

Monday Morning, October 29, 2012

Electronic Materials and Processing

Room: 9 - Session EM+TF+OX+GR-MoM

High-k Dielectrics for MOSFETs I

Moderator: A.C. Kummel, University of California San

Diego

8:20am **EM+TF+OX+GR-MoM1 Surface Preparation and Dielectric Growth for Graphene-based Devices, R.M. Wallace**, University of Texas at Dallas **INVITED**

In addition to interesting physics, numerous device applications are under investigation for graphene. Many of these devices require an interaction of graphene with dielectrics, and require a thorough understanding of the graphene/dielectric interface. As practical device applications require large area graphene, CVD methods have been employed to synthesize graphene and typically involve a wet chemical transfer process, which can leave residues that impact device behavior. This talk will review recent progress in the investigation of CVD graphene growth, transfer and dielectric growth processes with an emphasis on in-situ studies of the surfaces produced by these processes and the resultant electrical behavior. This work is supported by the NRI SWAN Center.

9:00am **EM+TF+OX+GR-MoM3 Antimonide-Based P-Channel MOSFET: Progress and Challenges, S. Oktyabrsky, A. Greene, S. Madiseti, P. Nagaiah, M. Yakimov, R. Moore, S. Novak, H. Bakhru, V. Tokranov**, University at Albany-SUNY **INVITED**

Development of p-type MOSFETs using new materials is an important goal to provide a further scaling of CMOS circuits. Although Ge is still considered as a main candidate for novel p-channels due to its superior bulk transport properties, recent progress in strained III-Sb channels and MOS technologies makes it a good competitor in particular for deeply scaled devices. The materials parameters affecting MOSFET's figures-of-merit are reviewed with the emphasis on strain in quantum wells (QWs), effective mass, density of states and mobility.

Progress in development of materials for III-Sb channels is reported. Optimization of MBE growth of metamorphic buffers and GaSb on lattice-mismatched GaAs substrates has resulted in "step-flow" growth mode of GaSb with monolayer-high steps on the surface, $\sim 10^7 \text{ cm}^{-2}$ dislocation density and bulk hole mobility $860 \text{ cm}^2/\text{Vs}$. Optimization of strain in QWs provided the highest Hall mobility of $1020 \text{ cm}^2/\text{Vs}$ at sheet hole density of $1.3 \times 10^{12} \text{ cm}^{-2}$ obtained for $\text{In}_{0.36}\text{Ga}_{0.64}\text{Sb}$ with compressive strain of 1.8%. Hole mobility in QW channel was benchmarked against the thickness of top semiconductor AlGaSb barrier. The effect of interface-related scattering hole mobility in the channel was found to be significantly less than e.g. for n-InGaAs, that might be due to stronger localization of holes in QWs.

Two approaches to fabricate high-quality III-Sb/high-k interface were studied: all *in-situ* Al_2O_3 or HfO_2 gate oxides, and *ex-situ* atomic layer deposited (ALD) Al_2O_3 with InAs top semiconductor capping layer. Interface with *in-situ* MBE gate oxides was found to improve with *in-situ* deposited a-Si interface passivation layer (IPL). Interfaces with better thermal stability, reduced interface trap density and hysteresis were observed on both n- and p- type GaSb MOSCaps with the IPL. P-type MOSFETs with HfO_2 showed a maximum drain current of 23 mA/mm for a $3 \mu\text{m}$ gate length. Use of a-Si IPL has also resulted in a significant (over an order of magnitude) reduction of the hole density in QWs and corresponding negative flat band voltage shift and drop of mobility which becomes remote Coulomb scattering-limited. An interface with ALD Al_2O_3 was improved by a thin 2nm interface layer of InAs which was treated with HCl or $(\text{NH}_4)_2\text{S}$ immediately prior to ALD process. Optimized annealing further improved the C-V characteristics, reduced interface trap density down to $10^{12} \text{ cm}^{-2}\text{eV}^{-1}$, leakage current and MOSFET subthreshold slope down to 200 mV/dec. Increasing annealing temperature to and above 450°C drastically degraded C-V characteristics due to low thermal budget of antimonides.

9:40am **EM+TF+OX+GR-MoM5 Interface Study of the Atomic Layer Deposited Al_2O_3 on $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$, X. Qin, B. Brennan, H. Dong, R.M. Wallace**, The University of Texas at Dallas

Due to the high two-dimensional electron gas (2-DEG) density, AlGaIn/GaN high electron mobility transistors (HEMTs) are recognized as key devices for high power and low noise applications. However, the associated large gate leakage current degrades the performance of AlGaIn HEMTs. In order to solve this problem, MOS-HEMTs have been

developed, in which the incorporation of a high-k gate dielectric layer can overcome the drawbacks.

In this work, the native and treated $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ surface chemical states and structure of were studied by x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS) and low energy electron diffraction. Different chemical treatment processes including $(\text{NH}_4)\text{OH}$, $(\text{NH}_4)_2\text{S}$ and HF were studied, followed by atomic layer deposition (ALD) Al_2O_3 layers on $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$. The oxidation states of the $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ interface and Al_2O_3 deposition process were studied by in-situ XPS analysis. In addition, ex-situ atomic force microscopy (AFM) was used to observe the surface topography before and after the Al_2O_3 deposition. According to the XPS results, it is found that chemical treatments could remove the native Al_2O_3 but were not effective to eliminate the Ga oxide, and the growth rate of Al_2O_3 is low on the native and treated $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ samples. The AFM images show that there are many pin holes in the surface of $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$. Studies of HfO_2 deposition will also be presented.

This work is supported by the AOARD under AFOSR Grant No. FA2386-11-1-4077

10:00am **EM+TF+OX+GR-MoM6 Ideal Monolayer Nitridation of Semiconductors using a Nitrogen Radical Generator, A.T. Lucero, J. Kim**, University of Texas at Dallas

Thin silicon nitride films have long been desirable for various applications. Suggested uses range from surface and interface passivation to ultra-thin dielectric layers. Traditional deposition techniques are low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD). High quality LPCVD films require high processing temperatures, and PECVD exposes the substrate to damaging plasma and electric potentials. While both techniques are suitable for many applications, there are some instances where both processes are too harsh.

In this paper, we report the growth of silicon nitride using a remote nitrogen radical generator system. Growth temperatures range from room temperature to 400°C , and growth time is varied from two minutes to one hour. Film composition is analyzed using x-ray photoelectron spectroscopy (XPS) and morphology is checked using atomic force microscopy. Results indicate that surface nitrogen saturation can be reached at both low temperatures and short exposure times, and that the reaction is self limiting, terminating at one monolayer. Film thickness is approximately one Angstrom, as determined by XPS. Results for silicon and III-V passivation will be discussed.

We would like to thank Toshiba Mitsubishi-Electric Industrial Systems Corporation for providing the nitridation system used in this study.

11:00am **EM+TF+OX+GR-MoM9 Characterization of ALD Laminated Gate Dielectrics on GaN MOSCAPs, D. Wei, T. Hossain**, Kansas State University, N. Nepal, N.Y. Garces, Naval Research Laboratory, H.M. Meyer III, Oak Ridge National Laboratory, C.R. Eddy, Jr., Naval Research Laboratory, J.H. Edgar, Kansas State University

To improve the efficiency of GaN based power electronic devices there is tremendous and growing interest in employing metal-insulator-semiconductor (MIS) transistors. As with all compound semiconductors, there is a significant challenge in forming an electronic quality dielectric-semiconductor interface. Thus, there is a need to better understand and improve the dielectric-semiconductor interface quality in order to improve the overall performance of the device.

This research focuses on the benefits and properties of Al_2O_3 , TiO_2 and $\text{TiO}_2\text{-Al}_2\text{O}_3$ nanolaminate thin films deposited on GaN and GaOx/GaN by plasma-assisted atomic layer deposition (PA-ALD) for gate dielectric development. Correlations were sought between the films' structure, composition, and electrical properties. The gate dielectrics were approximately 15nm thick as determined by spectroscopic ellipsometry. The interface carbon concentration, as measured by x-ray photoelectron spectroscopy (XPS) depth profile, was lower for $\text{Al}_2\text{O}_3/\text{GaN}$ than TiO_2/GaN , and the nanolaminate structure did not decrease the carbon concentration. However, carbon was not detected at the interface for the GaN samples pretreated by annealing in O_2 for 30 minutes at 800°C . Also, according to XPS, the Al_2O_3 films had a better coverage than TiO_2 . The RMS roughness of TiO_2 and Al_2O_3 top layers were $\sim 0.53\text{nm}$ and $\sim 0.20\text{nm}$ respectively, as determined by atomic force microscopy. The dielectric constant of Al_2O_3 on GaOx/GaN was greatly increased compared to that of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ and pure Al_2O_3 on GaN substrate. In addition, the Al_2O_3 deposited on the GaOx/GaN showing no hysteresis in capacitance-voltage (C-V) characteristics, which is corresponding with a negligible carbon concentration from the XPS depth profile. These results indicate the

promising potential of plasma ALD deposited Al₂O₃ serving as the gate oxide on GaOx/GaN based MOS devices.

11:20am **EM+TF+OX+GR-MoM10 Passivation of Interfacial Defects in GaAs and Other III-Vs**, *J. Robertson*, Cambridge University, UK
INVITED

It has always been harder to make FETs from GaAs than Si, because of 'Fermi level pinning' and the difficulty of passivating its surfaces. These issues were discussed by Spicer et al [1] in the 'unified defect model' and Hasegawa [2] is his 'Disorder Induced Gap states' model. Since 1997 it was possible to make inverted GaAs MOSFETs using the epitaxial Gadolinium gallium oxide [3]. The main impetus now is to use atomic layer deposition (ALD) to make scalable FETs [4], as recently achieved by Intel [5]. The obvious question is why (In)GaAs is much harder to passivate than Si. The early answer was its poor native oxide. But since the advent of good ALD HfO₂ or Al₂O₃ oxides on Si, this answer is deficient, as they should also work on GaAs [6]. The underlying reason for defects is not stress, it must be chemical. I show that it arises from the polar bonding of GaAs [7], and a driving force to keep the surface Fermi level in a gap. The electron counting rule of Pashley [8] that describes surface reconstructions is shown to be a variant of auto-compensation, and it works more generally [9]. It leads to a continuous generation of defects if it is not satisfied. So the answer is to deposit oxide layers that meet this rule, and also to break any surface reconstructions that may lead to As-As dimers [9]. Diffusion barriers are also crucial to a good passivant, on GaAs or on Ge.

