# Wednesday Afternoon, October 31, 2012

**Late Breaking Session**
**Room: 14 - Session LB+EM+GR+MN+TR-WeA**

**Select Topics in Surface and Interface Science**
**Moderator:** C.R. Eddy, Jr., U.S. Naval Research Laboratory, J.M. Fitz-Gerald, University of Virginia

**2:00pm  LB+EM+GR+MN+TR-WeA1  Degradation Kinetics of Hard Gold Tribofilms**, *N. Argibay, M.T. Dugger, M.T. Brumbach, S.V. Prasad*, Sandia National Laboratories

Hard gold coatings are low alloy (> 98% Au) films exhibiting relatively low friction, electrical contact resistance (ECR) and chemical reactivity, making them uniquely suited for use in dynamic electrical connections. Hardness is primarily a result of grain refinement achieved through alloying. At relatively low temperature (approx < 0.5Tm) the diffusion of codeposited and underlayer species toward the free surface, dominated by grain boundary and pipe diffusion, has been identified as a principal degradation pathway. The consequent formation of metal oxides deteriorates ECR and often contributes to increased wear and friction. A clear antagonistic relationship exists between the hardening mechanism that improves tribological performance and the diffusion phenomena that reduce useful lifespan. This talk focuses on the role of diffusion and film morphology on the aging and degradation of the tribological and electrical characteristics of hard gold films.

**2:20pm  LB+EM+GR+MN+TR-WeA2  Effect of Nitrogen Concentration on the Surface Properties of Plasma Nitrided Tool Steels**, *P. Abraha, J. Miyamoto*, Meijo University, Japan

The nitriding of tool steel was performed in electron beam excited plasma using neutral nitrogen species and nitrogen ions. The plasma apparatus is composed of three regions: the discharge region, the acceleration region and the processing region. This set up has the advantage of controlling the energy and number of electrons involved in producing the plasma independently.

In this study, the control of the nitrogen concentration on the formation of the hard but brittle compound layer and the effect on the tribology of the tool steel surface were investigated. Electron probe micro-analyzer (EPMA) results revealed that nitrogen concentration of samples nitrided by neutral nitrogen species had deep diffusion layer before reaching the threshold value of 6% nitrogen concentration that is necessary for the formation of the compound layer. Whereas in the samples nitrided by nitrogen ions, compound layer was confirmed right from the onset of the nitriding process.

The results of our experiments show that in nitriding the tool steel for 6h, below the threshold value, a mirror finish surface (Ra=14nm) with a deep diffusion layer of (up to 80 micrometers) and a surface hardness of more than two times (1300 Hv) that of the untreated sample (600 Hv) were produced. Our results demonstrate that neutral species based nitriding is effective for high performance and high precision mechanical components that require high hardness and wear resistance without altering the as finished dimensional accuracy, surface roughness and appearance.

**2:40pm  LB+EM+GR+MN+TR-WeA3  High Strength Carbon Fiber Composite Wafers for Microfabrication**, *L. Pei, K. Zufelt, R. VanFleet, R.C. Davis, J. Lund, K. Jones, B.D. Jensen*, Brigham Young University, *J. Abbott, M. Harker, M. Zappe, S. Liddiard*, Moxtek

Carbon fiber composites are very high strength materials that could be enabling materials for micro and mesoscale applications. These materials have comparable strength to silicon but are much less brittle and can achieve four times higher strain. Several challenges must be overcome before carbon fiber composite devices can be fabricated on this scale. One challenge is the fabrication of ultra-thin wafers with low void density and low surface roughness. Another challenge is the ability to reliably machine the material into desired patterns. Here we present a method for curing carbon fiber wafers (~100 μm thick) with low surface roughness, low void density, a modulus of 50 GPa, and a yield strength of ~3.6 GPa. These wafers are suitable for laser machining into high fidelity micro and mesoscale structures. We will present laser micromachined devices made from these wafers including a series of high strength support structures for ultrathin membranes and a high-dynamic-range accelerometer.

