

# Tuesday Afternoon Poster Sessions

## Graphene Focus Topic

Room: Southwest Exhibit Hall - Session GR-TuP

### Graphene Focus Topic Poster Session

**GR-TuP1 Electronic and Magnetic Properties of Functionalized Graphene Nano-Ribbons**, *Y. Fujii, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Oxidation and reduction are the basic and most important processes for the carbon-based materials as initial processes for producing very thin graphitic materials composed of a single or several graphene layers [1]. Recently, Kosynkin *et al.* have reported that the graphene nano-ribbons (GNRs) can be produced using an oxidative process, and the edges of these GNRs are functionalized by carboxylic acids even after the reduction treatment [2]. On the other hand, it has been well-known that a certain type of GNR with zigzag edges exhibits the so-called flat-band magnetism, which stems from the localized states at the edges [3,4]. In this study, we reveal the electronic and magnetic properties of zigzag GNRs functionalized by carboxyl groups using the first-principles total-energy calculations within the spin density functional theory.

The zigzag GNRs employed in this study have widths from  $N=2$  to  $N=8$ . We have found that the ground state of the GNR with the zigzag edges functionalized by the carboxyl groups is ferromagnetic, if  $N$  is even. For the GNR with  $N=4$ , the ferromagnetic state is more stable by 17 meV per unit cell than the anti-ferromagnetic one. However, if  $N$  is odd, the ground state of the functionalized GNR becomes the anti-ferromagnetic: e.g., for  $N=3$ , the anti-ferromagnetic state is more stable by 12 meV per unit cell than the ferromagnetic one. We have also investigated the energy dispersions of the GNRs. In the anti-ferromagnetic states, the energy bands for both spins are degenerate, and their dispersions near the Fermi level are nearly-flat at the edge of the Brillouin zone, while for the ferromagnetic states, the up-spin and down-spin bands split from each other. The spin density for the ferromagnetic states is localized near the GNR edges. Thus, the onset of the finite magnetic moment of the functionalized GNR is due to the so-called flat-band magnetism.

- [1] S. Horiuchi *et al.*, Appl. Phys. Lett. **84**, 2403 (2004)
- [2] D. V. Kosynkin *et al.*, Nature Lett. **458**, 872 (2009)
- [3] M. Fujita *et al.*, J. Phys. Soc. Jpn. **65**, 1920 (1996)
- [4] J. Nakamura, T. Nitta, and A. Natori, Phys. Rev. B, **72**, 205429 (2005)

**GR-TuP2 Aminocaproic Graphene Sheet Synthesized by Solution Plasma**, *N. Tsuda, Y. Aoki, J. Hieda, O. Takai, N. Saito*, Nagoya University, Japan

Plasma in gas phase is widely used in many industrial fields such as electronic device manufacturing processes (plasma etching, sputtering, plasma-enhanced CVD, etc.), hard coating processes (ion plating, sputtering, etc.), surface treatment processes (low or atmospheric pressure plasma treatments, sputtering, plasma etching, etc.) and so on. Plasma in solid phase has been utilized finally for surface plasmon resonance (SPR) spectroscopy, nanoparticles, etc., and plasmonics is developing as a new research field. On the other hand, plasma in liquid phase is not generally well-known, although it has been partially utilized in water treatments and electrical discharge machining. The fundamentals of plasma in liquid phase have not been established, including its generation techniques, its state, and activated chemical species. However, it would be reasonable to expect a higher reaction rate under lower-temperature conditions, and the greater chemical reaction variability since the molecular density of liquid is much higher than that of gas phase. So we have named the plasma in liquid phase "solution plasma" because we make variety of plasma by choosing the combinations of solvents and solutes in solutions, and are developing solution plasma processing (SPP). In SPP, aqueous solutions, nonaqueous ones, liquid nitrogen, supercritical fluids, etc. can be utilized as solutions. Recently, we have investigated the features of SPP and the applications such as syntheses of nanoparticles and mesoporous silica, and surface modification of particles.

