

# Tuesday Morning, October 19, 2010

## Graphene Focus Topic

Room: Brazos - Session GR+TF-TuM

## Characterization, Properties, and Applications

Moderator: M. Chhowalla, Rutgers University

### 8:00am GR+TF-TuM1 Near-field Scanning Microwave Microscopy of Few-Layer Graphene, N.G. Kalugin, New Mexico Tech

Near-field microwave microscopy can be used as an alternative to atomic-force microscopy or Raman microscopy in determination of graphene thickness. We evaluated the values of AC impedance for few layer graphene. The impedance of mono and few-layer graphene at 4GHz was found predominantly active. Near-field microwave microscopy allows simultaneous imaging of location, geometry, thickness, and distribution of electrical properties of graphene without device fabrication. Our results may be useful for design of future graphene-based microwave devices.

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### 8:20am GR+TF-TuM2 Molecular Simulation of the Indentation of Free-Standing Graphene Films in the Presence of Defects, J.D. Schall, R.V. Petrach, Oakland University

Recent experimental advances in the synthesis of graphene have enabled the construction of free-standing graphene-based "nanobridges" (for example: Shivaraman, Nanoletters, 9, 2009, 3100 ). This has allowed for the first time to probe the mechanical properties of this unique material directly through experiment. In the past, mechanical properties had been estimated theoretically via various molecular simulation techniques. With these new experimental advances, many new questions arise. To list a few: How do defects affect mechanical properties? How do molecular adsorbates modify these materials? Again, molecular simulation is expected to play a significant part in the future of graphene research. In this talk, results of simulated indentation of free-standing graphene films mimicking recent force-probe experiments will be presented. Simulations are conducted using Brenner's second generation reactive empirical bond order potential. This method allows for accurate determination of mechanical properties and chemical modification of the films. Using indentation and a simple force balance approach, the Young's modulus of a pristine free-standing graphene nano-bridge was estimated to be in excess of 1 Terapascal. Results from films with Stone-Wales defects, vacancies, and chemical adsorbates also will be presented.

### 8:40am GR+TF-TuM3 Mechanical Characterization of Freestanding Graphenoid Nanomembranes from Self-Assembled Monolayers, X. Zhang, C.T. Nottbohm, A. Turchanin, A. Beyer, A. Götzhäuser, Bielefeld University, Germany

We report on the fabrication and mechanical characterization of novel graphenoid nanomembranes with a thickness of approximately 1 nm. The nanomembranes are prepared from electron cross-linked aromatic self-assembled monolayers (SAMs). The membranes are then transferred to window-substrates (Si) for mechanical characterization. Bulge testing of such freestanding nanomembranes within an atomic force microscope is utilized to investigate their mechanical properties.

A series of biphenyl-based molecules were used to prepare the nanomembranes, such as carbonitrile-biphenyl-trimethoxysilyl (CBPS), biphenyl-thiol (BPT) and nitro-biphenyl-thiol (NBPT). Biphenyl-based nanomembranes have elastic moduli ranging from 6 to 12 GPa. They display outstanding performance in the ultimate tensile strength with values of 400 to 500 MPa, which is several times higher than the values of other carbon based membranes. Furthermore, annealing of the cross-linked nanomembranes in ultra high vacuum systematically increase of the Young's moduli from 10 GPa to ~45 GPa for an annealing temperature of ~1000 K. Strain relaxation lowers the residual strain from 0.9 % to ~0.35 % for temperatures of 800 K and above. This is caused by a structural transformation in which the nanomembrane is converted into nanocrystalline graphene.

### 9:00am GR+TF-TuM4 Chemical Vapour Deposition (CVD) Growth of Graphene on Copper, C. Mattevi, H.K. Kim, G. Eda, M. Chhowalla, Imperial College London, UK