**4:00pm  LB+EM+GR+MN+TR-WeA7  Selective Graphitization using Multi-Ion Beam Lithography**, *J. Fridmann*, Raith USA Inc., *S. Tongay*, University of California, Berkeley, *M. Lemaitre, A.F. Hebard, B. Gila*, University of Florida, *A. Nadzeyka*, Raith GmbH, Germany, *F. Ren, X. Wang*, University of Florida, *D.K. Venkatachalam, R.G. Elliman*, Australian National University, Australia, *B.R. Appleton*, University of Florida

Promising techniques for growing graphene on SiC single crystals for electronic device fabrication include heating in UHV above the graphitization temperature $(T_G)$[1]; or processing them in vacuum using pulsed excimer laser[2].

We report recent findings on the graphitization of SiC using a patterned Ga implantation, in which the implanted regions exhibit reduced $T_G$ and enhanced graphitization above $T_G$. Here we report an approach that combines ion implantation, thermal or pulsed laser annealing (PLA), and multi-ion beam lithography (MIBL) to both pattern and synthesize graphene nanostructures on SiC single crystals at low temperatures. This approach utilizes a MIBL system developed at the University of Florida in collaboration with Raith for implantation/nanofabrication, in combination with thermal annealing in vacuum or PLA with a 25 ns pulsed ArF laser in air. To investigate the mechanisms and the effects of the implanted species, ion damage, and annealing, samples were also subjected to broad-area ion-implantations using facilities at the Australian National University.

It has recently been shown that implantation of Si, Ge, Au, or Cu followed by thermal annealing in vacuum below the $T_G$ of SiC can selectively grow graphene only where the ions are implanted, and that graphene nanoribbons a few nanometers to microns wide can be formed using MIBL[3]. Additionally, we will show that graphene can be formed on implanted and/or unimplanted SiC by ArF PLA in air, at fluences from 0.4-1.2 J/cm². AES, SEM, X-sectional TEM, micro-Raman analyses and heat flow simulations are presented to verify graphene growth and explain the effects and mechanisms involved.

1. C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H.Conrad, P. N. First, and W. A. de Heer, J. Phys. Chem. 108, 19912 (2004)

2. Sangwon Lee, Michael F. Toney, Wonhee Ko, Jason C. Randel, Hee Joon Jung, Ko Munakata, Jesse Lu, Theodore H. Geballe, Malcolm R. Beasley, Robert Sinclair, Hari C. Manoharan, and Alberto Salleo; ACS Nano Vol.4, No. 12, 7524-7530 (2010).

3. S. Tongay, M. Lemaitre, J. Fridmann, A. F. Hebard, B. P. Gila, and B. R. Appleton, Appl. Phys. Lett. 100, 073501 (2012).

**4:20pm  LB+EM+GR+MN+TR-WeA8  Unrippling and Imaging of Extra-Large Free-Standing Graphene with Atomic Precision**, *W.W. Pai, R. Breitweiser, Y.C. Hu, Y.C. Chao*, National Taiwan University, Taiwan, Republic of China, *Y.R. Tzeng*, Institute of Nuclear Energy Research of Taiwan, Republic of China, *L.J. Li*, Academia Sinica, Taiwan, Republic of China, *K.C. Lin*, Catholic Fu Jen University, Taiwan, Republic of China