1. W E Spicer, et al, J Vac Sci Technol 16 1422 (1979); Phys Rev Lett 44 420 (1980)
2. H Hasegawa, et al, J Vac Sci Technol B 5 1097 (1987)
3. M Hong et al, Science 283 1897 (1997)
4. P D Ye et al, App Phys Lett 83 180 (2003)
5. M Radosavljevic, et al, Tech Digest IEDM (2009) p13.1
6. C Hinkle, et al, Curr Opin Solid State Mat Sci 15 188 (2011)
7. W Harrison, J Vac Sci Technol 16 1492 (1979)
8. M D Pashley, Phys Rev B 40 10481 (1989)
9. J Robertson, L Lin, App Phys Lett 99 222906 (2011); 98 082903 (2011)

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+EM+NS+PS+SS+TF-MoM

Graphene Growth

Moderator: M. Spencer, Cornell University, V.D. Wheeler, U.S. Naval Research Laboratory

8:20am **GR+EM+NS+PS+SS+TF-MoM1 Synthesis Ingredients Enabling Low Noise Epitaxial Graphene Applications**, *D.K. Gaskill, L.O. Nyakiti, V.D. Wheeler*, U.S. Naval Research Lab, *A. Nath*, George Mason Univ., *V.K. Nagareddy*, Newcastle University, UK, *R.L. Myers-Ward, N.Y. Garces, S.C. Hernandez, S.G. Walton*, U.S. Naval Research Lab, *M.V. Rao*, George Mason Univ., *A.B. Horsfall*, Newcastle Univ., UK, *C.R. Eddy, Jr.*, U.S. Naval Research Lab, *J.S. Moon*, HRL Labs LLC

Sensors made from graphene flakes have demonstrated single molecule detection [Schedin *et al.*, Nat Mat 6, 652 (2007)]; this ultra-sensitivity is likely due to the high crystalline quality of the graphene and the associated relative lack of defects that give rise to noise. The low noise nature of high quality graphene should also facilitate other applications, e.g., low-noise amplifiers. Combined with the unique ambipolar property of graphene field effect transistors (FETs), the low noise character of graphene would significantly advance the performance of frequency multipliers, mixers and high-speed radiometers. To exploit these applications, high quality, reproducible wafer-scale epitaxial graphene (EG) with minimal thickness variations and defects are essential requirements. Here, crucial graphene synthesis elements required to achieve the wafer-scale quality goal are described. Understanding the effect of substrate misorientation as well as hydrogen etch and Si sublimation conditions for graphene synthesis on the (0001) SiC surface is essential to achieve improved and reproducible wafer-scale graphene quality. For example, the impact of processing factors such as temperature control, laminar gas flow and substrate rotation on large area EG uniformity are described using examples created in an Aixtron SiC epitaxy reactor. In addition, managing SiC step formation on the nominal (0001) orientation is significant for achieving uniform EG thickness on terraces and to minimize additional growth at the step edges; this is illustrated using data from atomic force microscopy and scanning electron microscopy images in combination with Raman spectroscopy maps and x-ray photoelectron spectroscopy analysis. Managing step formation

combined with optimal growth leads to the suppression of the Raman defect "D" band confirming minimal grain boundaries and defects, which are additional sources of electronic noise. Lastly, contactless Leighton resistivity maps of 75 mm wafers are used to illustrate the overall uniformity of optimally synthesized graphene as well as to show the resistance state-of-the-art, with individual wafers exhibiting about a ±3% relative variation. Examples of the impact of this synthesis approach on chemical sensors devices and FETs will be shown, each exhibiting 1/f noise behavior down to 1 Hz and possessing noise spectral densities similar to reports from exfoliated graphene. Hence, careful control of EG formation across the wafer results in improved quality which subsequently leads to the reduction or elimination of additional noise sources from graphene defects that would then adversely affect device performance.

8:40am **GR+EM+NS+PS+SS+TF-MoM2 Growth of Graphene by Catalytic Decomposition of Ethylene on Cu(100) and Cu(111) With and Without Oxygen Pre-dosing**, *Z.R. Robinson, P. Tyagi, T. Mowll, C.A. Ventrice, Jr.*, University at Albany- SUNY, *K. Clark, A.-P. Li*, Oak Ridge National Laboratory

Graphene growth on Cu substrates has become one of the most promising techniques for the mass production of graphene, and therefore significant effort has been put into developing growth conditions that lead to large area, defect and grain boundary free graphene films. One key consideration is the influence that the underlying copper substrate has on the growth of the graphene. In order to study this, graphene growth on Cu(100) and Cu(111) was carried out in a UHV system. The samples were heated using an oxygen series button heater. The hydrocarbon pressure was measured using a capacitive manometer instead of an ion gauge, which could cause dissociation of the hydrocarbon molecules. Initially, it was found that annealing the crystals to 900 °C resulted in impurity segregation at the surface. Several cycles of sputtering at 600 °C were required to remove all bulk impurities so that the surface remained clean even after annealing to 900 °C. Initial attempts to grow graphene by annealing each crystal to temperatures as high as 900 °C in UHV, followed by backfilling the chamber with up to 5 x 10⁻³ torr of C₂H₄ did not result in graphene formation. It was found that by first backfilling the chamber with C₂H₄ and then raising the temperature from 25 °C to 800 °C, graphene growth could be achieved. A four-domain epitaxial overlayer is observed for the Cu(100) surface. Pre-dosing the Cu(100) with oxygen at 300 °C, which forms a saturation coverage of chemisorbed oxygen, was found to result in a 2-domain graphene overlayer using similar growth conditions. A study of the effect of oxygen pre-dosing on the growth of graphene on Cu(111) has been initiated.

9:00am **GR+EM+NS+PS+SS+TF-MoM3 Impact of Growth Parameters on Uniformity of Epitaxial Graphene**, *L.O. Nyakiti, V.D. Wheeler, R.L. Myers-Ward, J.C. Culbertson*, U.S. Naval Research Laboratory, *A. Nath*, George Mason University, *N.Y. Garces*, U.S. Naval Research Laboratory, *J. Howe*, Oak Ridge National Laboratory, *C.R. Eddy, Jr., D.K. Gaskill*, U.S. Naval Research Laboratory

Epitaxial graphene (EG) offers a facile method for attaining large area graphene for device applications. Since wafer uniformity and thickness control is vital, a systematic study of the parameters affecting the EG growth process was performed and the optimal conditions for obtaining uniform morphology and high electronic quality were determined. EG was synthesized in a low pressure Ar flowing ambient on 8x8mm² 6H-SiC(0001) substrates that were offcut 0.8° from the basal plane, using an Aixtron VP508 reactor. The samples were placed on a rotating ~100 mm diameter susceptor and excellent EG layer uniformity and run-to-run reproducibility were obtained. The investigation focused upon the critical synthesis parameters of temperature (T) (1520-1660°C) and time (t) (15-60 min), an *in-situ* H₂ etch conditions (1520-1600°C for 10-30min). Morphology, layer thickness, chemical analysis, and strain variations across the samples were characterized using electron microscopy, AFM, XPS and μ-Raman spectroscopy. Large-area van der Pauw Hall effect was performed to quantify the graphene mobility (μ), and carrier density. Results show that growth T and t had the most significant impact on EG electronic and morphological properties. For example, synthesis at 1660°C for 30min resulted in 4-8 monolayers (ML) and a step-bunched morphology with high concentration of wrinkles originating from the step-edge and pinned at the nearest terrace edge. Other morphological features were pits primarily located at the step edges having a depth ~20nm and density 6.4x10⁸ cm⁻². In contrast, EG synthesis at 1520°C for 30min results in uniform ML coverage along the terrace width that is devoid of pits and wrinkles. Mobility was found to have a drastic dependence on graphene thickness. Under optimal conditions, 1-2 ML were obtained and μ as high as 1240 cm²V⁻¹s⁻¹ was achieved; in contrast, for EG with >2 ML μ ~ 550 cm²V⁻¹s⁻¹, presumably due to interlayer interaction and electronic screening. XPS C1s and Raman 2D spectra of EG grown on substrates after undergoing *in-situ* H₂ etch at different times did not show shifts in peak position/intensity suggesting lack

of etch time dependence on EG electronic or structural quality. Yet etch conditions affect the final morphology, as EG synthesis performed after an *in-situ* H₂ etch at 1600°C resulted in step-bunched morphology with step heights 5-10nm, whereas, substrates etched at 1520°C had EG with step-heights 10-15nm. In addition other growth parameters investigated were found to be of secondary importance, including: Ar pressure, flow rates, and sample cool down conditions.

9:20am **GR+EM+NS+PS+SS+TF-MoM4 Uniform Epitaxial Growth of Charge Neutral Quasi-Free-Standing Monolayer Graphene on a 6H-SiC(0001) Surface by Combination of Metal Silicidation and Intercalation**, *H. Shin, I. Song, C.-Y. Park, J.R. Ahn*, Sungkyunkwan University, Republic of Korea

Intrinsic high mobility of graphene are much reduced in graphene devices by various factors. Two critical factors degrading mobility are uniformity in an atomic structure such as number of a layer and an interaction with a substrate. Recently Shuai-Hua Ji *et al.* reported quantitatively that conductivity is much reduced by one sixth when electrons pass through a boundary between monolayer and bilayer graphene at a step edge in comparison to conductivity of monolayer graphene. This suggests that uniformity of number of graphene layer is a more crucial factor than expected. In particular, in epitaxial graphene on SiC, the uniformity of number of layer is an intrinsic and serious problem because Si is more rapidly sublimated near a step edge in the formation of epitaxial graphene by thermal evaporation of Si and, subsequently, epitaxial graphene with different layers coexists intrinsically on a terrace. Another factor degrading mobility is an interaction between graphene and a substrate. In epitaxial graphene, the interaction was reduced by intercalation of metal or molecule such as H, F, and Au between graphene and a substrate, which results in quasi freestanding graphene. Various charge neutral quasi freestanding graphene has been reported, but the charge neutrality was found at an optimal coverage of an intercalated element and annealing temperature. This makes it difficult to achieve spatially homogeneous charge neutrality of quasi freestanding graphene, and a method with a broad range of coverage and temperature is demanded. We demonstrate that charge neutral quasi freestanding monolayer graphene can be grown uniformly without coexistence of a buffer layer and a bilayer graphene which limit mobility of epitaxial monolayer graphene. Because coexistence of two different phases is inevitable on a SiC surface, uniform monolayer graphene was produced based on two different phases, a Si-rich phase and a C-rich phase called a buffer. Pd was deposited on both the Si-rich and C-rich phases and annealed up to 900°C. The Si-rich phase produced Pd silicide and charge neutral quasi freestanding monolayer graphene was produced on the Pd silicide while, on the C-rich phase, Pd was intercalated between the buffer layer and SiC resulting in charge neutral quasi freestanding monolayer graphene, where the quasi freestanding monolayer graphene on two difference regions was connected atomically. The combination of Si silicidation and intercalation result in uniform charge neutral quasi freestanding uniform monolayer on a SiC surface, where the electronic and atomic structures were observed using angle-resolved photoemission spectroscopy and scanning tunneling microscopy.

9:40am **GR+EM+NS+PS+SS+TF-MoM5 Epitaxial Graphene on Ir(111) - A Playground for the Fabrication of Graphene Hybrid Materials**, *T.W. Michely*, Universität zu Köln, Germany **INVITED**

Carefully optimizing the growth of graphene on Ir(111) yields a virtually defect free, weakly bound epitaxial monolayer ranging from quantum dot sizes to macroscopic extension. In the talk I will show how this system can be used to construct new types of graphene based materials. Specifically, patterned adsorption of transition metals results in dense cluster arrays with exciting magnetic and catalytic properties. Intercalation underneath the graphene allows one to manipulate the properties of graphene itself, e.g. its ability to adsorb atoms and molecules as well as its magnetism.

10:40am **GR+EM+NS+PS+SS+TF-MoM8 Graphene Growth Studied with LEEM, PEEM, EELS, ARPES, MEIS, and STM**, *R.M. Tromp, J.B. Hannon, M.W. Copel, S.-H. Ji, F.M. Ross*, IBM T.J. Watson Research Center **INVITED**

We have studied the growth of graphene on a variety of substrates, including SiC (both Si and C terminated), polycrystalline Cu and Ni foils, as well as single-crystal Ni foils. Low Energy Electron Microscopy (LEEM) and Photo Electron Emission Microscopy (PEEM) offer the unique opportunity to follow the growth in real time, as it proceeds at high temperature, and in the presence of processing gases such as disilane (for growth on SiC) or ethylene (for growth on the metal substrates). Low Energy Electron Diffraction (LEED) allows us to determine crystallographic orientations as well as atomic structure of areas well below a micrometer in extent. Information on electronic structure can be obtained from the plasmon loss features using Electron Energy Loss Spectroscopy (EELS), or from Angle Resolved Photo Electron Spectroscopy (ARPES).

These spectroscopic experiments are carried out in the LEEM/PEEM microscope using an in-line energy filter with which energy and angle resolved analysis of the electrons can be performed on selected areas. Finally, to obtain information on the layer-by-layer evolution of the graphene films, particularly on SiC, we have used isotope sensitive Medium Energy Ion Scattering (MEIS), to follow the growth by thermal decomposition of ¹²C vs ¹³C graphene monolayers from a three-bilayer thick Si¹³C homoepitaxial film grown on a SiC substrate. Taken together, these results provide a comprehensive view of the growth of graphene films. In this talk, we will review the most salient results of these studies, and their relevance to the use of graphene films for electronic applications. To address the latter, we will discuss the results of three-probe STM experiments in which we measured the excess resistivity of a graphene sheet as it crosses an atomic step of the underlying substrate.