Uniform large-scale fabrication of graphene thin films with controllable thickness represents a key challenge for integration of graphene into

practical electronic devices. Recently, graphene of high quality has been synthesized by chemical vapor deposition (CVD) on transition metal catalysts [1,2]. The graphene growth by CVD on polycrystalline copper [2] is particularly interesting because it allows single graphene layer over 95% of the surface and the residual 5% is covered by 2-3 layered graphene film. Hence, this is the first [2] reported reproducible method to synthesize uniform graphene thickness over large area. Then the as grown graphene can be transferred by different processes, onto a variety of substrates. An appealing challenge is to selectively obtain different graphene thicknesses over large area, to satisfy different applications. Here we report a detailed study of the multilayer graphene domains that appear in limited regions of the copper surface. The lateral size as well as the graphene thickness and stacking order, has been carefully investigated as a function of copper pre-treatment and growth parameters. In particular the role of the feed stock gas pressure and ratio between the etching gas (H<sub>2</sub>) and the precursor (CH<sub>4</sub>) has been demonstrated to affect the lateral size and the thickness. Optoelectronic properties of the transferred graphene films onto SiO<sub>2</sub> are also presented.

#### References

1. K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature* **457**, 706 (2009).
2. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**, 1312 (2009).

### 9:20am GR+TF-TuM5 Structural and Electronic Properties of Graphene Synthesized by Chemical Vapor Deposition, Y. Chen, Purdue University

INVITED

We have studied the structural and electronic properties of large scale (up to several inches) graphitic and graphene thin films synthesized by chemical vapor deposition (CVD) on polycrystalline Ni<sub>1,2</sub> and Cu<sub>3</sub> foils then transferred onto insulating substrates (SiO<sub>2</sub> on doped Si). For films grown on Ni<sub>1,2</sub>, structural characterizations by atomic force microscopy (AFM), scanning tunneling microscopy (STM), cross-sectional transmission electron microscopy (XTEM)<sup>4</sup> and spectroscopic Raman mapping confirm that such large scale graphitic thin films contain both thick graphite regions and thin regions of few layer graphene. The films also contain many wrinkles, with sharply-bent tip and dislocations revealed by XTEM, yielding insights on the growth and buckling processes of the film. Measurements on mm-scale back-gated transistor devices fabricated from the transferred film show ambipolar field effect with resistance modulation ~50% and carrier mobilities reaching ~2000 cm<sup>2</sup>/Vs. We also demonstrate quantum transport of carriers with phase coherence length over 0.2 μm from the observation of 2D weak localization in low temperature magneto-transport measurements. Our results show that despite the non-uniformity and surface roughness, such large-scale, flexible thin films can have electronic properties promising for device applications. For films grown on Cu<sub>3</sub>, we show they consist dominantly of monolayer graphene as indicated by Raman mapping. STM imaging shows monolayer graphene lattice. Low temperature transport measurements are performed on micro devices fabricated from such CVD graphene, displaying ambipolar field effect (with on/off ratio ~5 and carrier mobilities up to ~3000 cm<sup>2</sup>/Vs) and "half-integer" quantum Hall effect, a hall-mark of intrinsic electronic properties of monolayer graphene. We also observe weak localization and extract information about phase coherence and scattering of carriers by disorder in the graphene. We have measured the thermal conductivity of suspended CVD graphene to be ~3000 W/m-K, comparable with that of exfoliated graphene, by combining electronic transport and Raman thermometry<sup>5</sup>. Finally, I will present some results on graphene layers grown by CVD directly on insulating substrates. Work in collaboration with Q. Yu, H. Cao, L. Jauregui, R. Colby, E. Stach, N. Guisinger and H. Li.

1. Q. Yu *et al.*, *Appl. Phys. Lett.* **93**, 113103 (2008)
2. H. Cao *et al.*, *J. Appl. Phys.* **107**, 044310 (2010)
3. H. Cao *et al.*, *Appl. Phys. Lett.* **96**, 122106 (2010)
4. R. Colby *et al.*, *Diamond Relat. Mater.* **19**, 143 (2010)
5. L. A. Jauregui *et al.*, *ECS Trans.* **28** (5), 73 (2010)

### 10:40am GR+TF-TuM9 Scanning Tunneling Spectroscopy of a Gated Single-Layer Graphene Device in the Quantum Hall Regime, S. Jung, G.M. Rutter, N.N. Klimov, D.B. Newell, N.B. Zhitenev, J.A. Stroscio, NIST