Nanoscale ripple is believed to be a common feature most manifested in free-standing graphene and is expected to play an important role in altering the coupling of graphene's electronic and geometric structures. Direct characterization of free-standing graphene ripple is challenging from atom-resolved transmission electron microscopy (TEM) due to its limited depth resolution. Recent scanning tunneling microscopy (STM) of free-standing graphene uses small suspended area (1 or 5 microns) samples and can introduce uncontrolled tension that alters the intrinsic graphene structure. Here we report an STM study of suspended extra-large (~4000 micron²) Cu CVD graphene that was prepared with a resist-free transfer and characterize its electromechanical response in details. In our study, a series of controlled "Z-V" spectroscopy were carefully conducted. In Z-V spectroscopy, the tip displacement vs. sample bias in close-loop condition is recorded. This gives hints on the nature of interaction forces and the mechanical response of graphene. In contrast to a solid surface, the graphene membrane is very compliant and Z-V curves are characterized by a fast-rise regime and a plateau regime that follows. Graphene deformation up to 100 nm with simply a small ~1 V bias ramp was observed. We discovered that our graphene is in best analogy with a curved rubber band that maintains quasi-static in shape until it is either pulled or pushed to tensile stress regimes. The graphene can be manipulated by the STM tip through electrostatic and van der Waals forces, with the latter being significant when it is repulsive. In its transit to tensile-stressed state, the graphene exhibits a series of sudden speed jump; we interpret these events as unrippling of graphene ripples and render support with molecular dynamics (MD) simulation. Atom-resolved graphene images provide direct evidence of nanoscale structure ripples in its intrinsic state and the smoothing out of such ripples in the tensile regimes. Surprisingly, on rippled monolayer graphene,

coexistence of triangular and hexagonal graphene lattices without tip condition change were observed. Our study provides a foundation to understand and control the electromechanical response of graphene (or other flexural atomic crystals) in its pristine two-dimensional form when subjected to a local proximal probe, therefore paves way to further investigate its structure-property correlation with atomic precision.

**4:40pm LB+EM+GR+MN+TR-WeA9 Ultrafast Charge Transfer at Monolayer Graphene Surfaces with Varied Substrate Coupling**, *S. Lizzit*, ELETTRA Sincrotrone Trieste, Italy, *R. Larciprete*, CNR , Institute of Complex Systems, Italy, *P. Lacovig*, ELETTRA Sincrotrone Trieste, Italy, *K. Kostov*, Bulgarian Academy of Sciences, Bulgaria, *D. Menzel*, Technische Universität München and Fritz Haber Institute, Germany

The importance and scientific appeal of graphene monolayers (Gr) are out of question, and investigations of its electronic properties abound. Most of these center on the most spectacular region, that around the Dirac cone, which is also the most relevant region for possible devices. But regions outside of this region are also important, since their correct representation requires basic understanding, and since they may relate to applications in photonics, photochemistry, and contact formation. Also, static investigations are more frequent than those of dynamics.

We present here the first investigation of electron dynamics at energies above the Fermi (and Dirac) energy but below the vacuum level [1]. To this purpose we used the core hole clock (CHC) method with adsorbed argon and measured the transfer rate of a localized electron (the 4s electron on core-excited Ar) to the surface of Gr monolayers with variable substrate coupling: strong but graded coupling for Gr on Ru(0001) ("valleys" and "hills"), and decoupled Gr ML on $SiO_2$. We obtained the latter system by using the recently developed transfer-free approach [2] based on the synthesis of $SiO_2$ layers directly below Gr epitaxially grown on Ru(0001), through a stepwise reaction between intercalated silicon and oxygen. This method provides the optimal system to study the electronic properties of Gr using spectroscopic approaches, such as the CHC method.

We find strong variations of CT time between ~3 fs (Gr ML strongly coupled to substrate on Ru(0001) "valleys") and ~ 16 fs (decoupled Gr on $SiO_2$). A ratio of 1.7 is found between the "hills" and "valleys" of the corrugated Gr/Ru. The very fast CT on Gr/Ru valleys is interpreted as due to hybridized Ru orbitals "reaching through" the Gr layer which change with the relative Gr/Ru alignment and distance. On the decoupled Gr layers the intrinsic coupling to the Gr empty π* states determines the CT time. The intermediate CT time for the Gr hills on Ru shows that these regions are far from the "decoupled" condition. The results contribute new information on the still controversial states of Gr/Ru, and shed light on the empty density of states above Gr surfaces and the coupling to them in an energy range possibly important for photonic applications of Gr, such as solar energy conversion.