In this research, graphene sheet were modified by a glow discharge in solution. A pulsed power supply was used to generate discharges. The pulsed width was 2 micro seconds, the repetition frequency was 15 kHz. The electrode was tungsten wire in the diameter of 1 mm with electrode gap of 0.3 mm. ammonium aqueous solution was used as the medium around plasma. Graphene sheets were separated by oxidation. The graphene sheets were added to the ammonium solution and irradiated by glow discharge in the solution. The solution and the productants after the discharge were analyzed by optical emission spectroscopy, IR spectroscopy, Uv-Vis

spectroscopy, AFM, XRD and TEM. After the discharge, the graphene sheets were modified by amino functional groups. Moreover, the aminocaproic acid was grafted into the amino functional groups on graphene sheets. Finally, graphene sheets were solidified because the space of sheets was measured.

**GR-TuP3 Investigation of Diffusion Process between Many-Layers Graphene and Metallic Contacts**, *A.R. Vaz, CTI/CCS - UNICAMP, Brazil, F.P. Rouxinol, C.F. Fischer, S.A. Moshkalev, UNICAMP, Brazil, J.W. Swart, CTIRA, Brazil*

Nanoscale graphitic carbon forms like nanotubes and few-layer graphene (graphite) or FLG layers have attracted much attention recently due to their unique physical-chemical properties and many potential applications in microelectronics, like sensors, MEMS (micro-electromechanical systems) and interconnections [1]. However, successful applications of these materials in microelectronic devices require development of reliable and compatible technologies for their controlled growth or deposition, manipulation, contacting, processing and measurements of electrical other properties. In particular, mechanisms responsible for formation of high-quality electrical contacts between graphitic layers and metals (this is imperative for applications like interconnections) is poorly understood and need thorough study and optimization. In this work, we studied characteristics of the electrical contacts between FLG and metals like W, Ti, Ni, Cu, Pd and Au. For this, two different techniques were used. First, small flakes of FLG were prepared in solutions and deposited using ac dielectrophoresis [1] over metal electrodes pre-fabricated by photolithography and FIB milling processes that produced 5  $\mu\text{m}$  deep gaps with varying widths (Fig. 1). The thickness of FLG flakes was evaluated using Raman spectra, AFM measurements and SEM images [2]. Then, electrical properties of deposited structures were measured before and after thermal annealing, using 2 terminals I-V method (Fig. 2). Electrical contacts between graphitic layers and metal electrodes were found to improve strongly with annealing. It was also found that metal-FLG contacts give usually the major contribution to the total measured 2-terminals resistance, and the contact resistivities were then evaluated for different metals. Better contacts were achieved using Ti and W electrodes. To study interaction between metals and graphitic layers during annealing (metal diffusion), a special study was undertaken. For this, metal layers of certain thickness were deposited in deep trenches prepared in thick HOPG layers using FIB based lithography followed by deep reactive ion etching of graphite in oxygen with high-density plasma source [3]. Then, after annealing in vacuum, FIB was used to make cross-sections and to study lateral (in-plane) and normal (between planes) diffusion of metal inside the graphite structure. For such study, several microscopy techniques with spatial resolution like EDX, EELS, HRSEM were employed.