11:20am **GR+EM+NS+PS+SS+TF-MoM10 Spatial Confinement of Epitaxy of Graphene on Microfabricated SiC to Suppress Thickness Variation**, *H. Fukidome, T. Ide, H. Handa*, RIEC, Tohoku Univ., Japan, *Y. Kawai*, Tohoku Univ., Japan, *F. Fromm*, Univ. Erlange-Nürnberg, Germany, *M. Kotsugi, T. Ohkouchi*, JASRI/SPring-8, Japan, *H. Miyashita*, Tohoku Univ., Japan, *Y. Enta*, Hirosaki Univ., Japan, *T. Kinoshita*, JASRI/SPring-8, Japan, *Th. Seyller*, Univ. Erlange-Nürnberg, Germany, *M. Suemitsu*, RIEC, Tohoku Univ., Japan

Epitaxial graphene on SiC (EG) is promising owing to a capability to produce high-quality film on a wafer scale [1]. One of the remaining issues is microscopic thickness variation of EG near surface steps, which induces variations in its electronic properties and device characteristics. To suppress the variation, spatial confinement of surface reactions is effective. The spatial confinement using substrate microfabrication, for instance homoepitaxy and sublimation on microfabricated Si substrates, can induce self-ordering of steps, and even produce step-free surfaces [2]. The spatial confinement is therefore anticipated effective to obtain EG without the thickness variation.

We have for this reason applied the spatial confinement to the epitaxy of graphene on 6H-SiC(0001). For the spatial confinement, 6H-SiC(0001) substrates were microfabricated by using electron beam lithography and fast atomic beam etching using sulfur hexafluoride [3, 4]. Epitaxial graphene on the microfabricated 6H-SiC(0001) substrates was obtained by annealing at 1923 K in Ar ambience [2]. It is verified by using low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) that step-free SiC surface and EG without thickness variation can be formed on smaller patterns [4]. This result clearly demonstrate that the spatial confinement is effective for the epitaxy of graphene on SiC. Furthermore, Raman spectroscopy and LEEM reveals that the spatial confinement can suppress the fluctuations of the electronic properties, e.g. (unintentional) doping in EG [4].

In conclusion, we have demonstrated that the spatial confinement of EG is effective to control both structural and electronic properties. This novel technique can boost the development of electronic devices based on EG.

[References]

- [1] K. V. Emstev *et al.*, Nature Mater. 8 (2009) 203.
- [2] Y. Homma *et al.*, Jpn. J. Appl. Phys. 35 (1996) L241.
- [3] T. Ide *et al.*, accepted for the publication in Jpn. J. Appl. Phys.
- [4] H. Fukidome *et al.*, submitted.

11:40am **GR+EM+NS+PS+SS+TF-MoM11 Three-Dimensional Graphene Architecture Growth and Its Facile Transfer to Three-Dimensional Substrates**, *J.-H. Park*, Sungkyunkwan University, Republic of Korea, *H.-J. Shin, J.Y. Choi*, Samsung Advanced Institute of Technology, Republic of Korea, *J.R. Ahn*, Sungkyunkwan University, Republic of Korea

Recent development of large area graphene synthesis on metal layer by chemical vapor deposition (CVD) or epitaxial growth on silicon carbide (SiC) opened the possibility for applications such as transparent electrodes for ITO replacement. For instance, graphene has been demonstrated for use in a liquid crystal display (LCD) and/or organic light emitting diode (OLED) test cell as a bottom electrode. However, the actual device, e.g., an active-matrix (AM) LCD, operates by switching individual elements of a display, using a thin-film transistor (TFT) for each pixel. Here, the pixel electrode of a display should extend down to the transistor's source or drain, thereby making contact with a via hole, which demands that a three-dimensional (3D) architecture electrode be deposited on a flat surface as well as its side walls. Although large-area graphene growth can be applied for a wide range of applications, 3D graphene architecture growth has not been realized for actual devices due to the original limitation of planar graphene growth. Herein, we demonstrate for the first time 3D graphene architecture growth and its facile transfer to a planar and/or 3D substrate. To prevent agglomeration of nano-scale metal catalyst by the CVD process,

we chose a SiC system. Graphene, a few layers thick, was epitaxially grown on a pre-patterned SiC substrate with nano-size thickness which was produced by photolithography and dry etching. Graphene on a vertical facet of the SiC pattern with a few-hundred nanometers in height was perfectly prepared using this approach, contrary to the CVD method. Furthermore, we suggest the use of a facile transfer method of graphene on SiC to a SiO₂ substrate using thermal release tape after hydrogen intercalation. In spite of the troublesome transfer issue of SiC, the geometry of the 3D graphene was perfectly transferred onto the planar SiO₂ as well as the 3D SiO₂ structure. In other words, the 3D graphene architecture was maintained as a floating cap structure on planar SiO₂ and the vertical facet of the 3D SiO₂ structure was well covered. Moreover, the graphene bottom layer without a 3D cap and the inverted bowl structure in the 3D graphene architecture were selectively transferred by controlling intercalation and pressure. These approaches could provide a beneficial method for preparing a 3D graphene architecture as well as for modifying the ordered structure to be utilized in real devices.

Monday Afternoon, October 29, 2012

Electronic Materials and Processing

Room: 9 - Session EM+TF+OX+GR-MoA

High-k Dielectrics for MOSFETS II

Moderator: C.L. Hinkle, University of Texas at Dallas, H.J. Kim, National Institute of Aerospace (NIA)

2:00pm **EM+TF+OX+GR-MoA1 "6.1" Family: The Next Generation of III-V Semiconductors for Advanced CMOS: Epitaxial Growth and Passivation Challenges.** C. Merckling, A. Alian, A. Firrincelli, S. Jiang, M. Cantoro, J. Dekoster, M. Caymax, M. Heyns, IMEC, Belgium **INVITED**

The integration of high carrier mobility materials into future CMOS generations is presently being studied in order to increase drive current capability and to decrease power consumption in future generation CMOS devices. If III-V materials are the candidates of choice for n-type channel devices, antimonide-based III-V semiconductors present the unique property of owning both high electrons (InSb) and holes (GaSb) mobilities, which triggered much of the interest in these III-Sb compounds for advanced CMOS. Moreover recent simulations have demonstrated that higher hole mobility could be found in strained III-antimonides compounds, suggesting the possibility of an all III-antimonide solution for full III-V based CMOS. In this work we studied the heteroepitaxy of 6.1 family semiconductors (GaSb, AlSb & InAs) on various III-V and Si substrates as well as the passivation of such semiconductors.

The relatively large lattice parameter of "6.1" semiconductors makes the growth and the integration on standard surfaces difficult. But is it possible to grow such semiconductors fully relaxed with low defect density due to the formation of a highly periodic array of 90° misfit dislocations at the III-Sb/substrate interface. In this contribution both MBE and MOVPE growth techniques have been studied in order to propose novel integration scheme on Si substrate.

In a second part, we will focus on the passivation of these III-V semiconductors. Because III-V surfaces are very sensitive to oxygen compounds, this will generate the formation of native oxide. This undesirable interlayer will contribute aggressively to the high density of surface states within the energy band gap, resulting in Fermi level pinning which disturbs the basic III-V MOSFET-operation. In this context both ex-situ and in-situ Al₂O₃ high-κ gate dielectric deposition by standard ALD or MBD processes is reported. The interface is abrupt without any substantial interfacial layer, and is characterized by high conduction and valence band offsets. Finally, MOS capacitors showed well-behaved C-V with relatively low D_{it} along the band gap. Such a D_{it} profile is promising for the future devices and suggests possibility to attain a low subthreshold swing.

2:40pm **EM+TF+OX+GR-MoA3 Improving Nucleation and Passivation of Ge(100) via H₂O and H₂O₂ Dosing.** T. Kaufman-Osborn, K. Kiantaj, J.S. Lee, A.C. Kummel, University of California San Diego

Germanium is a promising candidate for potential channel materials due to its higher hole and electron mobility. To minimize the oxide-semiconductor interfacial defect density, a proper passivation layer must be used before the oxide layer is deposited. In this study, a monolayer of H₂O chemisorbates is shown to activate TMA chemisorption due to the Ge-OH bonds catalyzing the formation of an ultrathin passivation layer which can serve as an ideal ALD nucleation template on a Ge surface. However, since H₂O chemisorption results in equal density of Ge-H and Ge-OH sites on the Ge(100), H₂O can only provide a maximum of 0.5 monolayer of Ge-OH sites, limiting the TMA nucleation density. By using H₂O₂ dosing, the density of Ge-OH sites can be doubled thereby increasing the potential TMA nucleation density. This study compares the passivation of the Ge(100) surface via H₂O and H₂O₂, for the application of nucleating ALD growth on the surface, using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS).

A saturation H₂O dose onto Ge(100) resulted in 0.85 ML coverage of -OH and -H species chemisorbed on the surface. The remaining unreacted atoms on the surface have half filled dangling bond states causing a large local amount of conduction band edge states in the bandgap. The Ge-OH and Ge-H sites on the surface have limited thermal stability. Annealing the H₂O/Ge(100) sample to 100°C significantly reduces the H₂O coverage due to the recombinative desorption of H₂ or H₂O.

A saturation dose of H₂O₂ on Ge(100) at 250°C results in a coverage of 0.95 ML of Ge-OH species chemisorbed on the surface with very few unreacted sites. Compared to a H₂O dose, H₂O₂ provides more than double the number of reactive Ge-OH sites thereby increasing the number of potential ALD nucleation sites. In contrast to the H₂O passivated surface, annealing

the H₂O₂/Ge surface to 100°C generates no additional dangling bond sites and even eliminates the dangling bonds present from the 250°C dose and forms a highly ordered surface of Ge-OH bonds. The improved coverage of Ge-OH sites allows for increased nucleation density of O-Al bonds and also minimizes the dangling bonds which are considered as the major source of interfacial trap states (D_{it}). The improved thermal stability allows for an increased thermal budget during ALD cycles. STS measurements show that TMA nucleation on the H₂O₂ functionalized Ge(100) surface unpins the Fermi level and has a wide bandgap with no band edge states demonstrating very good interface quality.

3:00pm **EM+TF+OX+GR-MoA4 Electrical and Physical Characteristics of High-k/Metal Gate MOS Devices on MBE-Grown Germanium on Silicon Using Aspect Ratio Trapping.** S.R.M. Anwar, C. Bui, N. Lu, M.J. Kim, C.L. Hinkle, University of Texas at Dallas

Due to its high hole mobility and relative compatibility with Si CMOS processing, Ge has long been considered as a replacement channel material for PMOS devices. Selective area growth of Ge channels on bulk Si substrates would be ideal for minimizing fabrication costs and allowing the co-implementation of other materials (III-Vs for NMOS). However, due to the 4.2% lattice mismatch between Ge and Si, unacceptably high dislocation densities (~10⁹ cm⁻²) are created during this heteroepitaxy.

In this work, we investigate the fabrication of MOS gate stacks on MBE-grown Ge on Si using Aspect Ratio Trapping (ART)^{1,2} to reduce Ge defect density. ART is a growth technique that allows for the reduction of defects for lattice mismatched materials by trapping the threading dislocations into the sidewalls of patterned nanoscale trenches in which the epitaxial growth takes place. This technique has the added benefit of producing the necessary geometric structure required for highly scaled tri-gate devices while reducing defect density simultaneously. Surface roughness and defect density dependence on growth temperature and growth rate will be discussed as will be the effect of varying the trench geometry. RHEED, XRD, XPS, TEM, EPD, AFM, SEM, and IPE data are correlated with growth conditions to produce high quality heteroepitaxial growth. Data will be presented demonstrating the use of low-temperature buffer layers in conjunction with low-growth rate bulk Ge results in a reduction in threading dislocations of 2-3 orders of magnitude.

MOS devices were fabricated on the MBE-grown Ge on Si samples. A high-quality interface was obtained using a DI-H₂O surface functionalization by pre-pulsing the H₂O 50 times in the atomic layer deposition (ALD) chamber at 250 °C.³ A thin interfacial Al₂O₃ film was deposited by ALD at 250 °C followed by forming gas anneal (FGA) performed for 30 minutes at 350 °C. This FGA step converts the surface functionalized oxide to a thin layer of GeO₂ resulting in improved electrical performance. 2.5 nm of HfO₂ was then deposited by ALD. 10 nm of RF sputtered TiN was deposited as the gate metal followed by low-temperature anneals in various ambients to tune the effective work function of the HfO₂/TiN gate stack.⁴ A final FGA for 30 minutes at 350 °C completed device processing. These devices show excellent PMOS characteristics and will be discussed.