[1] S. Lizzit, R. Larciprete, P. Lacovig, K.L.Kostov, D. Menzel, *in preparation*

[2] S. Lizzit *et al*. Nanoletters (2012) DOI: 10.1021/nl301614j

**5:00pm LB+EM+GR+MN+TR-WeA10 Fano Interference Effects in Hydrogen Intercalated Graphene**, *A. Boosalis, T. Hofmann*, University of Nebraska-Lincoln, *R. Elmquist, M. Real*, National Institute of Standards and Technology (NIST), *M. Schubert*, University of Nebraska-Lincoln

Graphene has been the focus of much recent research due to its unique electronic and optical properties, with potential for high performance electronics, tunable ultra-fast lasers, and transparent electrodes. Further development of graphene for commercial use requires effective large-area epitaxial production that maintains the desirable properties of exfoliated graphene. One such method of epitaxial graphene growth is thermal sublimation of Si from SiC. Sublimation of Si from the Si-face (0001) is the most controllable but produces a $(6\sqrt{3} \times 6\sqrt{3})R30°$ surface reconstructed layer prior to graphene formation. This layer can be altered by subsequent hydrogen intercalation, resulting in quasi-free-standing (QFS) epitaxial graphene.

In order to determine the effect of hydrogen intercalation on the optical properties of graphene we performed spectroscopic ellipsometry experiments in a spectral range of 3 to 9 eV before and after hydrogen intercalation of buffer layer only carbon growth on 6H SiC (0001). Spectroscopic ellipsometry is a widely used technique for determining the optical properties of thin films, and can provide sensitivity to film quality, morphology, and strain. In the case of graphene sensitivity is obtained through the critical-point (CP) located at 5.1 eV and modified by a Fano interference. Analysis of absorption near the CP is achieved through a parameterized model dielectric function (MDF) which is varied until a best-match between model and experimental data is obtained.

Best-match model results show drastic changes in the imaginary part of the MDF between previous measurements of buffer layer only growth on SiC,

and buffer layer growth after hydrogen intercalation. Buffer layer only growth exhibits a far greater absorption throughout the spectrum, with an exciton produced maximum energy point that is shifted toward the infrared from the CP energy. After hydrogen intercalation, the QFS graphene layer exhibits a lowered absorption with a maximum closer to that of the CP energy; displaying an MDF closer to that of theoretical predictions for graphene.

In conclusion, hydrogen intercalation of buffer layer carbon growth on SiC (0001) has been shown to produce QFS graphene with optical properties closest to that of theoretical predictions for graphene, further proving its effectiveness as a tool for large-area epitaxial graphene production. In addition, buffer layer carbon growth shows optical properties sufficiently different from that of graphene to allow spectroscopic ellipsometry to become a viable in-situ monitor for commercial production of hydrogen intercalated graphene on SiC.

**5:20pm LB+EM+GR+MN+TR-WeA11 *In Situ* Dry-Cleaning of Ge(100) Surface using $H_2O_2$**, *K. Kiantaj, T. Kaufman Osborn, T.J. Kent, A.C. Kummel*, University of California San Diego

