz, M. Kaminski, Argonne National Laboratory**

The design and fabrication of arrays of electronic molecular devices as sensors for plutonium and uranium at the nanoliter volume will be discussed. Computational calculations performed at Texas A&M University and experiments performed at Argonne National Laboratory (Center for Nanoscale Materials and Chemical Sciences and Engineering Division), will be presented. In particular, we are studying graphene, which is a vibronic, plasmonic, and electronic material for molecular circuits and sensors. The idea is to use the plasmonic features of graphene molecules in order to transfer the electrical, magnetic, vibrational, and optical characteristics of nuclear agents into the graphene plasmon, which produces an enhancement (amplification) of observable quantities as successfully done with chemical and biological agents. For nuclear agents, we have additional possibilities due to their radiation features. Theoretical simulations have shown the possible use for sensors to identify single molecules with high selectivity and sensitivity that will contribute to the miniaturization, as well as efficient transport and processing of signals using graphene based devices. It is expected that this approach will allow us not only to sense targeted agents, but also to perform chemical recognition using molecular potentials, which have become the signature at the nanoscale, perfectly suitable for detection and identification of atoms and small molecules. Maps of the molecular potentials around complexes of U and Pu allows us to distinguish their main signatures similar to those observed in biological systems where receptors are able to distinguish to its transmitters or when a donor of electrons is able to match with an acceptor. The information obtained, especially following a supercritical nuclear event, would severely limit the list of potential actors and provide critical information to guide a proper and timely response.

Acknowledgments

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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3:00pm **GR+AS+BI+PS+SS-ThA4 Damage-free Etching of Graphene using Oxygen Neutral Beam towards Edge State Control, T. Okada, K. Igarashi, S. Samukawa, Tohoku University, Japan**

The band gap of graphene needs to be controlled for electronic device applications because it is a zero band gap semiconductor. Narrow width graphene, which is called graphene nanoribbon (GNR), has an effective band gap and solves several problems. Although there are several approaches to fabricating GNRs, top-down lithographic patterning is the most attractive method for the well-arranged GNRs required for large-scale device integration. However, conventional plasma etching always produces high density defects around the edges of the GNRs due to UV irradiation. This makes it difficult to obtain a sufficiently large band gap and the high mobility necessary for GNR-based FETs using wide GNRs (>10 nm). We developed an etching process using a damage-free neutral beam (NB) to

fabricate the GNRs that can eliminate the UV irradiation to overcome this issue. We compared oxygen neutral beam etching to oxygen plasma etching within the same flux and energy conditions to clarify the defect generation mechanism at the edges of graphene.

Graphene sheets were extracted by micromechanical cleaving them from the HOPG and depositing them onto the substrate. The graphene was then etched using a stencil mask. The laser spot for taking the Raman measurement was shifted step by step to measure the defects at the edges. The Raman peaks at approximately the D-band and G-band were examined.

At the edges, the D/G ratio was increased, indicating that the defects were not generated on the plane but on the edge of the graphene. We also found that the D/G ratio on the edge etched by using oxygen NB was extremely lower than that for plasma. These results suggest that high-quality graphene edges can be easily fabricated using NB etching. The defects on the edges from the plasma etching were caused by UV radiation. Several studies have reported this defect generation on materials by high-energy UV photons during the plasma processing. Since UV photons have a non-orientation, they irradiated to the edges during etching. In contrast, in the case of neutral beam etching, damage-free etching was possible because the UV radiation was suppressed.

We concluded that NB etching is a promising candidate for GNR fabrication for high-mobility graphene transistors. In addition, this damage-less etching technique can be used for defect free formation of graphene nano structures, like nano dots and its periodic array when using the top-down process.

3:40pm **GR+AS+BI+PS+SS-ThA6 Controlling the Chemistry of Graphene.** *S. Hernández, E.H. Lock, Naval Research Laboratory, C. Bennett, Nova Research, C. Junkermeier, F. Bezares, S. Tsoi, Naval Research Laboratory, R. Stine, Nova Research, J.T. Robinson, J. Caldwell, T. Reinecke, P.E. Sheehan, C.R. Tamanaha, S.G. Walton, Naval Research Laboratory*

Graphene has attracted widespread interest because of its unique structural and electronic properties. Given its pure two dimensional nature, adsorbates have a strong impact on these properties and so global chemical modification provides opportunities towards homogeneous control of graphene films. However, control over the spatial distribution of chemical moieties provides an even greater functionality in that the properties can be manipulated locally, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Global and spatial chemical functionalization of graphene using electron beam generated plasmas will be discussed. The resulting chemical, structural, and electrical properties of the functionalized graphene as they originate for -oxygen, -fluorine, and -nitrogen functionalities will be demonstrated. This work is supported by the Naval Research Laboratory Base Program.

4:00pm **GR+AS+BI+PS+SS-ThA7 Covalent Functionalization of Graphene with Fluorine by Plasma Treatment.** *G. Mordí, S. Jandhyala, S. McDonnell, R.M. Wallace, J. Kim, The University of Texas at Dallas*

As the performance of graphene based devices has continued to improve over the years (mobility, contact resistance, transconductance), the realization of novel logic devices as the BiSFET (Bi-layer Pseudospin Field-Effect Transistor) for ultra-fast switching speeds and ultra-low power consumptions may not be far off. One of the challenges in realizing BiSFET¹ is the integration of a thin (1-2 nm), low-k (~2) dielectric material which can electrically isolate the two graphene layers in which a condensate is formed and at the same time act as a tunnel barrier.