We have performed scanning tunneling spectroscopy (STS) measurements to investigate Dirac particle interactions and localization by local impurities in a gated single-layer exfoliated graphene device in the quantum Hall

regime at a temperature of 4.3 K. At the Dirac point, electron-hole puddles created by the disorder potential in SiO<sub>2</sub> substrate are observed at zero magnetic field. In an applied magnetic field, the carriers are condensed into well-resolved Landau levels (LLs), whose general evolution as a function of both charge density and magnetic field is well described by the context of ‘massless’ Dirac particles. Tunneling spectroscopy measurements as a function of magnetic field and applied gate potential are shown to give insight into the localization of carriers and their relation to the disorder potential. At low magnetic fields, tunneling spectra display long-range scattering features related to the graphene disorder potential variation. The disorder potential also determines the spatial distribution of LLs in higher magnetic fields. We observe that isolated compressible LL regions surrounded by incompressible strips behave like graphene quantum dots (QDs). Single-electron charging of the QDs is seen as four-fold Coulomb oscillations in individual  $dI/dV$  curves. These results show that the plane of the graphene 2DEG breaks into a checkerboard pattern of electron- or hole-rich QDs localized at either maxima or minima of the disorder potential.

11:00am **GR+TF-TuM10 Scanning Tunneling Spectroscopy of Gated Bilayer Graphene Device in the Quantum Hall Regime**, *N.N. Klimov*, CNST/EEEL/NIST and Maryland NanoCenter UMD, *G.M. Rutter*, CNST/NIST, *S. Jung*, CNST/NIST and Maryland NanoCenter UMD, *D.B. Newell*, EEEL/NIST, *N.B. Zhitenev*, *J.A. Stroscio*, CNST/NIST

It has been shown recently, both theoretically [1] and experimentally [2-3], that a bandgap can be opened and even tuned continuously in bilayer graphene (BLG) in the presence of a strong electrical field, which induces asymmetry of the electrostatic potential of the two graphene layers. This makes BLG an attractive material for future digital electronic applications, infrared nanophotonics, pseudospintronics, and terahertz technology. On the other hand a complete understanding of the physics of BLG and the effect of disorder on a microscopic scale is missing. In this work, we present local tunneling measurements of bilayer graphene exfoliated on SiO<sub>2</sub>/Si using scanning tunneling spectroscopy at a temperature of 4.3 K. The graphene bilayer is probed with both the application of a perpendicular magnetic field and with an external gate voltage applied to the Si substrate. We study the effect of disorder potential induced by SiO<sub>2</sub>/Si on the electronic properties of bilayer graphene. We find that disorder potential causes a bandgap opening in BLG, while a backgate voltage has a secondary effect on the density of states. We also find that the magnetic quantization of the carriers, evidenced by the formation of Landau levels (LL), does not obey the simple scaling of LL energy versus magnetic field for an ideal graphene bilayer.[4] The LL spectra are seen to vary greatly depending on the local potential variation and associated charge density. We have investigated these variations with detailed spectroscopic maps of the LL spectra as a function of energy, gate voltage, and local potential variation. We find the assignment of the spectral features to be much more complex than expected, and may require the introduction of an intrinsic electrical bias in the bilayer system. In this talk, we will discuss the possible theoretical models that may account for our observations.

[1] E. McCann, V. I. Fal’ko, *Phys. Rev. Lett.* **96**, 086805 (2006).

[2] J. B. Oostinga, *et. al.*, *Nature Mater.* **7**, 1510157 (2008).

[3] E. V. Castro *Phys. Rev. Lett.* **99**, 216802 (2007).

[4] E. A. Henriksen *et al.*, *Phys. Rev. Lett.* **100**, 087403 (2008).

11:20am **GR+TF-TuM11 Monolayer Graphene on 150mm Substrate**, *H.J. Chung*, *J. Heo*, *H. Yang*, *S.-H. Lee*, *S. Seo*, Samsung Advanced Institute of Technology, Korea

Monolayer graphene over a 150 mm substrate was fabricated using Cu-Ni multilayer growth substrates with Inductively Coupled Plasma-Enhanced Chemical Vapor Deposition (ICPCVD) over 700°C. It was confirmed with Raman spectroscopic mapping after metal etching and transfer process. Over 2000 FETs were fabricated on a 150 mm wafer and on-off ratio and Dirac shift were measured for each device and compared to ones from the graphene grown on Ni substrate. In addition, the result from SPM investigation will be presented.

