

Tuesday Morning, November 10, 2009

Graphene Topical Conference

Room: C3 - Session GR+EM+MS-TuM

Graphene and Carbon-based Electronics

Moderator: J.E. Rowe, North Carolina State University

8:00am **GR+EM+MS-TuM1 Graphene: Quantum Transport in a 2D Membrane**, *C.N. Lau*, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a promising candidate for electronic materials, as well as a new model system for condensed matter physics. It also has the double identity of an extraordinary conductor and the thinnest isolated membrane. In this talk I will present our results on both of these aspects: (1) our observation of novel transport phenomena in graphene, including coherent interference of multiply-reflected charge waves and properties of p-n-p junctions in zero and high magnetic fields; and (2) our work on ripple formation and manipulation on suspended graphene sheets. I will conclude the talk with a brief discussion on the fascinating prospect of strain-based graphene engineering.

8:40am **GR+EM+MS-TuM3 Air Induced Suppression of n-Type Conduction in Field-Effect Transistors**, *P. Levesque*, Université de Montréal, Canada, *C.M. Aguirre*, École Polytechnique de Montréal, Canada, *M. Paillet*, *F. Lapointe*, Université de Montréal, Canada, *B.C. St-Antoine*, *P. Desjardins*, École Polytechnique de Montréal, Canada, *R. Martel*, Université de Montréal, Canada

Carbon nanotube, graphene, and organic semiconductor based devices share common features when exposed to atmospheric environment. For carbon nanotube field-effect transistors (FET), the effect is an almost exclusive p-type character in air. N-type conduction can only be observed under certain conditions, for instance when the devices are annealed in vacuum. By performing experiment under controlled atmosphere, we investigated the impact of the chemical nature of the substrate and of gas adsorbates on the field-effect switching behavior of both nanoscale and thin-film nanotube FETs. Our study revealed that the intrinsic material properties are modified and lead to the reduction of n-type conduction when an adsorbed water layer containing solvated oxygen is present on the SiO₂ surface. This finding demonstrates that an electrochemical charge transfer reaction between the semiconducting channel and the aqueous oxygen redox couple is the underlying phenomenon behind the suppression of electron conduction in nanotube devices. The impact of this redox couple on graphene FET explored in this context will also be discussed. We forecast that these redox active species generally influence the transport properties of transistors operating in air and propose a general mechanism that explains behaviors observed in many material systems on SiO₂/Si substrates, also including nanowires, polymers and organic materials.

9:00am **GR+EM+MS-TuM4 Epitaxial Graphene Device Technology**, *D.K. Gaskill*, U.S. Naval Research Laboratory, *J. Moon*, HRL Laboratories, LLC, *J.L. Tedesco*, U.S. Naval Research Laboratory, *J.A. Robinson*, The Pennsylvania State University, *A.L. Friedman*, *P.M. Campbell*, *G.G. Jernigan*, *J.K. Hite*, *R.L. Myers-Ward*, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory, *M.A. Fanton*, The Pennsylvania State University

Recently, the world's first graphene RF field effect transistors (FETs) have been fabricated using photolithography on epitaxial graphene (EG) grown on 50 mm SiC semi-insulating wafers. The RF FETs had f_{\max} of 14 GHz at 5 V_{ds} for 2 μm gate widths and results are expected to improve as gate widths are scaled down. Continued research addressing key materials issues is needed to push the performance metrics for devices fabricated on wafer-scale EG significantly higher. Some of these key materials issues are morphology and thickness control, enhanced mobility, uniformity of sheet carrier density and resistivity, and optimizing atomic layer deposition (ALD) of high dielectric constant oxides on EG. In this presentation, we will present details on our approach using Si sublimation from SiC substrates for growing EG on 50.8 and 76.2 mm diameter SiC wafers and discuss the impact of key material issues on RF device performance.

Epitaxial graphene was synthesized using a commercial Aixtron VP508 SiC epitaxial growth reactor on the Si- and C-faces of 4H- and 6H-SiC semi-insulating 0° oriented substrates at temperatures from approximately 1225 to 1700°C and for times ranging from 10 to 300 min. Substrates were 16 x 16 mm² coupons and 50.8 and 76.2 mm diameter wafers. Both *in-vacuo* (10⁻⁶ to 10⁻⁴ mbar) and Ar ambient (50-200 mbar) Si sublimation synthesis conditions were investigated. Dielectrics were deposited using a Cambridge NanoTech Savannah 200 ALD system. EG was characterized by a wide

array of tools including atomic force, Nomarski and scanning tunneling microscopies, Raman spectroscopy, Hall effect, and Leighton contactless resistivity and mobility wafer probe.