This work is supported by the SRC Global Research Corporation.

- 1 J.-S. Park, *et al.*, Appl. Phys. Lett. **90**, 052113 (2007).
- 2 J. Bai, *et al.*, Appl. Phys. Lett. **90**, 101902 (2007).
- 3 S. Swaminathan, *et al.*, J. Appl. Phys. **110**, 094105 (2011).
- 4 C. L. Hinkle, *et al.*, Appl. Phys. Lett. **100**, 153501, (2012).

3:40pm **EM+TF+OX+GR-MoA6 In Situ Infrared Spectroscopy Study on the Temperature Dependence on the Growth Mechanism of Atomic Layer Deposition of Al₂O₃ on InP(100).** W. Cabrera, The University of Texas at Dallas, I.M. Povey, Tyndall National Institute, Y.J. Chabal, The University of Texas at Dallas

One of the current challenges in fabricating III-V-based electronics is the growth of an interfacial layer during the atomic layer deposition (ALD) of high-k dielectrics on III-V substrates, which has led to poor quality electrical properties. A process that can mitigate this problem is the "clean-up" effect that occurs when trimethylaluminum (TMA) is deposited by atomic layer deposition during the formation of Al₂O₃. A recent theoretical study suggests that the principal pathway in the "clean-up" effect of TMA on the native oxides of GaAs and InGaAs involves oxygen gettering¹. In this work, *in-situ* infrared absorption spectroscopy has been used to investigate the temperature dependence of the native oxide and the interface formation during Al₂O₃ deposition using TMA and deuterium oxide (D₂O) on chemically-treated InP(100) surfaces. Upon annealing a degreased sample to 300°C, compositional changes are observed, as evidenced by new absorption features in the region of 900-1250 cm⁻¹ of the infrared spectrum

prior to TMA exposure. The initial native oxide, comprised in part of $\text{In}(\text{PO}_3)_3$ is transformed into an InPO_4 -rich surface. Upon TMA exposure at 300°C , there is a clear loss of $\text{In}(\text{PO}_3)_3$ and gain of InPO_4 (at 1007 and 1145 cm^{-1} , respectively) along with the formation of Al-O bonds (absorption band at 800 cm^{-1}). These observations are consistent with the “clean up” effect observed on GaAs₃ and InGaAs₄, and on InP(100)₅ where TMA preferentially withdraws oxygen from the native oxide forming Al-O bonds. However, the TMA reduces $\text{In}(\text{PO}_3)_3$ and fosters the formation of InPO_4 . Furthermore, TMA exposure of the native oxide at lower deposition temperatures (150°C) gives rise to methoxy (CH₃) formation as evidenced by the appearance of a band centered at 1475 cm^{-1} . This indicates that TMA not only withdraws oxygen from the native oxide but also transfers a methyl group to the surface oxygen, which may lead to carbon contamination at the interface. Al_2O_3 oxide films are formed after 10 TMA and D₂O cycles on both degreased native oxide and chemically treated (HF and (NH₄)₂S) InP(100) substrates, although the quality is higher on the (HF and (NH₄)₂S)-treated surface. A more clearly defined LO phonon mode is detected for that surface, suggesting that a denser oxide is formed.

- 1 S. Klejna et. al, *J. Phys. Chem. C*, **116**, (2012) 643-654
- 2 M. M. Frank et. al, *Appl. Phys. Lett.* **82** (2003) 4758
- 3 C. L. Hinkle et. al, *Appl. Phys. Lett.*, **92** (2008) 071901
- 4 M. Milojevic, et. al *Appl. Phys. Lett.*, **93**, (2008) 202902
- 5 B. Brennan et. al, *Appl. Phys. Exp.*, **4** (2011) 125701

4:00pm **EM+TF+OX+GR-MoA7 Ultimate Scaling of High-k Gate Dielectrics: Current Status and Challenges**, T. Ando, M.M. Frank, E.A. Cartier, B.P. Linder, J. Rozen, IBM T.J. Watson Research Center, K. Choi, GLOBALFOUNDRIES, V. Narayanan, IBM T.J. Watson Research Center
INVITED

Current status and challenges of aggressive equivalent-oxide-thickness (EOT) scaling of high-k gate dielectrics via higher-k (>20) materials and interfacial layer (IL) scavenging techniques are reviewed [1]. La-based higher-k materials [2, 3] and La-silicate IL with HfO_2 [4] showed aggressive EOT values (0.5–0.8 nm), but with large effective workfunction (EWF) shifts toward the Si conduction band edge, limiting their application to nFET. Further exploration for pFET-compatible higher-k materials is needed. Meanwhile, IL scavenging is a promising approach to extend Hf-based high-k dielectrics to future nodes [4, 5]. Remote-scavenging techniques enable EOT scaling below 0.5 nm. We will review IL scavenging techniques from the viewpoints of (1) IL growth condition; (2) Choice of scavenging element; (3) Location of scavenging element; (4) Choice of high-k material and (5) Maximum process temperature. Careful choice of materials and processes based on these considerations is indispensable. Mobility-EOT trends in the literature suggest that short-channel performance improvement is attainable with aggressive EOT scaling via IL scavenging or La-silicate formation. However, extreme IL scaling is accompanied with loss of EWF control [6] and with severe penalty in reliability [7]. Therefore, highly precise IL thickness control in an ultra-thin IL regime (<0.5 nm) will be the key technology to satisfy both performance and reliability requirements for future CMOS devices.

This work was performed by the Research alliance Teams at various IBM Research and Development Facilities.

- [1] T. Ando, *Materials* **2012**, *5*, 478-500 [2] H. Arimura et al., *Electron Device Lett.* **2011**, *32*, 288–290 [3] L. F. Edge et al., *Appl. Phys. Lett.* **2011**, *98*, 122905 [4] T. Ando et al., *IEDM* 2009, 423-426 [5] L. Å. Ragnarsson et al., *IEDM* 2009, 663-666 [6] T. Ando et al., as discussed at *SISC* 2011 [7] E. A. Cartier et al., *IEDM* 2011, 18.4.1-18.4.4

4:40pm **EM+TF+OX+GR-MoA9 AR-XPS Study of $\text{Al}_2\text{O}_3/\text{In}$ -based III-V Interfaces after Annealing under Vacuum at Low Temperature**, E. Martinez, H. Grappeix, O. Desplats, CEA, LETI, MINATEC Campus, France, A. Herrera-Gomez, O. Ceballos-Sanchez, CINVESTAV-Unidad Queretaro, Mexico, J. Guerrero, K. Yckache, F. Martin, CEA, LETI, MINATEC Campus, France

III-V semiconductor substrates are a potential solution for MOSTETs down scaling below the 16 nm technological node. Indium based semiconductors, such as InGaAs, InAs and InP are promising compounds to improve the speed of operation. The quality of the interface between these high mobility substrates and the gate oxide is of crucial importance to preserve the devices electrical properties. Aluminium oxide is used to remove the As oxide (“self-cleaning” effect). The gate-last scheme is preferred to control of the high-k/III-V since it involves low temperature post deposition annealing [1]. State-of-the-art control of this interface has been obtained with annealing at 400°C under vacuum [2]. In this work we focus on the impact of low temperature annealing under vacuum on the quality of the $\text{Al}_2\text{O}_3/\text{In}$ -based III-V interfaces. We have studied the interfacial oxides formed between alumina and III-V substrates such as InGaAs, InAs and InP.

Annealing at 600°C under ultra high vacuum (UHV) is first performed and compared to thermal treatments at 600°C and 400°C at 3×10^{-4} mbar. Substrate passivation is done with NH_4OH (4 %). The 3-nm thick alumina is deposited by Atomic Layer Deposition (ALD) using TMA and H_2O as precursor and oxidant. Angle-resolved photoelectron spectroscopy (AR-XPS) has been carried out to investigate the interfacial chemical bonding states. Consistent and robust analysis of the As 3d, P 2p, Ga 3d and In 3d core levels was carried out through the simultaneous fitting method [3]. At 600°C , we show that, on InGaAs, no interfacial oxides are created after annealing under UHV, whereas a thin interfacial InGaO_x is observed under secondary vacuum. A clear difference between the three substrates is observed after annealing at 400°C under 3×10^{-4} mbar. In particular, the indium oxidation and the relative stability of interfacial oxides are substrate dependant. On InAs, indium hydroxide is formed after annealing, by OH release from TMA/ H_2O deposited alumina. This is not the case with additional elements such as Ga and P, which react with residual species to create their respective oxides. On InGaAs, a regrowth of InGaO_x is observed after anneal, as a result of preferential oxidation of Ga. On InP, the InPO_x interfacial oxide seems to decrease after anneal. **Acknowledgements** This work was performed with financial support from the MOS35 project funded by the French National Research Agency. Measurements were carried out at the NanoCharacterization Centre (NCC) of MINATEC. [1] H. Zhao et al., *Appl. Phys. Lett.* **95**, 253501 (2009)[2] Y. Urabe et al., *Appl. Phys. Lett.* **97**, 253502 (2010)[3] J. Muñoz-Flores et al., *J. Electron. Spec. Rel. Phen.* **182**, 81 (2011)

5:00pm **EM+TF+OX+GR-MoA10 Effect of a H_2 Plasma Pre-treatment on the Reduction of Native Oxides at the PEALD $\text{Al}_2\text{O}_3/\text{InAs}$ Interface**, E. Cleveland, L. Ruppalt, J.B. Boos, B. Bennett, J. Champlain, S.M. Prokes, Naval Research Laboratory

The integration of high-k dielectrics with high mobility III-V semiconductor materials has attracted extensive interest recently as an alternative to Si-based complementary metal-oxide semiconductor (CMOS) applications at the 16 nm node and beyond. Among the III-V semiconductors, InAs is a promising material as the channel material in metal-oxide-semiconductor field-effect transistors (MOSFETs) due to its extremely high electron mobility and high saturation velocity. However, problems arise in the fabrication of high performance channel MOSFETs due to the poor quality of the gate oxide/InAs interface. InAs has a highly reactive surface and on exposure to air will form a native oxide layer composed of In_2O_3 and As_2O_3 . The complexity of these native oxides leads to the formation of a relatively high density of interface states which in turn act as charge traps thus pinning the Fermi level and degrading device performance. Wet-chemical treatments based on HCl and (NH₄)₂S have been found to be an effective means of removing these oxides, however, due to the rapid re-oxidation and lack of reproducibility a better means of interface cleaning is needed. Recently, there has been much interest in the field of surface cleaning combined with atomic layer deposition (ALD) in order to deposit high quality dielectrics on III-V semiconductor materials, such as InAs and GaSb. Therefore, we examined the use of a H_2 plasma as a means to obtain an oxide-free InAs interface prior to the deposition of high-k Al_2O_3 via plasma enhanced atomic layer deposition (PEALD). Ex-situ XPS, AFM, and C-V measurements were performed to establish the effect of the plasma exposure time, temperature and rf power on the removal of the native oxide. It will be demonstrated that by removing or reducing the native oxides on the InAs surface that the density of interface defects at the $\text{Al}_2\text{O}_3/\text{InAs}$ interface can be reduced and enhance the electrical performance. Similar work done on GaSb will be discussed, where XPS spectra revealed a significant reduction in Sb-O features for longer H_2 plasma exposures as the peaks associated with Ga-O increased. C-V measurements of fabricated MOSCAPS also found that samples treated with longer H_2 plasma exposures exhibited better C-V characteristics.