- 1 R.Gelamo *et al.*, Chem.Phys.Lett. (2009)
- 2 F.P. Rouxinol *et al.*, to be published
- 3 H. Jansen *et al.*, J. of Micromech. Microeng. 16 (1995)

**GR-TuP4 Optoelectronic Properties of Large Area Graphene Thin Films**, *C. Mattevi, H.K. Kim, G. Eda, M. Chhowalla*, Imperial College London, UK

A scalable method to isolate graphene on insulating substrates is still a challenge. Recently it has been demonstrated that graphite can be exfoliated in certain solvents [1] and in water-surfactant solution [2] forming a stable colloidal suspension. Amongst several solvents investigated, exfoliation with 1-Methyl-2-pyrrolidone (NMP) has yielded the highest concentration of 1-5 graphene layers [1,3]. Here we present Langmuir-Blodgett (LB) films of pure graphene exfoliated in NMP and their optical and electronic characteristics [3]. For flakes with large lateral size, the films displayed sheet resistance of 5 K $\Omega$ /sq and transmittance of 75% at wavelength of 550 nm. Thin film transistor (TFTs) have been fabricated and tested at temperatures ranging from 77 K to 340 K. The field effect measurements displayed high degree of p-doping and this is possibly due to interaction between graphene and residual oxygen functional groups, as suggested by X-ray photoelectron spectroscopy (XPS). Below 150 K, the temperature dependence of the conductivity suggests transport by two-dimensional variable range hopping. Above 180 K, thermal activation of the charge carriers appears to be the dominant mechanism. A clear dependence of the optoelectronic properties with the lateral size of graphene flakes has been observed. A critical analysis on the prospects of improving the electrical

properties of graphene obtained *via* non covalent exfoliation will be discussed.

- [1] Y. Hernandez et al. *Nature Nanotech.* Vol. 3, pp. 563-568, 2008.
- [2] M. Lotya et al. *J. Am. Chem. Soc.* Vol 131, pp.3611-3620, 2009.
- [3] H. Kim et al. *submitted.*

**GR-TuP5 Tunneling Spectroscopy of Image Potential Derived States of Epitaxial Graphene on SiC(0001): Sample Annealing Effects, A. Sandin, A. Pronshinske, D.B. Dougherty, J.E. Rowe, North Carolina State University**

Constant current tunneling spectroscopy has been used to study the high energy unoccupied electronic structure of single layer and bilayer epitaxial graphene on the Si-terminated face of SiC(0001) prepared with several different sample-annealing conditions that give different thicknesses of graphene film coverage. We identify a series of intense peaks in vertical sample-tip spacing versus voltage as derived from image-potential states of epitaxial graphene. These peaks shift in energy position between single-layer and bilayer graphene in a manner somewhat like the known work function difference (of ~4.4 eV and ~4.6 eV for single-layer and bilayer graphene respectively). We compare the series of image-potential-like-state energies measured experimentally with simple models of the tunneling potential due to a sharp tip protrusion and a flatter average tip radius that shows a variability of the energy series with spatial variation of the potential. In addition, we argue that variability in peak positions for nearly all of the observed image potential derived states arises from the variations in the 3-D tip shape, which then determines the field dependent tunneling potential.

**GR-TuP6 Characterization of Graphene Films Grown on Cu-Ni Foil by XPS and LEED, D.D. Moody, W. Priyantha, R. Droopad,, C.A. Ventrice Jr., Texas State University - San Marcos, S. Chen, W. Cai, R.D. Piner, R.S. Ruoff, The University of Texas at Austin**

