

Tuesday Morning, October 16, 2007

Thin Film

Room: 613/614 - Session TF-TuM

Two-Dimensional Carbon Nanostructures

Moderator: B.C. Holloway, Luna Innovations Incorporated

8:00am TF-TuM1 Study of Growth Process and Structures of Carbon Nanowalls Synthesized Using Radical Injection Plasma Enhanced CVD. S. Kondo, Nagoya University, Japan, K. Yamakawa, Katagiri Engineering Co., Ltd., Japan, M. Hiramatsu, Meijo University, Japan, M. Hori, Nagoya University, Japan

Carbon nanostructures, such as fullerene, carbon nanotubes and carbon nanowalls (CNWs) have received great attention for several applications, due to their outstanding physical, chemical and mechanical properties. Among a variety of nanocarbons, CNWs are considered as two-dimensional carbon nanostructures. CNWs are the graphite nanostructure with edges, which comprise the stacks of plane graphene sheets standing almost vertically on the substrate, forming a unique nanostructure similar to a maze with high aspect ratio. The large surface area and sharp edges of CNWs are useful as templates for the fabrication of other types of nanostructured materials, which have potential various applications such as in energy storage and electrodes for fuel cell as well as an electron field emitter. We have successfully synthesized CNWs using the radical injection plasma enhanced chemical vapor deposition (RI-PECVD) employing C_2F_6 and H_2 gases. The system consists of a parallel-plate capacitively coupled plasma (CCP) region and a surface wave microwave excited H_2 plasma (H_2 -SWP) region over the CCP. Using this system, the heated substrate was showered with fluorocarbon radicals as well as plenty of H atoms in a controlled manner. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structures and properties. Furthermore, it would be useful to investigate the etching characteristics of CNWs for the modification of CNWs structure or pattern transfer of CNWs to other materials. CNWs were evaluated by Raman spectroscopy, TEM, ellipsometry and XPS measurements. In the initial stage of CNWs growth on a Si substrate by RI-PECVD, we have confirmed that a thin layer of approximately 10 nm in thickness was deposited in the first 1 min, and subsequently CNWs grew in the vertical direction from a lot of nuclei on this thin film. This thin film was found to be amorphous carbon with a little amount of fluorine. The CNWs film with the bottom amorphous carbon layer was exfoliated from the Si substrate. Both sides of the detached CNWs film were etched by Ar/H_2 plasma. The etching rates of CNWs and amorphous carbon thin film were 140 and 15 nm/min, respectively. It is noted that after the removal of amorphous carbon thin film, the morphology of the CNWs was still maintained on the backside, resulting in the formation of free-standing CNWs filter or membrane.

8:20am TF-TuM2 Evaluation and Control of Electric Conduction of Carbon Nanowalls Fabricated by Plasma-Enhanced CVD. W. Takeuchi, M. Ura, Nagoya University, Japan, Y. Tokuda, Aichi Institute of Technology, Japan, M. Hiramatsu, Meijo University, Japan, H. Kano, NU Eco-Engineering Co., Ltd., Japan, M. Hori, Nagoya University, Japan

Carbon nanowalls (CNWs), two-dimensional (2-D) carbon nanostructure, consisting of graphite sheets standing vertically on the substrate, have attracted much attention for several applications, including field emitter arrays, gas storage, and membranes for electrochemical energy storage. Recently, it was reported that 2-D multilayer graphene sheet offers high mobility and huge sustainable currents. Therefore, CNW films potentially would possess high mobility and huge sustainable current density, since the CNWs are basically graphene sheet. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structure and properties. In this study, we focused on the evaluation and control of electric properties of CNWs. CNWs were fabricated on the quartz substrate by the plasma enhanced CVD with H radical injection employing a mixture of C_2F_6/H_2 . We investigated the influence of N_2 or O_2 addition to the process gas mixture on the morphology and electric properties of CNWs. Hall measurement and Raman spectroscopy were used to evaluate the electric properties and structure of CNWs. The Hall coefficient was positive for the CNW film grown without additives. When O_2 was added to the plasma, it was still positive. In the case of N_2 addition, it displayed negative value. The positive or negative value of the Hall coefficient implies p- or n-type, respectively. Therefore, it was found that the conduction type of CNW films was