The growth of EG on 50.8 mm Si-face wafers using the *in-vacuo* process was optimized and excellent relative resistivity uniformity of 2.8% and record 300 K Hall mobilities up to 2700 cm²V⁻¹s⁻¹ were found. Raman spectroscopy mapping of the 2D peak on the wafers determined: (1) the majority of the film was monolayer EG, (2) two layers of EG could be found at step edges and (3) the EG was continuous across the wafer. RF FETs fabricated using the latest optimized wafer-scale EG exhibited state-of-the-art ambipolar behavior, I_{on}/I_{off} ratios and peak transconductances. Frequency performance metrics were established for these devices such as f_T•L_g products of 10 GHz•μm and f_{max} of 14 GHz. To our knowledge, the highest field effect mobilities reported to-date have been measured using these devices. We will discuss the impact of key material parameters associated with EG for these record results as well as the impact of Ar ambient controlled graphenization on future RF devices.

9:20am **GR+EM+MS-TuM5 Hydrogen Adsorption at Surfaces of the Epitaxial Graphene on the 6H-SiC(0001)**, *Y. Aoki*, *H. Hirayama*, Tokyo Institute of Technology, Japan

Recently, adsorption of a small amount of atomic hydrogen was reported to transform the exfoliated graphene from highly conductive semimetal into an insulator [1]. In this case, the C-atom is only the site for hydrogen adsorption. However, at the epitaxial graphene on the SiC(0001) substrate, hydrogen could adsorb on both C- and Si-site. Furthermore, the surface structure changes by stages from Si-rich 3x3, √3x√3 to C-rich 6√3x6√3 phase in the epitaxial growth of graphene on SiC substrates [2]. In this study, we investigated the hydrogen adsorption at these surfaces appeared in the way of epitaxial growth of graphene on the Si-terminated 6H-SiC(0001) surfaces.

Experiments were carried out in an ultra-high vacuum apparatus equipped with a Si dozer, a LEED/AES, a TPD (Temperature Programmed Desorption), a hydrogen gas inlet, and a hot W-filament. We prepared the 3x3, √3x√3, and 6√3x6√3 surfaces by heating the sample at 850°C under the Si flux, heating at 1150°C for 3min, and heating at 1250°C for 3min, respectively. We exposed these surfaces to atomic hydrogen, and measured their TPD spectra. Our TPD indicated that the saturation coverage of H was ≈0.1 monolayer (ML) at these surfaces independent of the surface structure. However, the TPD spectrum changed drastically at the stage from 3x3 to √3x√3. The 3x3 surface showed a shoulder at ≈500K, and a dominant peak at 700K, while the √3x√3 and the 6√3x6√3 surface had a single peak at 400K. Comparing to the previous TPD studies at graphite [3], we attributed to the single peak at 400K to the hydrogen desorption from the graphene layer. Meanwhile, the peak at 700K of the 3x3 surface is very close to the hydrogen desorption peak from the Si(111) surface. Both TPD and AES suggests that the π-bonded C-induced benzene ring structure started to grow at the appearance of the √3x√3 surface structure. This interpretation is supported by our electron energy loss spectroscopy (EELS) measurements in which the π-plasmon loss peak of the benzene ring started to evolve at the √3x√3 surface.

[1] Science 323,610(2009), [2]JPC,B208,19912(2004), [3]JCP117,8486(2002)

9:40am **GR+EM+MS-TuM6 Graphitic Carbon Growth on Si(111) from Solid Source Molecular Beam Epitaxy**, *J.C. Hackley*, *D. Ali*, *J. Di Pasquale*, *C.J.K. Richardson*, University of Maryland, College Park

Since the recent discovery of isolated graphene through mechanical exfoliation of bulk graphite, a number of methods have been developed to produce graphene. However, there have been no reports of graphene growth by direct carbon deposition such as solid source molecular beam epitaxy (MBE). Carbonization of a silicon surface is a commonly used first step in the epitaxial growth of SiC films, and is often accomplished by solid source MBE of carbon onto a Si substrate to form a thin SiC buffer layer. Annealing SiC wafers in ultra-high vacuum is a reliable method of producing graphene layers, and is frequently referred to as an epitaxial technique. Consequently, graphene may be synthesized via MBE through a two-step process consisting of first growing SiC, and then annealing this film at high temperatures to desorb Si. A shorter processing route which bypasses the SiC formation would be quite beneficial. In this project, we investigate the growth of graphene directly on Si using solid source MBE at growth temperatures which are much lower than a SiC process.