One approach for obtaining a low-k dielectric is using two dimensional materials similar to graphene which can be manufactured independently and transferred on top of graphene. Covalent functionalization of graphene is a process of adding functional groups which covalently bind to the graphene network, changing its structure from sp^2 to sp^3 hybridization resulting in opening of a band gap. Fluorination among other processes (graphene oxide¹, graphene²) can be used to covalently functionalize graphene. Fluorinated graphene (GrF) is an interesting material because of its atomically thin nature, thermodynamically more stable compared to graphene oxide and graphane, has a wide band gap (~3-7.5 eV) and a potentially low-k dielectric (expected to have dielectric constant of ~2)².

In this study we utilized fluorine based plasma (CF₄) to covalently functionalize graphene films. We established suitable CF₄ plasma exposure parameters and then investigate the conduction mechanisms across GrF based devices. Raman spectroscopy studies showed the evolution of Raman active D (~1350 cm⁻¹), G (~1595 cm⁻¹), D' (1620 cm⁻¹) and 2D (~2680 cm⁻¹) peaks as function of plasma exposure (fluorination) time. XPS studies revealed the type of bonding that exists between fluorine and carbon atoms of the graphene lattice. Conductive atomic force microscopy (C-AFM) showed the *out-of-plane* conductivity on the GrF films were significantly

small compared to non-fluorinated films. *In-plane* transport characteristics of GFETs displayed two minima (or Dirac points) for short CF₄ exposures possibly attributed by both ionic and covalent doping effects simultaneously. Longer exposures result in a single minimum conductivity point possibly due to dominant covalent functionalization effects.

References

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4:20pm **GR+AS+BI+PS+SS-ThA8 Field Effect Control of Carrier Conduction in Helium Ion Irradiated Graphene.** *S. Nakaharai, T. Iijima, S. Ogawa, AIST, Japan, S.-L. Li, K. Tsukagoshi, NIMS, Japan, S. Sato, N. Yokoyama, AIST, Japan*

We demonstrate the gate control of carrier conduction in graphene which is functionalized by Helium ion beam irradiation in a Helium Ion Microscope (HIM) [1]. Carrier conduction control is important for graphene application to electronics, but it has long been an obstacle to realization of graphene electronics. We found that an appropriate amount of He ion dose to graphene induced point defects which enabled gate bias control of current with an on-off ratio of two orders of magnitude at room temperature.

Helium ions were applied to graphene with ion doses from 2.2×10^{15} ions/cm² to 1.3×10^{16} ions/cm². The induced defect density was estimated by numerical calculation to be 0.2% to 1.3% [2]. The introduction of defects was confirmed by the D-mode peak of Raman spectroscopy. A series of samples with different ion doses exhibited a drastic decay of current by more than five orders of magnitude as the defect density increased from 0.2% to 1.3%. In spite of such a drastic change in current, the basic structure of graphene remained, as evidenced by G-mode peak of the Raman spectra. Room temperature current switching with an on-off ratio of two orders of magnitude was realized at a moderate defect density of 0.9%. We also found that the current exhibited an exponential decay as the irradiated region length increased from 5 to 50 nm. These results suggest that the carriers in graphene are spatially localized due to interference of waves which are scattered at the randomly distributed defect sites. A theoretical investigation of localization in a defective graphene has predicted that 1% point defects will cause a strong localization of carriers [3], which shows good agreement with our experimental results. Therefore, it should be argued that the gate control of carrier conduction is realized by a transport gap which is generated by defect-induced localization.

Since the presented technique of graphene functionalization is a "top-down" process, it is easily introduced to the fabrication process of future electron devices. We will also present the application of our ion irradiation technique to the channel of graphene transistors [4] which achieved nearly four orders of magnitude on-off ratio at 250 K.

This research is granted by JSPS through FIRST Program initiated by CSTP.

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5:00pm **GR+AS+BI+PS+SS-ThA10 Epitaxial Graphene Oxide.** *E. Riedo, A. Bongiorno, Georgia Institute of Technology, Y.J. Chabal, University of Texas at Dallas, C. Berger, Georgia Institute of Technology, C. Aruta, CNR*

INVITED

Graphene and graphene-based materials hold great promise for the next generation of nanodevices. One of the most pressing issues for the technological use of graphene is the possibility to control physical and chemical properties by means of ad hoc functionalization. Thermal, chemical and optical reduction of graphene oxide have been explored as a route to produce graphene-based materials with the desired electron transport, mechanical and optical properties. Here, we demonstrate the ability to reduce graphene oxide at the nanoscale by using hot AFM tips (thermochemical nanolithography, TCNL). The resulting nanostructures have a conductivity that can be tune over 4 orders of magnitude [1]. Graphene oxide is indeed a material of great interest for its potential applications in nanoelectronics, nanoelectromechanical system, sensors, polymer composites, catalysis, energy storage devices and optics. However, the chemistry of graphene oxide and its response to external stimuli such as temperature and light are not well understood and only approximately controlled. This understanding is crucial to enable future applications of this material. We have carried over a combined experimental and density functional theory study [2] which shows that multilayer graphene oxide

produced by oxidizing epitaxial graphene through the Hummers method is a metastable material whose structure and chemistry evolve at room temperature with a characteristic relaxation time of about one month. At the quasi-equilibrium, graphene oxide reaches a nearly stable reduced O/C ratio, and exhibits a structure deprived of epoxide groups and enriched in hydroxyl groups. This study shows that the structural and chemical changes are driven by the availability of hydrogen in the oxidized graphitic sheets, which favors the reduction of epoxide groups and the formation of water molecules. Furthermore, we have discovered that a mild chemical oxidation of multilayer epitaxial graphene produces uniform oxidized films showing no propensity to exfoliate. XRD measurements show that the epitaxial graphene oxide films are extremely well ordered with an interlayer distance of 10 Å [3].

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