Electronic Properties and Charge Transport

Moderator: T.W. Michely, Universität zu Köln, Germany

2:00pm **GR+EM+ET+NS+TF-MoA1 Influence of Substrate Offcut on Electrical and Morphological Properties of Epitaxial Graphene, R.L. Myers-Ward, V.D. Wheeler, L.O. Nyakiti, T.J. Anderson, F.J. Bezares, J.D. Caldwell, A. Nath, N. Nepal, C.R. Eddy, Jr., D.K. Gaskill**, U.S. Naval Research Laboratory

The promise of graphene-based device technologies is critically dependent on uniform wafer-scale graphene films and is most directly met through epitaxial graphene (EG) growth on silicon carbide (SiC) substrates. An essential parameter which influences this uniformity is the substrate offcut, as any deviation will result in a local change in the terrace width, impacting the growth rate and step-bunched heights observed after EG formation. For nominally on-axis SiC substrates, typical offcuts can range from $\sim 0^\circ$ to $\sim 1^\circ$ off-axis toward the [11-20] direction. Offcuts approaching 0° produce wide terraces with short step-bunched heights which offers the possibility of reduced anisotropy of transport properties [M. Yakes, et al., Nano Lett. **10**(5), 1559 (2010)] and improved EG layer uniformity. Thus, it is of interest to understand the influence of substrate offcut on carrier mobility, surface morphology, step heights, and graphene growth rate. This study investigates EG grown on a unique single 3-inch substrate possessing a large variation in offcut, from $+0.1$ to -1° toward the [11-20] direction, enhancing the information obtained on offcut influence while eliminating other substrate influences. X-ray diffraction rocking curve and peak position maps of the (0012) reflection were performed prior to growth to evaluate the crystalline quality and local offcut, respectively. Electron mobilities of EG films were determined by van der Pauw Hall measurements. Surface morphology of the EG was investigated with scanning electron microscopy, while the step heights and terrace widths were measured using atomic force microscopy.

For a given set of conditions (1620°C for 30 min in 10 slm Ar), the EG morphology is dominated by straight steps that become wavy in character as the offcut decreases to zero degrees. Close to zero degrees, the step direction rotates from [11-20] to the [1-100] direction and the steps become further distorted. The step bunch heights generally decreased (from 8 to 3 nm) as the offcut decreased and the terrace widths increased (from 0.3 to ~ 3 μm); however, for the latter, the trend is interrupted near zero degrees offcut. In addition to such morphological assessments, the impact of growth parameters, where the growth temperatures investigated were 1540, 1580 and 1620 °C and growth times were 15, 30 and 45 min, on the electrical and structural properties of EG grown on this unique substrate will be reported. For example, samples grown at 1540 °C for 30 min on witness substrates with offcuts ranging from ~ 0.4 to 0.9° had large area mobilities ranging from 780 to 1100 cm^2/Vs , where larger offcuts led to lower mobilities.

2:20pm **GR+EM+ET+NS+TF-MoA2 Direct Determination of Dominant Scatterer in Graphene on SiO₂, J. Katoch, D. Le, T.S. Rahman, M. Ishigami**, University of Central Florida

Freely suspended graphene sheets display high-field effect mobility, reaching 2×10^5 $\text{cm}^2/\text{V s}$. Yet, suspended graphene sheets are fragile and impractical for most experiments and applications. Graphene sheets on SiO₂ are easier to handle but possess low-carrier mobilities, which can vary by an order of magnitude from sample to sample. Poor and unpredictable transport properties reduce the utility of SiO₂-bound graphene sheets for both fundamental and applied sciences. Therefore, understanding the impact of substrates is crucial for graphene science and technology.

We have measured the impact of atomic hydrogen with kinetic energy less than 250 meV on the transport property of graphene sheets as a function of hydrogen coverage and initial, pre-hydrogenation field-effect mobility. The saturation coverages for different devices are found to be proportional to their initial mobility, indicating that the number of native scatterers is proportional to the saturation coverage of hydrogen. In order to understand this correlation between the field effect mobility and the apparent affinity of atomic hydrogen to graphene, we have performed a detailed temperature programmed desorption study on hydrogen-dosed graphene sheets. Atomic hydrogen is found to physisorb on graphene with activation energy for desorption of 60 ± 10 meV, consistent with our theoretical calculations. The associated charge transfer expected for such small desorption energy indicates that atomic-scale defects and ripples are not responsible for determining the mobility of graphene on SiO₂ and that charged impurities in substrates define the transport property of graphene on SiO₂.

1. J. Katoch, J.H. Chen, R. Tsuchikawa, C. W. Smith, E. R. Mucciolo, and M. Ishigami, Physical Review B Rapid Communications, **82**, 081417 (2010).

2:40pm **GR+EM+ET+NS+TF-MoA3 Tuning Electronic Properties of Graphene by Controlling its Environment, K.I. Bolotin**, Vanderbilt University

Every atom of graphene, a monolayer of graphite, belongs to the surface. Therefore, the environment of graphene -- the substrate onto which graphene is deposited and any coating on top of graphene -- intimately affects the properties of graphene. In this talk, we demonstrate that both the mechanical and electrical properties of graphene can be tuned by varying its environment.

First, we discuss the dependence of electrical transport in graphene on the dielectric constant (k) of graphene's environment. For graphene in vacuum ($k=1$) we observe very strong electron-electron interactions leading to robust fractional quantum Hall effect at temperatures up to 15K. By suspending graphene in liquids, we explore the regime of dielectric constants between ~ 1.5 and ~ 30 . We observe the dependence of carrier scattering in graphene on k and demonstrate large values for room temperature mobility ($>60,000$ cm^2/Vs) in ion-free liquids with high k . We also explore the rich interplay between the motion of ions inside liquids and transport of electrons in graphene. We observe signatures due to streaming potentials and Coulomb drag between ions in the liquid and electrons in graphene.

We also briefly address the mechanical properties of graphene and their dependence on graphene's environment. We demonstrate that the built-in strain, the substrate adhesion force and even the thermal expansion coefficient of graphene depend on the substrate supporting graphene.

3:40pm **GR+EM+ET+NS+TF-MoA6 Study of Impurity-Induced Inelastic Scattering on Suspended Graphene by Scanning Confocal Micro-Raman Spectroscopy, L.W. Huang, C.S. Chang**, Academia Sinica, Taiwan, Republic of China

We utilized a polymer-based procedure to transfer the CVD-grown graphene onto a TEM copper grid. The heat treatment was performed on the graphene membrane in an argon/ hydrogen (Ar/H₂) atmosphere at 400 °C. After the transfer and heat treatment, TEM images, acquired by an ultra-high-vacuum transmission electron microscopy (UHV-TEM), demonstrated areas with distinguishable impurity distribution on the suspended graphene membrane. These areal impurity distributions can also be mapped by the scanning Raman spectroscopy correspondingly, indicating the influence of impurity-induced inelastic scattering. The results of this experiment show that the intensity ratio of Raman spectra 2D band over G band (I_{2D}/I_G) is proportional to minus fourth power of the inelastic scattering rate.

4:00pm **GR+EM+ET+NS+TF-MoA7 The Adsorption of Molecules with Large Intrinsic Electrostatic Dipoles on Graphene, L. Kong**, Univ. of Nebraska-Lincoln, G.J. Perez Medina, Univ. of Nebraska-Lincoln, Univ. of Puerto Rico, J. Colón Santana, Univ. of Nebraska-Lincoln, L. Rosa, Univ. of Nebraska-Lincoln, Univ. of Puerto Rico, L. Routaboul, P. Braunstein, Maître de conférences de l'Université de Strasbourg, France, B. Doudin, Institut de Physique et Chimie des Matériaux de Strasbourg, France, C.-M. Lee, J. Choi, Kyung Hee Univ., Korea, P.A. Dowben, Univ. of Nebraska-Lincoln

Both gold and graphene are excellent conductors, and one might expect that both conductors would fully screen the photoemission and inverse photoemission final states of a molecular adsorbate, but in fact this is not the case. The comparison of the electronic structure of p-quinonoid zwitterionic type molecules with a large intrinsic dipole of 10 Debyes adsorbed on both gold and graphene on copper substrates, shows that the interaction between the adsorbate molecules and graphene is very weak, confirming that graphene is chemically inert. We find that the photoemission and inverse photoemission final states are well screened for p-quinonoid zwitterionic dipolar molecules on gold. This is not observed in the case of this quinonoid zwitterion adsorbed on graphene on copper. This weaker screening is evident in a larger highest occupied molecular orbital to lowest unoccupied molecular orbital gap for the molecules on graphene. The larger highest occupied molecular orbital to lowest unoccupied molecular orbital gap for the molecules on graphene indicates that a much weaker screening on the photoemission and inverse photoemission final states for these dipolar molecules on graphene than that on gold. This work is reviewed in the context of other studies of molecular adsorption on graphene.

4:20pm **GR+EM+ET+NS+TF-MoA8 Growth of and Interactions in Epitaxial Graphene Layers**, *A. Bostwick*, Lawrence Berkeley National Laboratory, *A. Walter*, *Th. Seyller*, Lawrence Livermore National Laboratory, *K. Horn*, *E. Rotenberg*, Lawrence Berkeley National Laboratory **INVITED**

The electronic properties of graphene has been investigated using angle-resolved photoemission spectroscopy at the MAESTRO* facility of the ALS** synchrotron in Berkeley, California. This laboratory is unique in its ability to grow sophisticated samples for *in situ* study using angle-resolved photoemission spectroscopy, and to subtly alter their properties by engineering their surfaces by chemical doping or thickness control. In this talk I will discuss the electronic properties of graphene, focusing on the role of dopants to control the charge density and as defects to disrupt the metallic conduction. By measuring the spectrum of “plasmaronic” quasiparticle excitations, we can demonstrate the scale-free nature of the Coulomb interaction in Dirac systems. Such effects are readily observed on quasi-free standing graphene samples doped with long-range scatterers. Doping with short-range scatterers, on the other hand, results in a loss of conduction which we interpret as a manifestation of strong (Anderson) localization.

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5:00pm **GR+EM+ET+NS+TF-MoA10 Squeezing of the Graphene Dirac Cone Observed by Scanning Tunneling Spectroscopy**, *J. Chae*, *S. Jung*, *Y. Zhao*, *N.B. Zhitenev*, *J.A. Stroscio*, Center for Nanoscale Science and Technology / NIST, *A. Young*, *C. Dean*, *L. Wang*, *Y. Gao*, *J.C. Hone*, *K.L. Shepard*, *P. Kim*, Columbia University

The single-particle spectrum of graphene is described by massless Dirac quasiparticles with a linear energy-momentum dispersion relation. In this talk I examine the effect of electron interactions on the graphene energy dispersion as a function of both excitation energy E away from the Fermi energy and density n . To analyze the dispersion, we measure the Landau levels (LLs) in graphene on a hexagonal boron nitride (hBN) insulator in low magnetic fields by scanning tunneling spectroscopy. The experiments were performed in a custom designed cryogenic scanning tunneling microscope system operating at 4 K with applied magnetic fields from 0 T to 8 T. The graphene devices were fabricated by the method detailed in Dean *et al.* [1]. The disorder in graphene on hBN is reduced in comparison with the previous measurements in graphene on SiO₂ [2] allowing us to observe the LLs in fields as low as 0.5 T. By fitting the LL energies obtained at constant density, we find that the energy dispersion remains linear, characterized by a momentum-independent renormalized velocity. However, the renormalized velocity is density dependent, showing a strong increase as the charge neutrality point is approached. The overall spectrum renormalization can be described as a *squeezing* of the Dirac cone angle due to electron-electron interactions at low densities. Interestingly, we also find that the renormalization of the dispersion velocity is affected by the local disorder potential and magnetic field, which is not described by current theory.

[1]. C. Dean, A. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone, *Nature Nanotech.* 5, 722–726 (2010).

[2]. S. Jung, G. M. Rutter, N. N. Klimov, D. B. Newell, I. Calizo, A. R. Hight-Walker, N. B. Zhitenev, and J. A. Stroscio, *Nature Phys.* 7, 245–251 (2011).

5:20pm **GR+EM+ET+NS+TF-MoA11 Interfacial Interaction of Graphene and Metal Surfaces Investigated by Resonant Inelastic X-ray Scattering**, *L. Zhang*, University of Science and Technology of China, Advanced Light Source, *J.H. Guo*, Advance Light Source, *J.F. Zhu*, University of Science and Technology of China

The synthesis of graphene on metal surfaces by chemical vapor deposition (CVD) is the most promising method to prepare single-layer and large-area graphene, which is a prerequisite for the fabrication of graphene-based electronic devices. Therefore, the graphene/metal interfaces have attracted much attention due to their importance in graphene synthesis by CVD processes. In this presentation, we report our recent studies on the electronic structure and band dispersion of graphene on different metal surfaces (Cu, Ir and Ni) by the means of X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS). The XAS spectra for graphene on metal surfaces show strong π^* and σ^* resonant features, indicating that the single-layer graphene films preserve the intrinsic symmetry of graphite. The resonant XES spectra of graphene on different metal surfaces change dramatically, especially for the features of π^* resonances, which can be directly related to the different strength of hybridization between graphene and metal substrates. These significant spectra changes have been proved to be an effective measure for the bonding strength of graphene on different substrates: strong band

dispersion can be observed when the interaction between graphene and metal substrate is weak (such as Cu), while the band dispersion is seriously disturbed when a strong hybridization between graphene and metal substrate (such as Ni) exists. These results provide basic understanding of graphene/metal interfacial interaction, which helps to develop graphene-based electronic devices with high performances.