An EPI-Model 930 MBE system which has been modified to accommodate a Si electron beam source is used for carbon sublimation onto 3" Si wafers. Our carbon source is a Thermionics rod-fed electron beam gun with a

highly oriented pyrolytic graphite (HOPG) target. Reflective high-energy electron diffraction (RHEED) measurements are used to monitor the carbon film growth in situ. The film bonding structure is investigated ex-situ with x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman scattering spectroscopy. Film topology is examined ex-situ with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hall measurements in a Van der Pauw configuration are implemented for electrical characterization of the films. Through preparing the Si surface with seeding layers and choosing an appropriate C flux we have been able to suppress SiC formation and grow graphitic carbon at temperatures < 700°C. Raman scattering measurements show the G mode at ~1600 cm⁻¹ and the D mode at ~1320 cm⁻¹ (Fig. 1), as well as weak overtones of these phonon modes. XPS analysis of the C 1s region shows no significant sp³ carbon bonds, and no SiC formation, which is also verified by FTIR measurements (Fig. 2). SEM and AFM analysis show that the films are smooth and continuous.

We are currently refining our growth process in order to increase graphite grain size and subsequently downscale to 2-dimensional growth. These initial results appear promising for the future development of graphene growth via direct deposition of carbon.

10:40am **GR+EM+MS-TuM9 Epitaxial Graphene: Designing a New Electronic Material.** *W.A. de Heer*, Georgia Institute of Technology **INVITED**

Since 2001 the Georgia Tech epitaxial graphene research team and its collaborators have developed the new field of epitaxial graphene electronics. The current status of epitaxial graphene research will be presented, including the production methods and recent results from various characterization investigations. Methods have been developed to grow continuous multilayered epitaxial graphene (MEG) on the C-face of hexagonal silicon carbide with of up to 100 graphene sheets and its extraordinary transport properties have been demonstrated.

Surprisingly, the properties of MEG are closely related to monolayer graphene rather than graphite, as a result of an unusual rotational stacking of the graphene layers that causes the graphene sheets to electronically decouple. Consequently the electronic band structure of MEG is composed of Dirac cones. The charge carriers are chiral and exhibit a non-trivial Berry's phase. Weak anti-localization and quantum confinement has been demonstrated. Landau level spectroscopy further exhibits record-breaking room temperature mobilities and well resolved Landau levels below 1 T, indicating extremely low carrier densities and good homogeneity of the material. Efforts towards large scale electronic device patterning will be reviewed.

11:20am **GR+EM+MS-TuM11 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene.** *Q.H. Wang**, *M.C. Hersam*, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al₂O₃ on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,¹ and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.² In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.³ We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

* Morton S. Traum Award Finalist

- ¹ X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).
- ² P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).
- ³ Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

11:40am **GR+EM+MS-TuM12 Effects of Reducing Conditions on Conductivity Change of Graphene Oxide.** *H. Asano*, *Y. Shimogaki*, The University of Tokyo, Japan

Graphene is an attractive material for electronic devices since it has remarkable electronic properties, such as super high electron mobility. There are some methods to form graphene on SiO₂, however, it is difficult to cover SiO₂ substrate fully by flat graphene flakes on a wide area. For example, micromechanical cleavage of graphite can make graphene sheet on SiO₂, but the largest size of it will be within several micrometers. There is a demand, however, to graphene to use as conductive materials such as wiring material for ULSI interconnects and transparent and conductive electrode for solar cells and flat panel displays. These applications require large area coating and low process temperature. Then, graphene oxide (GO) coating and its reduction to form conductive graphene gets much attention. In the present work, we tried to reduce GO by gas-phase reduction and examined the resistivity change.

To obtain GO dispersion, graphite (Nippon Graphite Industry Co., LTD, SCB-100) was oxidized through the modified Hummer's methods. The dispersion was determined to be 0.965 wt% from the weight change of the dispersion. The dispersion was exfoliated by sonication, diluted by ethanol to 0.20 wt% and spin-coated on SiO₂/n-Si substrate, which was pre-treated by aminopropyltriethoxysilane (APTES). Spin-coated GO film was dried at room temperature. Reduction of GO film to form graphene was carried out in a vacuum, H₂, or formic acid ambient. The temperature of the substrate was ranged from 200°C to 1000°C, base pressure was 2.6×10⁻⁷ Torr, pressure of reducing agent (hydrogen or formic acid) was 5 Torr.

Thickness of spin-coated GO film was 30±5 nm and the film contents were 90 at% of C and 10 at% of O. Sheet resistance of the film was decreased by annealing in vacuum. The reciprocal of sheet resistance showed the Arrhenius type behaviour and minimum sheet resistance obtained in our work was 0.7 kΩ/sq. This result suggests some thermal activation phenomena that controls resistivity of GO. Thermal Desorption Spectroscopy (TDS) analysis showed that almost all O atoms were removed at 200°C, but very small amount of H₂O, CO, CO₂ was also detected above 200°C. The elimination of remaining oxygen as H₂O, CO, CO₂ at high temperature may be responsible for the Arrhenius type behaviour of the sheet resistance. Sheet resistance became one-third by the reduction using formic acid at 290°C compared with the reduction in vacuum or H₂. The sheet resistance treated over 700°C did not show any ambient dependency. We will also discuss the chemical bond state change observed by XPS and carrier concentration / mobility change measured by Hall measurement.

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