11:40am **GR+TF-TuM12 Probing the Electronic Structure, Surface Chemistry, and Alignment of Graphene using Soft X-ray Absorption Spectroscopy**, *C. Jaye*, NIST, *V. Lee*, SUNY at Buffalo, *P. Lysaght*, SEMATECH, *S. Banerjee*, SUNY at Buffalo, *D.A. Fischer*, NIST

Graphene, a single layer of graphite packed in a honeycomb lattice, has been the subject of intense scientific research since its discovery in 2004 owing to its remarkable properties such as the half-integer quantum Hall effect, ballistic conduction, and the extremely high mobilities of its charge carriers. Graphene has numerous potential applications in the electronics industry including within ultra-high frequency transistors, electrical interconnects and as a replacement for indium-tin-oxide. Nevertheless, the fabrication of large-area graphene remains a challenge. We present

systematic studies of the electronic structure, defect density, and alignment of relatively large-area graphene thin films prepared by a) solution/sonochemical methods and b) chemical vapor deposition (CVD). The solution-chemistry-based approaches have the advantage of ease of scalability, making it an attractive approach for industry. We have been able to achieve the fabrication and transfer of large-area graphene films on both conductive and non-conductive substrates. The fabricated films have been characterized by Raman spectroscopy, near-edge X-ray absorption spectroscopy, and four-point-probe conductivity measurements. This battery of measurements allows evaluation of the role of different reducing agents in reducing graphene oxide to graphene. We have also performed systematic measurements of single- and few-layered graphene grown by CVD onto Cu and Ni substrates. X-ray absorption spectroscopy in particular provides strong evidence for substrate hybridization and rippling of graphene. The rippling of graphene induced during transfer to insulating substrates represents a formidable challenge that will need to be solved since corrugations and electronic asperities in graphene induce local scattering potentials. Finally, we will present some X-ray absorption spectroscopy imaging data showing local electronic asperities in graphene.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Banerjee, S.: GR+TF-TuM12, **2**  
Beyer, A.: GR+TF-TuM3, **1**

## — C —

Chen, Y.: GR+TF-TuM5, **1**  
Chhowalla, M.: GR+TF-TuM4, **1**  
Chung, H.J.: GR+TF-TuM11, **2**

## — E —

Eda, G.: GR+TF-TuM4, **1**

## — F —

Fischer, D.A.: GR+TF-TuM12, **2**

## — G —

Gölpzhäuser, A.: GR+TF-TuM3, **1**

## — H —

Heo, J.: GR+TF-TuM11, **2**

## — J —

Jaye, C.: GR+TF-TuM12, **2**

Jung, S.: GR+TF-TuM10, **2**; GR+TF-TuM9, **1**

## — K —

Kalugin, N.G.: GR+TF-TuM1, **1**  
Kim, H.K.: GR+TF-TuM4, **1**  
Klimov, N.N.: GR+TF-TuM10, **2**; GR+TF-TuM9,  
**1**

## — L —

Lee, S.-H.: GR+TF-TuM11, **2**  
Lee, V.: GR+TF-TuM12, **2**  
Lysaght, P.: GR+TF-TuM12, **2**

## — M —

Mattevi, C.: GR+TF-TuM4, **1**

## — N —

Newell, D.B.: GR+TF-TuM10, **2**; GR+TF-TuM9,  
**1**  
Nottbohm, C.T.: GR+TF-TuM3, **1**

## — P —

Petrach, R.V.: GR+TF-TuM2, **1**

## — R —

Rutter, G.M.: GR+TF-TuM10, **2**; GR+TF-TuM9, **1**

## — S —

Schall, J.D.: GR+TF-TuM2, **1**  
Seo, S.: GR+TF-TuM11, **2**  
Stroscio, J.A.: GR+TF-TuM10, **2**; GR+TF-TuM9,  
**1**

## — T —

Turchanin, A.: GR+TF-TuM3, **1**

## — Y —

Yang, H.: GR+TF-TuM11, **2**

## — Z —

Zhang, X.: GR+TF-TuM3, **1**  
Zhitenev, N.B.: GR+TF-TuM10, **2**; GR+TF-TuM9,  
**1**