Tuesday Morning, October 30, 2012

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+AS+EM+MI+MN-TuM

Optical, Magnetic, Mechanical and Thermal Properties
Moderator: K.I. Bolotin, Vanderbilt University

8:00am **GR+AS+EM+MI+MN-TuM1 Characterization of Magnetically Tunable Iron Nanorod Coated Graphene Nanoplatelets, S.D. Johnson, M.H. Gowda, S.-F. Cheng, N.Y. Garces, B. Feigelson, F.J. Kub, C.R. Eddy, Jr., U.S. Naval Research Laboratory**

Composites made from iron coated graphene nanoplatelets (GNPs) show promise for applications such as, magnetic switches, electromagnetic interference shielding, and electromagnetic waveguides due to the large conductivity of GNPs combined with the magnetism of iron. Additionally, this composite can be easily formed into millimeter thick sheets making it a promising composite for other applications.

We report a novel method to synthesize iron oxide compound onto GNP using microwave hydrothermal synthesis at 60° C and reaction times between 10 and 120 minutes. Scanning electron microscopy imaging reveals iron oxide nanorods approximately 100 nm long adhered to the GNPs for reaction times as short as 10 minutes. X-ray photoemission spectroscopy reveals that the iron/carbon ratio remains constant across these reaction times. The resistivity of the composite increases with reaction time from 0.2 to 0.6 ohm-cm. Saturation magnetization and coercive field values follow a decreasing trend with increasing reaction time. From 10 to 120 minutes saturation magnetization decreases by 70% from 170 emu/g and coercive field decreases by 40% from 52 Oe. Remnant magnetization of around 0.7 memu/g remains constant throughout. We also report the temperature-dependent magnetic response of the compound across the Morin transition, which for submicron particles of α -Fe₂O₃ is near 250 K.

Preliminary results suggest that while the nanorod size and quantity remains constant with reaction time, the resistive and magnetic properties change. This may suggest that we are tuning the magnetism of the system by changing the iron structure between the ferromagnetic γ -Fe₂O₃ and the antiferromagnetic α -Fe₂O₃.

8:20am **GR+AS+EM+MI+MN-TuM2 Dynamical Origin of Blue Photoluminescence from Graphene Oxide, A.L. Exarhos, M.E. Turk, P.M. Vora, J.M. Kikkawa, University of Pennsylvania**

The tunable broadband emission from graphene oxide (GO) has sparked significant interest in research regarding its potential for band gap engineering. Here, we use polarization sensitive time-resolved optical spectroscopy to study the spectral diffusion and sub-picosecond dynamics of the excited carriers in GO and photo-exposed GO, where photo-exposure has been demonstrated to constitute a reducing condition. In steady state measurements, a significant blueshifting of the photoluminescence (PL) is observed with photo-exposure. This blueshift correlates with a marked difference in the temporal behavior of the PL from GO and photo-exposed GO. The PL spectra are very similar at short delay times, but an increased non-radiative recombination rate in the exposed GO leads to a decreased lifetime in the material. Utilizing in-plane polarization memory measurements, we examine the electron-hole polarization in these systems which can probe excitonic effects and help to provide a better understanding of the role of the sp² graphene lattice in GO and exposed GO. We further discuss the relevance of our data to the origins of PL in these systems.

A.L.E. gratefully acknowledges the support of NSF DMR-0907226. M.E.T., P.M.V., and the construction of a Kerr gate system are supported by the Department of Energy Office of Basic Energy Sciences Award DE-SC0002158.

8:40am **GR+AS+EM+MI+MN-TuM3 Spin-Transport and Magnetism in Graphene, R. Kawakami, University of California, Riverside INVITED**

Graphene is an attractive material for spintronics due to its high mobility and the low intrinsic spin-orbit and hyperfine coupling, which should lead to excellent spin transport properties. In 2007, graphene became the first material to exhibit gate tunable spin transport and spin precession at room temperature. However, the spin injection efficiency was low and the spin lifetime was much shorter than predicted theoretically. In this talk, I will report on our progress in this area. The low spin injection efficiency into graphene is due to the conductivity mismatch between the ferromagnetic metal (Co) spin injector and the single layer graphene (SLG). To alleviate this problem and enhance the spin injection efficiency, we developed atomically smooth MgO tunnel barriers by utilizing a TiO₂ seed layer. With tunneling contacts, the non-local spin signal is found to be as high as 130

ohms at room temperature, with a spin injection efficiency of 30%. In addition to improving the spin injection efficiency, the tunneling contacts were found to improve the spin lifetime as well. This indicates that the short spin lifetimes reported before are due to the contact-induced spin relaxation from the ferromagnetic electrodes. Using tunneling contacts, we investigate spin relaxation in single layer graphene (SLG) and bilayer graphene (BLG). At low temperatures, contrasting behaviors of gate voltage dependence of the spin lifetime are observed between SLG and BLG, which suggest different mechanisms for spin relaxation in SLG and BLG. A final topic of interest is magnetism and the formation of magnetic moments in graphene. While there is substantial theoretical work on magnetic moments generated by hydrogen adatoms and lattice vacancies, the experimental situation is less clear. We have developed a new method for detecting magnetic moment formation based on scattering of pure spin currents in graphene spin valves. We will report the progress on our efforts to identify magnetism with this approach.

10:40am **GR+AS+EM+MI+MN-TuM9 A "How To" for Magnetic Carbon, H. Ohldag, SLAC National Accelerator Laboratory, E. Arenholz, T. Tyliczszak, Lawrence Berkeley National Laboratory, D. Spemann, R. Hoehne, P. Esquinazi, M. Ungureneau, T. Butz, University of Leipzig, Germany**

While conventional wisdom says that magnetic materials have to contain some metallic atoms, the confirmation of intrinsic magnetic order in pure metal free carbon represents an ultimate and general scientific breakthrough because of the fundamental importance of carbon as an elemental building block of organic as well as inorganic matter. The common controversy raised across all disciplines is whether the magnetism of carbon is intrinsic or induced by other elements. We address this controversy by providing clear experimental evidence that metal free carbon can be ferromagnetic at room temperature using dichroism x-ray absorption spectro-microscopy. For this purpose we acquired soft x-ray microscopy images of magnetic structures on a thin carbon film that have been produced by irradiation with a focused 2.25MeV proton beam. Our element specific magnetic probe shows no indication of magnetically ordered Fe, Co or Ni impurities in these samples. In a second step we investigate the particular electronic states that are involved in carbon magnetism and find that the carbon p-states as well as C-H bonds show a magnetic moment, indicating that hydrogenation plays a crucial role in developing the ferromagnetic order. Our surface sensitive approach reveals that the magnetism at the surface of the irradiated graphite samples is much larger than in the bulk of the sample. We observe a surface magnetic moment similar to what is typically present in classical ferromagnetic 3d transition metals.

REFERENCES

P.Esquinazi et al., *Magnetic order in graphite: Experimental evidence, intrinsic and extrinsic difficulties*, Journal of Magnetism and Magnetic Materials, Vol 322, 1156 (2010).

H. Ohldag et al., *p-Electron ferromagnetism in metal free carbon probed by soft x-ray dichroism*, Phys. Rev. Lett. 98, 187204 (2007) H. Ohldag et al., *The role of hydrogen in room temperature ferromagnetism at graphite surfaces*, New J. Phys. 12 123012 (2010)

11:00am **GR+AS+EM+MI+MN-TuM10 From Graphene to Amorphous Carbon by Sublimation and Condensation, B. Steele, R. Perriot, V. Zhakhovsky, I.I. Oleynik, University of South Florida**

The mechanisms of the non-equilibrium melting process of graphene and the structure of the liquid phase of carbon was studied by molecular dynamics (MD). Graphene undergoes a non-equilibrium melting process at high temperature and low pressure as the carbon chains are formed out of the graphene sheet, thus making up a transient liquid phase of carbon. As the chains expand the material sublimates to a low dense gas of carbon chains. Under higher pressure the gas phase will condense to an intermediate porous phase of carbon with a significant sp² fraction of atoms, followed by the liquid phase, and finally an amorphous phase. Mechanisms of melting of graphene, including formation of topological and Stone Wales (SW) defects in two and three dimensions will be discussed.

Tuesday Afternoon, October 30, 2012

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+AS+NS+SP+SS-TuA

Graphene Characterization Including Microscopy and Spectroscopy

Moderator: J.C. Hone, Columbia University

2:00pm **GR+AS+NS+SP+SS-TuA1 High Resolution Real and Reciprocal Space Photoelectron Emission Microscopy on Heterogeneous Graphene/SiC(000-1)**, *K. Winkler, B. Kroemker*, 10micron NanoTechnology, Germany, *N. Barrett*, IRAMIS, Saclay, France, *E. Conrad*, GeorgiaTech

We present energy filtered electron emission spectromicroscopy with high spatial and wave-vector resolution on few-layer epitaxial graphene on SiC(000-1) grown by furnace annealing.

Conventional electron spectroscopy methods are limited in providing simultaneous real and reciprocal or k-space information from small areas under laboratory conditions. Therefore, the characterization of materials with only micron scale sample homogeneity such as epitaxially grown graphene requires new instrumentation. Recent improvements in aberration compensated energy-filtered photoelectron emission microscopy (PEEM) can overcome the known limitations in both synchrotron and laboratory environments. Here we report 2D maps of the k-parallel π - π band dispersion in micron-scale regions and correlate them with spatially resolved chemical information on the same regions. Only the combination of high lateral, high energy, high k-resolution and controlled switching between real space and k-space allows detailed understanding of micron size sample sites with 1-3 layers graphene. The experiments underline the importance of simultaneous lateral, wave vector and spectroscopic resolution on the scale of future electronic devices in order to precisely characterize the transport properties and band alignments.

2:20pm **GR+AS+NS+SP+SS-TuA2 Evidence of Nanocrystalline Semiconducting Graphene Monoxide during Thermal Reduction of Graphene Oxide in Vacuum**, *C. Hirschmugl, E. Mattson, H. Pu, S. Cui, M. Schofield, S. Rhim, G. Lu, M. Nasse*, University of Wisconsin Milwaukee, *R.S. Ruoff*, University of Texas at Austin, *M. Weinert, M. Gajdardziska-Josifovska, J. Chen*, University of Wisconsin Milwaukee

As silicon-based electronics are reaching the nanosize limits of the semiconductor roadmap, carbon-based nanoelectronics has become a rapidly growing field, with great interest in tuning the properties of carbon-based materials. Chemical functionalization is a proposed route, but syntheses of graphene oxide (G-O) produce disordered, nonstoichiometric materials with poor electronic properties. We report synthesis of an ordered, stoichiometric, solid-state carbon oxide that has never been observed in nature and coexists with graphene. Formation of this material, graphene monoxide (GMO)[1], is achieved by annealing multilayered G-O. A combination of transmission electron microscopy and infrared microspectroscopy have provided critical experimental evidence to identify the novel structure. These results indicate that the resulting thermally reduced G-O (TRG-O) consists of a two-dimensional nanocrystalline phase segregation: unoxidized graphitic regions are separated from highly oxidized regions of GMO. GMO has a quasi-hexagonal unit cell, an unusually high 1:1 O:C ratio, and a calculated direct band gap of approximately 0.9 eV.

This work was supported by the NSF (CMMI-0856753 and CMMI-0900509). This work is based upon experiments performed at the Synchrotron Radiation Center. The SRC is funded by the University of Wisconsin-Madison and the University of Wisconsin-Milwaukee. Work performed at the SRC IRENI beamline been done with support from an NSF Major Research Instrumentation grant (DMR-0619759). The authors thank Bruker Technologies for the Grazing Angle Objective used for this work.