controllable by adding N_2 or O_2 to the C_2F_6/H_2 plasma. Morphology and crystallinity of CNWs were also changed by the addition of N_2 and O_2 . In the Raman spectroscopy, all samples have a strong peak at 1590 cm^{-1} (G-band) indicating the formation of a graphitized structure, and another peak around at 1350 cm^{-1} corresponding to the disorder-induced phonon mode (D-band). The G-band width in the Raman spectrum increased when N_2 was added. In the case of O_2 addition, G-band width and peak intensity ratio of D band to G band of CNWs decreased. These results indicate that nitrogen would be included in CNWs and act as a donor, while accompanied by the slight degradation of graphite crystallinity. On the other hand, oxygen would play a role of etching of amorphous carbon content and contribute to the higher graphitization, while conduction type of CNW films would not change.

8:40am TF-TuM3 Low Temperature Deposition of Carbon Nanosheets by C_2H_2/H_2 Plasma Enhanced Chemical Vapor Deposition. M.Y. Zhu, R.A. Outlaw, K. Hou, P. Miraldo, D. Manos, College of William and Mary

Two-dimensional carbon nanosheets were previously deposited by radio frequency plasma enhanced chemical vapor deposition (PECVD) using CH_4/H_2 plasma on a variety of substrates. In this work, we report the deposition of the same nanostructure using C_2H_2/H_2 plasma at a substrate temperature more than 100°C lower than that for typical depositions using CH_4/H_2 plasma. The decrease of required substrate temperature is a great benefit to device fabrications. Carbon nanosheets were deposited on silicon substrates at temperatures ranging from 500°C to 600°C while other parameters were 100% C_2H_2 gas (5 sccm total gas flow rate), 35 mTorr gas pressure, 1000 W input RF power, and 10 minutes deposition duration. For substrate temperature from 550°C to 600°C , the carbon nanosheets deposited have sheet-like structures and flat surface morphologies, and are free-standing on substrate surfaces, as characterized by scanning electron microscope (SEM). High-resolution transmission electron microscopic (HR-TEM) results revealed that the edges of the nanosheets consist of about 3-8 atomic layers. Selected area electron diffraction pattern of carbon nanosheet samples matches that for polycrystalline graphitic structures. Raman spectra of carbon nanosheets have the characteristic D and G peaks for defective sp^2 graphitic structures. Detailed results showed faster growth rates and high Raman D/G peak ratios for samples deposited at higher substrate temperatures. Carbon nanosheets were also deposited using various (60-100%) C_2H_2 in H_2 concentrations while other parameters were fixed at 600°C substrate temperature, 5 sccm total gas flow rate, 1000 W input RF power, and 10 min deposition duration. With a decreasing C_2H_2 in H_2 concentration, both the nanosheet growth rate and the Raman D/G ratio were decreased, however, the basic nanosheet structures were maintained. Cross-sectional SEM images showed that carbon nanosheets deposited using C_2H_2/H_2 gas mixture have a straighter vertical orientation and a more uniform sheet height distribution than those deposited using CH_4/H_2 mixture, therefore are expected to have improved field emission properties. Field emission from C_2H_2/H_2 carbon nanosheets are measured under diode configuration and the results will also be presented.

9:00am TF-TuM4 Field Emission Performance of Carbon Nanosheets. K. Hou, R.A. Outlaw, College of William and Mary, M.E. Kordes, Ohio University, M.Y. Zhu, P. Miraldo, College of William and Mary, B.C. Holloway, Luna Innovations Incorporated, D. Manos, The College of William and Mary

Carbon nanosheet, a novel two-dimensional carbon nanostructure consisting of vertically oriented ultra-thin graphitic sheets terminating with 1-3 graphene layers, are fabricated by inductively coupled radio frequency plasma enhanced chemical vapor deposition. Carbon nanosheet, with its atomic-scale edge structure, high purity, and uniform height distribution have been confirmed to be a promising candidate for the application as the cold cathode material in vacuum electronic devices. In this study, we present the latest field emission test results of carbon nanosheet thin film including total current, lifetime in a slow pulse mode, and lifetime in a dc mode. These tests were conducted using a diode configuration having an anode-cathode distance of $254\text{ }\mu\text{m}$. Further, the emission uniformity of carbon nanosheet thin films was primarily studied by photoelectron emission microscopy. To date, we have routinely achieved total currents of more than 20 mA from $\sim 30\text{ mm}^2$ while maintaining a useful current density of $\sim 0.1\text{ A/cm}^2$. Among them, a maximum total current of 26 mA has been measured from a 32 mm^2 testing area at an applied electric field of $25.5\text{ V}/\mu\text{m}$. The test result suggests that the field emission of nanosheet film is not saturated at this field level but is limited by the test apparatus. The lifetime in a slow pulse mode was conducted by applying a series of identical voltage ramps over a long time period with a duty factor of 21%. The maximum current on the order of 13 mA in each voltage ramp was recorded for 96 hours. The test result reveals that the standard deviation of