Since Ge has higher hole and electron mobility compared to silicon, it is a good candidate for development of a new channel material in CMOS semiconductor devices. One of the obstacles in using Ge as a channel material is the high interface trap density between Ge and Ge native oxide. Air exposed Ge surfaces have a high density of defects and contaminants, but, in order to make optimal semiconductor devices, nearly perfect bonding between each unit cell and the gate oxide layer is required. Although there are many methods available for cleaning the Ge surface, the effectiveness of each of these methods highly depends on the cleanliness of the processing chambers. After cleaning, the Ge surface is typically functionalized with OH groups via water (H2O) or hydrogen peroxide (HOOH) during atomic layer deposition of the gate oxide. This OH functionalized surface ideally provides a high density of reactive sites for precursor nucleation. We have studied the effect of a very small amount of hydrocarbon in the processing chambers, and its effect on both the clean Ge surface and the OH functionalized surface since this may increase the density of interface traps and limit Equivalent Oxide Thickness (EOT) scaling. In-situ cleaned Ge surfaces as well as HOOH dosed surfaces have been studied after exposure to hydrocarbon contaminants with x- ray electron spectroscopy (XPS) and scanning tunneling microscopy (STM). An Argon ion source sputtering system was employed for in-situ cleaning of the Ge surface. After exposure to trace hydrocarbon contaminants, two different nanoscale features were observed by STM on the Ge and HOOH/Ge surfaces. One type of contamination denoted as carbon "nanoclusters" which are typically 0.3-0.5nm in height and 2-4nm in diameter. A distinctly different feature is observed on the Ge-OH terminated surface denoted as carbon "nanoflakes". In contrast to nanoflakes, nanoclusters were only observed on the Ge surfaces dosed with low concentration hydrogen peroxide. In the next step, a high concentration hydrogen peroxide source in combination with an ozone source was employed to study the removal of the contaminants from the Ge surface. Several dosing conditions and sample temperatures were studied and optimized. As the result, an atomically clean Ge surface were achieved by employing an all-dry in-situ process. The all-dry cleaning procedure does not involve any ion-milling or wet- cleaning procedures as both of these methods involve surface etching and result in surface roughness which is not desirable for semiconductor devices.

**5:40pm LB+EM+GR+MN+TR-WeA12 Hf-based High-k Dielectrics for Ge MOS Stacks**, *S. Fadida, M. Eizenberg*, Technion Israel Institue of Technology, Israel, *L. Nyns, D. Lin, S. Van Elshocht, M. Caymax*, IMEC, Belgium

Ge has drawn much attention recently, being a leading candidate to serve as the channel material of future metal oxide field effect transistors (MOSFETs) due to its high carrier mobility with respect to Si. The interest in Ge is mostly because of its high hole mobility. Most of Ge related researches were focused so far on the challenge of Ge surface passivation. In this research we have moved on to the next challenge - finding a suitable high-k dielectric for a Ge-MOS stack. The high-k dielectric has to be chemically and thermally stable on top of the chosen passivation layer, have sufficiently high energy barriers with respect to Ge energy band edges, and have a large dielectric constant in order to obtain the required low effective oxide thickness (EOT). We have studied the chemical, structural and electrical properties of various Hf-based high-k dielectrics: $HfO_2$, $Hf_xZr_{1-x}O_2$, $Hf_xAl_{1-x}O_2$ and $Hf_xGd_{1-x}O_2$. All high-k dielectrics (4 nm thick) were deposited by atomic layer deposition (ALD) on top of a constant passivation stack composed of a thin $GeO_2$ layer (0.7 nm thick) followed by a thin (2 nm) ALD $Al_2O_3$ layer. The $Al_2O_3$ layer, which has high band offsets to Ge and $GeO_2$, was added since $HfO_2$, as many of the leading candidates for high-k dielectrics, are unstable on top of Ge or $GeO_2$. A thorough and systematic electrical and chemical characterization of this complex gate

stack was carried out. The interesting results show that this challenge of seeking for a superior high-k is not detached from the passivation challenge. Surprisingly, we have found that although the passivation stack was kept constant for all systems studied, the apparent $D_{it}$ (density of interface states) changes when the top high-k material is modified. Another interesting phenomenon is revealed when different methods of $D_{it}$ characterization are compared - each method points out a different high-k as the one with the lowest $D_{it}$. These observations imply that the C-V characteristics do not reflect only the role of Ge interface traps, but also of traps throughout the whole stack, at least to a distance of 2.7 nm (the total thickness of the passivation stack) from the Ge surface . These results emphasize even more the great challenges in integrating Ge as a new channel material. We have also analyzed the band alignment for all high-k dielectrics using XPS with respect to the underlying layers. All high-k dielectrics have similar band gaps at the range of 5.2-5.9 eV. The conductance and valence band offsets with respect to Ge are all larger than 1 eV, which make them all suitable for Ge-MOSFETs in terms of band alignment.

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