[1] Mattson, E.C. et al., ACSNano (2011) 5 (2011) 9710-9717.

2:40pm **GR+AS+NS+SP+SS-TuA3 Scanning Tunneling Spectroscopy of Epitaxial Graphene: Local Band Mapping and Wavefunction Engineering**, *P.N. First*, Georgia Tech **INVITED**

Because the crystalline orientation is determined prior to growth, epitaxial graphene (EG) on silicon carbide is an excellent material to consider for 2D wavefunction engineering, where device properties are designed through wavefunction confinement and material strain. In pursuit of this goal, we use scanning tunneling microscopy (STM) and spectroscopy (STS) to characterize the local structural and electronic properties of EG and a

simple EG nanostructure. With some care, STS can be used to measure the full energy-momentum dispersion of both filled and empty states, on length scales determined by the coherence of the graphene wavefunctions. Applying a magnetic field introduces a field-tunable comb of discrete Landau level energies that we use to obtain high momentum resolution, to characterize the tip-induced surface potential, and to detect subtle interlayer interactions in a multilayer graphene stack. * Work performed in collaboration with NIST Center for Nanoscale Science and Technology ** Funded in part by NSF and by NRI-INDEX.

4:00pm **GR+AS+NS+SP+SS-TuA7 Intercalation of O₂ an CO Controlled by the Mesoscopic Structure of Graphene**, *E. Grånäs, J. Knudsen*, Lund University, Sweden, *U. Schröder, T. Gerber, C. Busse*, Universität zu Köln, Germany, *M.A. Arman, K. Schulte, J.N. Andersen*, Lund University, Sweden, *T.W. Michely*, Universität zu Köln, Germany

Intercalation of gases between epitaxial graphene and its substrate has become a topic of interest for studies due to, for example, the unique opportunities to modify the graphene-substrate interaction and the possibilities to perform chemistry under the graphene layer. Further, a profound knowledge about graphenes stability in gases at elevated temperatures and pressures is essential for, among other things, the correct interpretation of gas adsorption studies on graphene supported metal cluster arrays.

We have studied intercalation and etching of Ir(111) supported graphene upon gas exposure to common gasses such as O₂ and CO in the entire pressure interval from 10⁻⁸ to 0.1 mbar. Comparing perfect graphene layers without holes with graphene films, that only covers a fraction of the Ir(111) surface, we reveal that the holes - or more specific the graphene edges - are essential for intercalation.

For oxygen exposed graphene we develop a coherent picture of temperature dependent oxygen etching and intercalation. Using X-ray photoemission spectroscopy (XPS) and scanning tunnelling microscopy (STM) we show that a perfect graphene layer is stable against etching and intercalation up to 700 K, whereas at higher temperatures etching, but no intercalation, takes place. In contrast, a partial graphene coverage on Ir(111) enables dissociative oxygen adsorption on the bare Ir and subsequent intercalation underneath graphene flakes at 355 K and above. Intercalated oxygen remains stable up to a temperature of 600 K, above this temperature it desorbs in the form of CO or CO₂. We have determined XPS and STM fingerprints for the intercalated oxygen structure and we unambiguously assign it to a p(2x1)-O structure similar to the one observed on clean Ir(111). The decoupling of the intercalated graphene film from the metal substrate is directly visualized through the inability to form well-ordered Pt cluster arrays on the O-intercalated areas of graphene on Ir(111). Further, we have identified the rate limiting step for oxygen intercalation to be unlocking of the graphene edge and propose that this takes place through bond breaking between graphene edge bonds and the Ir substrate.

Using a combination of high pressure X-ray photoemission spectroscopy (HP-XPS) and STM we also show that CO intercalation takes place at room temperature and pressures in the 1 mbar range. The adsorption structure of intercalated CO is determined to be (3√3 × 3√3)R30°, identical to the structure observed on clean Ir(111) upon high pressure CO exposure.

4:20pm **GR+AS+NS+SP+SS-TuA8 Long-range Atomic Ordering and Variable Interlayer Interactions in Two Overlapping Graphene Lattices with Stacking Misorientations**, *T. Ohta, T.E. Beechem*, Sandia National Laboratories, *J.T. Robinson*, Naval Research Laboratory, *G.L. Kellogg*, Sandia National Laboratories

We report a method to examine the effect of stacking misorientation in bilayer graphene by transferring chemical vapor deposited (CVD) graphene onto monolithic graphene epitaxially grown on silicon carbide (SiC) (0001). The resulting hybrid bilayer graphene displays long-range Moiré diffraction patterns having various misorientations even as it exhibits electron reflectivity spectra nearly identical to epitaxial bilayer graphene grown directly on SiC. These varying twist angles affect the 2D (G')-band shape of the Raman spectrum indicating regions of both a monolayer-like single π state and Bernal-like split π states brought about by the differing interlayer interactions. This hybrid bilayer graphene fabricated via a transfer process therefore offers a means to systematically study the electronic properties of bilayer graphene films as a function of stacking misorientation angle.

The work at Sandia National Laboratories was supported by LDRD and by the US DOE Office of Basic Energy Sciences, Division of Materials Science and Engineering. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-

AC04-94AL85000. The work at NRL was funded by the Office of Naval Research.

4:40pm **GR+AS+NS+SP+SS-TuA9 Chemically-resolved Interface Structure of Epitaxial Graphene on SiC(0001)**, *J.D. Emery*, Northwestern Univ., *B. Detslefs*, European Synchrotron Radiation Fac., France, *H.J. Karmel*, Northwestern Univ., *V.D. Wheeler*, U.S. Naval Research Lab, *J.M.P. Alaboson*, Northwestern Univ., *L.O. Nyakiti*, *R.L. Myers-Ward*, *C.R. Eddy, Jr.*, *D.K. Gaskill*, U.S. Naval Research Lab, *M.C. Hersam*, Northwestern Univ., *J. Zegenhagen*, European Synchrotron Radiation Fac., France, *M.J. Bedzyk*, Northwestern Univ.

The implementation of graphene into next-generation electronics will require production high-quality graphene at the wafer scale. One promising route for the production of wafer-scale graphene is to grow epitaxial graphene (EG) via thermal decomposition of Si-terminated SiC (SiC(0001)). This method produces high-quality EG, but is accompanied by the formation of the so-called "buffer layer" at the interface, which is known to affect the electronic properties of the graphene. Despite numerous efforts to determine the nature of the buffer layer, debate persists concerning its atomic and chemical structure. Here, we use the X-ray Standing Wave (XSW) technique to create a precise chemically-sensitive description of the distributions of Si and C at the interface. This technique, which combines X-ray scattering and X-ray Photoelectron Spectroscopy (XPS), is capable of locating coherent distributions of chemically distinct species above a single crystal surface. This allows for a more detailed description of the interface than those afforded by scattering or XPS alone. Our analysis shows that the buffer layer, which is present in both UHV and furnace-grown EG/SiC(0001), contains no substantial non-bulk or oxide silicon component, and is thus purely carbon. We identify two chemically distinct carbon species within the interface layer, each with a distinct location above the Si-terminated surface, and report their positions and distributions with sub-angstrom precision. These results help to clarify long-standing uncertainties about the interfacial structure of graphene/SiC(0001). Further, we also highlight the potential for XSW with XPS as a valuable tool in the structural determination of complex interfaces, such as functionalized, doped, or intercalated epitaxial graphene.

5:00pm **GR+AS+NS+SP+SS-TuA10 Formation of Graphene on SiC(000-1) in Disilane and Neon Environments**, *G. He*, *N. Srivastava*, *R. Feenstra*, Carnegie Mellon University

We have prepared graphene on the SiC(000-1) surface (the so-called *C-face* of the {0001} surfaces), by heating the SiC in a Si-rich environment produced either by using disilane ($\approx 10^{-4}$ Torr) or cryogenically-purified neon (1 atm). With the Si-rich environments, we obtain considerably better uniformity in the thickness for thin, \approx ML-thick graphene on the C-face compared to that observed in samples prepared in vacuum or in an argon environment. We also find that different interface structures occur in these environments. In particular, we find a graphene-like buffer layer forming at the interface, analogous to the well known behavior of the SiC(0001) surface (the Si-face).

Studies are performed using atomic force microscopy (AFM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM). For graphene prepared in vacuum, LEED patterns show a characteristic 3×3 pattern together with graphene streaks. In contrast, for the graphene produced in either the disilane environment ($\approx 10^{-4}$ Torr) or 1 atm of neon, LEED patterns reveals a complex $\sqrt{43} \times \sqrt{43} - R \pm 7.6^\circ$ arrangement along with graphene spots. This structure is somewhat similar to the well known $6\sqrt{3} \times 6\sqrt{3} - R30^\circ$ "buffer layer" of the Si-face, with satellite spots surrounding the primary Si spots, and is interpreted as arising from a C-rich buffer layer on the SiC. Selected area diffraction on those surface areas reveals a wavevector magnitude precisely equal to that of graphene, thus proving that the buffer layer does indeed have structure very close to that of graphene (the pattern is interpreted as a distortion of the buffer-layer graphene due to bonding to the underlying SiC). Using LEEM, measurements from the buffer layer of the reflected intensity of the electrons as a function of their energy reveal a new characteristic reflectivity curve, not seen for vacuum-prepared graphene.

After oxidation of the samples, the $\sqrt{43} \times \sqrt{43} - R \pm 7.6^\circ$ spots disappear and $\sqrt{3} \times \sqrt{3} - R30^\circ$ spots appear on the surface. This latter behavior is interpreted as oxidation of the SiC surface beneath the buffer layer. Selected area diffraction on portions of the surface that were previously identified as buffer layer still reveal a wavevector magnitude precisely equal to that of graphene. However, LEEM reflectivity curves on those areas reveal a completely new spectrum, indicative of a "decoupling" of the buffer from the SiC. This decoupling is consistent with our interpretation of this new interface structure as being a graphene buffer layer on C-face SiC.

This work is supported by NSF.

5:20pm **GR+AS+NS+SP+SS-TuA11 Characterization of Few Layer Graphene Films Grown on Cu-Ni and SiC Substrates**, *P. Tyagi*, *J.D. McNeilan*, *J. Abel*, *F.J. Nelson*, *Z.R. Robinson*, *R. Moore*, *A.C. Diebold*, *V.P. LaBella*, *C.A. Ventrice, Jr.*, University at Albany - SUNY, *A.A. Sandin*, *D.B. Dougherty*, *J.E. Rowe*, North Carolina State Univ., *C. Dimitrakopoulos*, *A. Grill*, *C.Y. Sung*, IBM T.J. Watson Res. Center, *S. Chen*, *A. Munson*, *Y. Hao*, *C.W. Magnuson*, *R.S. Ruoff*, Univ. of Texas at Austin

The electronic structure of graphene depends on the number of graphene layers and the stacking sequence between the layers. Therefore, it is important to have a non-destructive technique for analyzing the overlayer coverage of graphene directly on the growth substrate. We have developed a technique using angle-resolved XPS to determine the average graphene thickness directly on metal foil substrates and SiC substrates. Since monolayer graphene films can be grown on Cu substrates, these samples are used as a standard reference for a monolayer of graphene. HOPG is used as a standard reference for bulk graphite. The electron mean free path of the C-1s photoelectron is determined by analyzing the areas under the C-1s peaks of monolayer graphene/Cu and bulk graphite and results in a value of $12.3 \pm 0.8 \text{ \AA}$. With this electron mean free path, the graphene coverage of a film of arbitrary thickness can be determined from the areas under the C-1s peaks of the sample of interest, the monolayer graphene/Cu, and HOPG samples. Analysis of graphene coverages for graphene films grown on Cu-Ni substrates shows that a uniform monolayer is first formed before the growth of a second layer. The thickness of both the graphene overlayer and intermediate buffer layer has been determined on 6H-SiC substrates. Raman spectroscopy data have also been taken on these samples and compared to the overlayer coverages determined with XPS. This research was supported in part by the National Science Foundation (grant no. 1006350/1006411).

5:40pm **GR+AS+NS+SP+SS-TuA12 Thickness-related Electronic Properties of Single-layer and Few-layer Graphene Revealed by Single-pass Kelvin Force Microscopy and dC/dZ Measurements**, *J. Yu*, *S. Wu*, Agilent Technologies, Inc.