the maximum is less than 2.1%. The lifetime in a dc mode was conducted by applying a constant negative bias to the sample. A stable ~1.5 mA emission current was obtained from the carbon nanosheet thin film for 200 hours. The standard deviation of the emission current is less than 3.6% during the test period. Photoelectron emission microscopy was used to investigate the field emission uniformity over the surface of carbon nanosheet thin films. In addition, field emission electron microscopy images, formed without photon illumination, were also captured. The analysis of these images show that a small number of nanosheet emission sites dominate the emission current.

9:20am TF-TuM5 Enhanced Field Emission from Mo₂C Coated Carbon Nanosheets, M. Bagge-Hansen, P. Miraldo, R.A. Outlaw, M.Y. Zhu, M. Hou, D. Manos, College of William and Mary

Carbon nanosheets, a new morphology of graphite, have shown remarkable promise as field emission cathodes for applications such as microwave tubes and flat panel displays. The sharp emission edges of the sheets are typically 1-3 graphite sheets thick (~1 nm) and thus provide a superior geometry for field emission enhancement. Fowler-Nordheim theory suggests further field emission enhancement is possible by lowering the work function. The effective work function of carbon nanosheets, previously undetermined, was calculated and found to be analogous to that of graphite, 4.8 eV. By applying a thin film coating of Mo₂C ($\Phi = 3.5$ eV), the field enhancement factor from the geometry, β , was reduced by only a factor of two, yet field emission current substantially increased. A molybdenum coating was deposited on a carbon nanosheets sample by physical vapor deposition in very high vacuum ($p \sim 1 \times 10^{-8}$ Torr) and determined to be ~3 monolayers thick by Auger electron spectroscopy. The coated sample was radiatively heated to T~250°C to promote molybdenum reaction with adventitious carbon found in defects of the carbon nanosheets' emission edges and the underlying graphite structure. Auger electron spectroscopy and scanning electron microscopy were used to verify the composition and conformity of the coating, respectively. Field emission testing in an ultrahigh vacuum ($p \sim 5 \times 10^{-10}$ Torr) diode assembly with 250 μ m spacing showed lowering of the effective work function after the coating procedure and consequently, increased emission current. At an applied field of 9 V/ μ m, the emission current was found to be 100 μ A compared ~0.1 μ A for the carbon nanosheets. A comparison of linear ($R^2 = .999$) Fowler-Nordheim plots of coated and uncoated samples yielded values for the work function of uncoated CNS and the fractional emitting area of ~2% for carbon nanosheets. The experimental data of Mo₂C-coated CNS was significantly more repeatable and stable than the uncoated CNS.

9:40am TF-TuM6 Production of Large Area Graphene Sheets by Si Desorption from SiC, G.G. Jernigan, J.C. Culbertson, B.L. VanMil, K.K. Lew, R.L. Myers-Ward, D.K. Gaskill, P.M. Campbell, E.S. Snow, U.S. Naval Research Laboratory