Previous studies have shown that monolayer graphene films can be grown on Cu substrates by the catalytic decomposition of methane molecules.[1-5] The solubility of carbon in Cu is negligible at the growth temperatures typically used for graphene growth. This results in the formation of films that self-terminate at a monolayer coverage since there is very little (if any) carbon in the sub-surface region that can precipitate to the graphene overlayer during the cooling phase. Indeed, our prior work suggests that the growth is entirely surface mediated with no contribution from segregation of carbon from the bulk.[2] In an attempt to enhance the catalytic activity of the surface and to grow multilayer graphene rather than solely monolayer graphene, use of a commercial 70%-30% Cu-Ni alloy foil (which also has some Fe and Mn present) has been investigated. Growth was performed in a home-made, cold-wall, chemical vapor deposition (CVD) system [6] at a growth temperature of 1000 ° C (as measured with a pyrometer through a quartz window) with pure CH<sub>4</sub> at a pressure of 8 Torr. To determine the surface alloy composition during the different phases of growth, X-ray photoelectron spectroscopy (XPS) measurements have been performed on the Cu-Ni foil before anneal, after anneal in H<sub>2</sub>, and after growth of graphene in a CH<sub>4</sub> environment. XPS measurements were made at both normal emission, and at an exit angle of 50° to enhance the surface sensitivity. Before anneal, the measurements indicate that the surface is Ni-rich and heavily oxidized. After annealing in H<sub>2</sub>, only a small amount of oxide remained, and the alloy fraction of the surface region was 21% Ni. This indicates that the outermost layer of atoms is probably Cu, but further study is indicated. Growth of the graphene overlayer resulted in an increase of the Ni composition of the surface region to 28%, with only trace amounts of oxygen present. Low energy electron diffraction (LEED) measurements of the foils showed only diffuse background for the Cu-Ni foils before anneal and after anneal in H<sub>2</sub>. The LEED measurements of the foil after graphene growth showed diffraction spots and ring structures at 70 eV, which are attributed to the formation of multidomain graphene. *Support from the Office of Naval Research is appreciated.*

- [1] X. S. Li, et al., *Science* **324**, 1312 (2009).
- [2] X. S. Li, et al., *Nano Letters* **9**, 4268 (2009).
- [3] X. S. Li, et al., *Nano Letters* **9**, 4359 (2009).
- [4] X. S. Li, et al., *ECS Transactions* **19**, 41 (2009).
- [5] W. Cai, et al., *Nano Letters* (in-press).
- [6] W. Cai, et al., *Nano Research* **2**, 851 (2009).

**GR-TuP7 Chemical Vapor Deposited Graphene-Based NEMS Resonators, I. Rivera, R. Joshi, J. Wang, University of South Florida**

Graphene is a superb structural material for NEMS resonators because of its unique electrical and mechanical properties. Excellent material properties of graphene such as good conductivity, single atomic thickness layers, large surface area, low mass density, and high Young's modulus as compared to

other materials allow optimization of the resonance response to approach the ultimate limit for two dimensional NEMSs. Single device resonator has been studied extensively in the past with very high Q-factor and resonant frequency. However, for device technology, arrays of resonators provide a wider range of applications which appear to be possible in graphene based resonators. Figure 1 summarizes the fabrication process of the graphene resonators and Figure 2 presents a 3D schematic of graphene resonator array, indicating key parts and the materials. We have grown the monolayer quality graphene using thermal chemical vapor deposition method on Ni coated substrates at 1000°C using a mixture of argon, hydrogen and methane as precursor gases. It was observed that growth time and thickness of Ni films are key parameters for controlling the number of layers of graphene. Initial results suggest the formation of 1-5 layers of graphene which was estimated from AFM, TEM and 2D peak intensity of Raman spectra [Figure 3]. Hall Effect data show mobility ~ 1500 cm<sup>2</sup>/V and resistivity of 2X10<sup>-6</sup> Ω-cm for 3 layer graphene. Graphene was released from Ni by wet chemical etching and the layers were transferred onto SiO<sub>2</sub>/Si substrate. In order to employ graphene as a major building block, NEMS resonator structures were created by transferring a patterned graphene layer onto a silicon-on-insulator (SOI) substrate to act as mechanical interconnects. The Si device layer in SOI substrate is patterned by deep reactive ion etching (DRIE) using SiO<sub>2</sub> as hard mask to create the resonator body. An ultra-thin layer of high-k dielectric material is uniformly deposited by atomic layer deposition (ALD) followed by deposition and doping of a poly-Si layer. A lithography process is done to create the shape of the double side electrodes. Thereafter, the graphene is transferred and attached to the resonator bodies to complete the array. Finally, the resonator array is released by removing the buried SiO<sub>2</sub> in the SOI substrate.

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