With DeHeer's¹ initial report of graphene formation by the thermal desorption of Si from SiC, efforts have been underway to use this method to make large area sheets of graphene for device fabrication purposes. Mobility measurements of graphene on SiC, however, have not approached the values obtained with graphene exfoliated from graphite, indicating that material issues and other factors may be affecting the quality of graphene from SiC. We will report on our efforts to produce large area graphene sheets using 2- and 3-, Si-face, 4H and 6H SiC wafers. Using x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), atomic force microscopy (AFM), Raman spectroscopy, and electrical characterization, we have studied graphene sheets and graphite films formed on SiC by Si desorption in ultra-high vacuum (UHV). The wafers were initially subjected to hydrogen etches at 1400 °C and 1580 °C to remove polishing damage and to produce smooth surfaces prior to entrance into UHV. XPS measurements show the hydrogen-etched surfaces are initially covered by an oxide, which can be desorbed at 1000 °C in UHV resulting in a surface containing excess Si. At ~1300 °C, the surface becomes stoichiometric in Si and C and a $\sqrt{3} \times \sqrt{3}$ R30 LEED pattern is observed. At ~1350 °C, we observe a $6\sqrt{3} \times 6\sqrt{3}$ R30 LEED pattern develop when graphene has formed, and a 1x1 LEED pattern for graphite films formed at temperatures greater than 1400 °C. AFM images show that the process of Si desorption from the surface results in the formation of hexagonal pits and that the liberation of carbon onto the surface produces the graphene layer. As more Si is desorbed from the surface, the carbon forms into 3-dimensional islands with a hexagonal shape. Interestingly, the sheet conductance remains constant while the islands coalesce into a thick graphite layer. Raman spectroscopy of the graphene sheets is complicated by strong transitions from the underlying SiC substrate. Nonetheless, D, G, and D' lines can be distinguished, and their intensities are observed to increase with increasing sheet thickness. The frequency of the D' line can also be used to distinguish the formation of graphene and graphitic material. We will discuss how process parameters affect the graphene quality as judged by the multiple techniques.

¹J. Phys. Chem. B 108, 19912-19916 (2004).

10:40am TF-TuM9 Epitaxial Graphene - A New Paradigm for Nanoelectronics, W.A. de Heer, Georgia Institute of Technology INVITED
Multilayer graphene grown on single-crystal silicon carbide by vacuum decomposition is a promising material for nanoelectronics. The material can be patterned using standard nanolithography methods. The transport properties, which are closely related to those of carbon nanotubes, are dominated by a single graphene layer at the silicon carbide interface. This epitaxial layer reveals the Dirac nature of the charge carriers. Unlike graphite, multilayer graphene is electronically related to single layer graphene with an anomalous Berry's phase as evidenced from transport measurements, from infrared absorption measurements and from Raman scattering measurements. Patterned structures show quantum confinement of electrons and phase coherence lengths beyond one micrometer at 4K, with mobilities exceeding 25000 cm²/Vs. These parameters suggest that all-graphene electronically coherent devices may be possible. Recent developments will be discussed including epitaxial graphene FETs.

11:20am TF-TuM11 Rotational Stacking of Graphene Films Grown on 4H-SiC(000-1), J. Hass, J.E. Millán-Otoya, M. Sprinkle, X. Li, The Georgia Institute of Technology, F. Varchon, L. Magád, LEPES-CNRS, France, P.N. First, E.H. Conrad, The Georgia Institute of Technology
The presence of Dirac electrons and micron scale coherence lengths have been demonstrated in multi-layer graphene grown on SiC, suggesting that an all-carbon paradigm for electronic circuits may be possible.¹ It is now critical to understand the source of these unique transport properties and explain their dependence on: 1) graphene stacking order and 2) graphene/SiC substrate interactions. We will present surface X-ray reflectivity data that suggest a new structural model for multilayer graphene grown on the SiC (000-1) (C-terminated) face.² Reflectivity modeling indicates a high density of stacking faults with distinct rotational alignments. These complex rotational phases will be discussed in the context of recent ab initio calculations which show that this type of stacking effectively decouples adjacent graphene layers. This provides a potential explanation for transport being confined to a single graphene layer.

¹ C. Berger, et al., Science 312, 1191 (2006).

² J. Hass, et al., Phys. Rev. B, in press (2007).

11:40am TF-TuM12 Probing the Interface between Graphene and SiC at the Atomic-scale*, N.P. Guisinger, National Institute of Standards and Technology, G.M. Rutter, Georgia Institute of Technology, J.N. Crain, E.A.A. Jarvis, M.D. Stiles, National Institute of Standards and Technology, P.N. First, Georgia Institute of Technology, J.A. Strosio, National Institute of Standards and Technology

Graphene films on SiC exhibit coherent transport properties that suggest the potential for novel carbon-based nanoelectronics applications. Through controlled processing of SiC graphitization, large domains of single layer graphene can be realized opening the possibility for large area fabrication of carbon structures. Recent studies suggest that the role of the interface between single layer graphene and silicon-terminated SiC can strongly influence the electronic properties of the graphene overlayer. In the present study we have investigated this interface at the atomic scale, utilizing scanning tunneling microscopy and spectroscopic measurements at 4 K. These techniques allow us to probe both the graphene adlayer and the underlying electronic states associated with the SiC surface reconstruction. A novel imaging of the underlying interface is demonstrated by exploiting the energy dependence of the density of states of the SiC substrate versus the graphene overlayer. The first layer of graphene becomes semi-transparent at energies of 1 eV above or below the Fermi-energy, yielding images of the SiC interface. Our analysis of calculations based on density functional theory shows how this transparency arises from the electronic structure of a graphene layer on the SiC substrate. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

12:00pm TF-TuM13 Quasiparticle Interference in Epitaxial Graphene*, G.M. Rutter, Georgia Institute of Technology, J.N. Crain, N.P. Guisinger, National Institute of Standards and Technology, P.N. First, Georgia Institute of Technology, J.A. Strosio, National Institute of Standards and Technology

Understanding the role that defects play in the transport properties of graphene is essential for realizing potential carbon-based electronics. In this study, scanning tunneling spectroscopy was used to measure scattering from defects in epitaxial graphene grown on SiC(0001). Energy-resolved maps of the differential conductance reveal standing-wave modulations of the local density of states on two different length scales, corresponding to two classes of allowed scattering vectors. While backscattering is normally suppressed due to the chiral symmetry of Dirac quasiparticles in graphene, the presence

of atomic defects is shown to mix quasiparticle wavefunctions of different symmetries. From Fourier transforms of the spectroscopic conductance maps we determine the energy-momentum dispersion relation for both occupied and unoccupied states near the Fermi level of single-layer and bilayer epitaxial graphene. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

Authors Index

Bold page numbers indicate the presenter

— B —

Bagge-Hansen, M.: TF-TuM5, **2**

— C —

Campbell, P.M.: TF-TuM6, **2**
Conrad, E.H.: TF-TuM11, **2**
Crain, J.N.: TF-TuM12, **2**; TF-TuM13, **2**
Culbertson, J.C.: TF-TuM6, **2**

— D —

de Heer, W.A.: TF-TuM9, **2**

— F —

First, P.N.: TF-TuM11, **2**; TF-TuM12, **2**; TF-TuM13, **2**

— G —

Gaskill, D.K.: TF-TuM6, **2**
Guisinger, N.P.: TF-TuM12, **2**; TF-TuM13, **2**

— H —

Hass, J.: TF-TuM11, **2**
Hiramatsu, M.: TF-TuM1, **1**; TF-TuM2, **1**
Holloway, B.C.: TF-TuM4, **1**
Hori, M.: TF-TuM1, **1**; TF-TuM2, **1**
Hou, K.: TF-TuM3, **1**; TF-TuM4, **1**
Hou, M.: TF-TuM5, **2**

— J —

Jarvis, E.A.A.: TF-TuM12, **2**
Jernigan, G.G.: TF-TuM6, **2**

— K —

Kano, H.: TF-TuM2, **1**
Kondo, S.: TF-TuM1, **1**
Kordes, M.E.: TF-TuM4, **1**

— L —

Lew, K.K.: TF-TuM6, **2**
Li, X.: TF-TuM11, **2**

— M —

Magáud, L.: TF-TuM11, **2**
Manos, D.: TF-TuM3, **1**; TF-TuM4, **1**; TF-TuM5, **2**
Millán-Otaya, J.E.: TF-TuM11, **2**
Miraldo, P.: TF-TuM3, **1**; TF-TuM4, **1**; TF-TuM5, **2**
Myers-Ward, R.L.: TF-TuM6, **2**

— O —

Outlaw, R.A.: TF-TuM3, **1**; TF-TuM4, **1**; TF-TuM5, **2**

— R —

Rutter, G.M.: TF-TuM12, **2**; TF-TuM13, **2**

— S —

Snow, E.S.: TF-TuM6, **2**
Sprinkle, M.: TF-TuM11, **2**
Stiles, M.D.: TF-TuM12, **2**
Strosio, J.A.: TF-TuM12, **2**; TF-TuM13, **2**

— T —

Takeuchi, W.: TF-TuM2, **1**
Tokuda, Y.: TF-TuM2, **1**

— U —

Ura, M.: TF-TuM2, **1**

— V —

VanMil, B.L.: TF-TuM6, **2**
Varchon, F.: TF-TuM11, **2**

— Y —

Yamakawa, K.: TF-TuM1, **1**

— Z —

Zhu, M.Y.: TF-TuM3, **1**; TF-TuM4, **1**; TF-TuM5, **2**