Graphene has attracted much attention recently due to their exotic electronic properties. Potential applications of graphene sheets as ultrathin transistors, sensors and other nanoelectronic devices require them supported on an insulating substrate. Therefore, a quantitative understanding of charge exchange at the interface and spatial distribution of the charge carriers is critical for the device design. Here, we demonstrate that atomic force microscopy (AFM)-based technique Kelvin force microscopy (KFM) can be applied as an experimental means to quantitatively investigate the local electrical properties of both single-layer and few-layer graphene films on silicon dioxide. Our measurements indicate that the surface potential of single-layer graphene is 60 mV higher than that of the silica interfacial layer. The effect of film thickness on the surface potential of few-layer graphene is observed. For example, a 66 mV increase in the surface potential is detected for an eleven-layered film with respect to a nine-layer film. Furthermore, with the introduction of multiple lock-in amplifiers (LIAs) in the electronics for scanning probe microscopes, single-pass kelvin force microscopy and probing of the other electric property such as local dielectric permittivity via the capacitance gradient dC/dZ measurements are allowed by the simultaneous use of the probe flexural resonance frequency ω_{mech} in the first LIA targeting the mechanical tip-sample interactions for surface profiling, and a much lower frequency ω_{elec} (both in the second LIA and its second harmonic in the third LIA) for sample surface potential and dC/dZ measurements, respectively. In contrast to surface potentials, the dC/dZ measurements show that local dielectric permittivity of few-layer graphene films maintain at the same level regardless of the film thickness. Such simultaneous monitoring of multiple electronic properties that exhibit different behaviors in response to the graphene layers provides us a way to achieve both a comprehensive characterization and a better understanding of graphene materials.

In Situ Microscopy and Spectroscopy Focus Topic **Room: 7 - Session IS+AS+BI+ET+GR+NS-TuA**

In Situ Studies of Organic and Soft Materials and In Situ Microscopy

Moderator: K. Artyushkova, The University of New Mexico, J.A. Eastman, Argonne National Laboratory

2:00pm **IS+AS+BI+ET+GR+NS-TuA1 Micronutrient Detection and Quantification from Data Obtained from Plasma Pencil Atmospheric Mass Spectrometry**, *M.J. Stein, E. Lo, C. Waterton, D.G. Castner, B.D. Ratner*, University of Washington

The analysis of micronutrient quantities is one component in the strategy to reduce the global burden of malnutrition-related disease. Accessibility of the proper equipment and equipment complexity impede nutrient testing in the areas that might benefit most from these studies. In this work, we present an analysis of micronutrients in a physiological range from blood plasma using plasma pencil atmospheric mass spectrometry (PPAMS), a method for sampling a sample's surface at ambient temperature and pressure conditions. The effectiveness of our PPAMS system is demonstrated using characteristic and tandem mass spectra on raw nutrient controls. Key micronutrient peaks and fragmentation patterns are observed. Next, we analyze a sample matrix of micronutrients in porcine plasma in which the nutrient concentrations are varied. Principal component analysis (PCA) is then employed on the spectra. The resulting PCA scores showed that these nutrients are separable at different nutrient concentrations to 95% confidence. The loadings peaks are shown to contain several of the key peaks observed in the raw nutrient powders as principal separators. The PPAMS technique is compared to several traditional techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrospray ionization mass spectrometry (ESI-MS). Separation of the nutrients at concentrations relevant for human blood-based nutrient detection is possible in both ESI-MS and PPAMS. However, ToF-SIMS is found to require 5x to 1000x higher concentrations than PPAMS for folate, vitamin A, and iodine in order to achieve similar separation of the micronutrients. In addition to the qualitative information obtained from the PCA results, quantitative predictive values are obtained by the application of a Bayesian wavelet-based functional mixed model. Since the mass spectra are modeled as functions in this model, peak detection methods are not required and the final results utilized the full spectral response. The final predicted values are compared to the known concentration values and the mean standard error of prediction (MSEP) is calculated. The accuracy of the predictive model was found to be dependent on the ionization potential of the individual nutrients. Metallic-nutrients were hypothesized to be more sensitive to outside cationization effects than their larger organic counterparts. In addition to quantitation, the physical properties of the ionization process were explored. Using XPS and ellipsometry in conjunction with carefully timed exposures and concurrent fragment PCA, it is determined that the PPAMS ionization is a softer form of ionization than most vacuum-based techniques.

2:20pm **IS+AS+BI+ET+GR+NS-TuA2 In Situ Real Time Examination of the Thin Film Growth of Pentacene on Polymeric Dielectrics Using X-Ray Synchrotron Radiation: Unexpected Changes in the Evolution of Surface Morphology with Substrate**, *T.V. Desai, A.R. Woll, J.R. Engstrom*, Cornell University

We have examined the thin film growth of pentacene on SiO₂ and on three different polymeric dielectrics using *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy (AFM). The polymeric dielectrics investigated spanned the range from a low surface energy hydrophobic surface (polystyrene, PS), to a medium surface energy hydrophobic surface (polymethylmethacrylate, PMMA), to a high surface energy hydrophilic surface [poly(ethylene imine), PEI]. We have also compared these results to pentacene growth on clean SiO₂. On all surfaces, pentacene forms a polycrystalline thin film, whose structure is that of the previously identified "thin film" phase. From *in situ* real-time x-ray scattering, we find that pentacene exhibits layer-by-layer (LbL) growth on all surfaces investigated, but the extent of LbL growth is a strong function of the underlying substrate. This result is unexpected as the transition to more 3D-like growth occurs for thicknesses where the underlying substrate is effectively almost entirely covered by the growing pentacene thin film. Layer-by-layer growth is significantly more prolonged on PEI (up to ~6 MLs), followed by SiO₂ and PMMA (up to ~4 MLs) and finally PS (up to ~3 MLs). This trend is also seen in the variation of both the roughness and the in-plane feature sizes of ~10 ML thick films, where the films are the smoothest, and the feature sizes are the largest for growth on PEI, whereas on PS, the films are roughest, and the feature sizes are the smallest. Concerning possible reasons for this behavior, we can exclude the effects of the structure of the

crystalline thin film (they were the same in all cases), and the roughness of the polymeric dielectric (rms roughness differed by < 0.1 nm) as major contributing factors. Surface energy of the polymeric thin films, however, provided the best explanation for the observed behavior, suggesting that thermodynamic driving forces play an important role in the evolution of thin film structure. In terms of molecular scale phenomena, interlayer transport and step-edge crossing events may be influenced by the mobility of the near-surface polymeric layers in the underlying substrate, which can be quite different for the ultrathin PEI layers vs. the much thicker PMMA and PS thin films.

2:40pm **IS+AS+BI+ET+GR+NS-TuA3 In Situ, Real-Time Diagnostics of Colon Cancer and Inflammatory Bowel Diseases by Direct Combination of Endoscopy and Rapid Evaporative Ionization Mass Spectrometry**, *Z. Takats*, Imperial College, UK, *L.A. Sasi-Szabo*, University of Debrecen, Hungary, *J. Kinross*, Imperial College, UK, *J. Balog*, Medimass Ltd., *L. Muirhead, K.C. Schafer, C. Guallar-Hoyas*, Imperial College, UK

INVITED

Rapid identification of biological tissues is a long-standing problem on various fields of interventional medicine, with special regard to cancer diagnostics and cancer surgery. While histological techniques provide the ultimate solution for the cellular-level identification of cancer cells, the approach is extremely complex and time consuming. Nevertheless, accelerated version of histopathology (so-called 'frozen section' method) is widely used for the intraoperative characterization of tissue samples removed from the surgical area. Since frozen section histology is less reliable than the traditional approaches, and the accelerated procedure still takes approx. 30 minutes for a single sample, there has been ongoing research for the development of more accurate and faster methods.

Molecular spectroscopy techniques including IR, Raman, solid state NMR and mass spectrometry have been used for the characterization of intact biological tissues and showed enormous potential for the differentiation of tissues with various histologies, including multiple different types of cancer.

Rapid Evaporative Ionization Mass Spectrometry is based on the observation that electrosurgical dissection of vital tissues involves the ionization of various tissue constituents, with special emphasis on membrane lipids. Electrosurgical methods employ electric current for the rapid heating and evaporation of tissue material and they are widely used both for dissection and coagulation on practically all fields of surgery. Hence, the direct combination of electrosurgery with mass spectrometry provides a tissue identification methodology, where the tissue manipulation part is already widely used by surgeons and fully approved from regulatory point of view. Electrosurgical methods are also employed on the field of endoscopy, both for coagulation and dissection. Combination of endoscopy with *in-situ* mass spectrometric tissue identification resulted in a diagnostic device which can potentially identify lesions in body cavities *in-situ*, in real-time.

Electrosurgical electrode assembly and ion transfer device were embedded into working channel of commercially available colonoscope. The device was coupled with a linear ion trap mass spectrometer, and the system was utilized during diagnostic colonoscopic interventions. Adenomae, adenocarcinomae and mucosal areas affected by inflammatory bowel diseases were successfully identified, in complete agreement with histopathological examination.

4:00pm **IS+AS+BI+ET+GR+NS-TuA7 Nanocrystal Phase Transformations in ZBLAN Glass Ceramics**, *J.A. Johnson*, University of Tennessee Space Institute, *C. Alvarez*, Northwestern University, *Y. Lui*, Argonne National Laboratory, *C.E. Johnson*, University of Tennessee Space Institute, *A. Petford-Long*, Argonne National Laboratory

In-situ and *ex-situ* TEM investigations of fluorochlorozirconate (FCZ) glass have led to the discovery of previously unreported BaF₂ in the face-centered-cubic (FCC) and orthorhombic phases. These FCZ glasses are a class of material based on ZBLAN glasses, which are being developed for uses in advance mammography systems. The FCZs of interest have been doped with Eu (II) for use as either a scintillator or a storage phosphor material but need to be partially crystalline to show good optical properties. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu²⁺ present in the BaCl₂ nanocrystals. The crystals formed from XRD experiments to be hexagonal and orthorhombic BaCl₂ depending on the annealing temperature, 265 and 295°C respectively. *In-situ* and *ex-situ* TEM heating experiments were used to study the nucleation and growth process of the nanocrystals at the EMC. The nanocrystals nucleate and grow through-out the glass matrix when annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The traditional BaCl₂ orthogonal phase in addition to the unreported FCC and orthogonal BaF₂ phase have been found in multiple ZBLAN compositions in which the content of Cl and F has been varied. This indicates that annealing FCZ

glasses produces polymorphic crystals of both BaCl₂ and BaF₂, which vary in size from 10 nm to 100 nm.

Mössbauer Spectroscopy has also given indisputable evidence that the divalent Europium enters the nanocrystals.

4:20pm IS+AS+BI+ET+GR+NS-TuA8 *In Situ* Microscopy of Organic Film Growth: Zn-Phthalocyanine on Ag(100), A. Al-Mahboob, J.T. Sadowski, Brookhaven National Laboratory

Metal phthalocyanines are attracting significant attention, owing to their potential for applications in chemical sensors, solar cells and organic magnets. As the electronic properties of molecular films are related to their crystallinity and molecular packing, the optimization of film quality is important for improving the performance of organic devices.

In this work, we studied the dynamics of nucleation and structural evolution of zinc-phthalocyanine (ZnPc) films on Ag(100) surface, employing real-time low-energy electron microscope (LEEM) complemented by DFT calculations. We have observed two different modes of ZnPc nucleation, depending on the growth temperature. At lower temperatures ZnPc nucleates in a double domain structure, with bulk-like square lattice similar to one reported by Dou et al. [2]. LEED patterns recorded in LEEM experiment show that ZnPc monolayer (ML) grows epitaxially, having a square lattice with $(4/3)\sqrt{13} \times (4/3)\sqrt{13} R33.69^\circ$ unit cell (denoted R33.69) with respect to the substrate lattice. At temperatures of 170°C or above, nucleation of less dense epitaxial ZnPc, having single domain orientation, was observed, with square lattice parameters exactly 5 times larger (5x5) than the Ag(100) substrate.

Utilizing LEEM to observe the ZnPc nucleation at varying substrate temperatures – from room temperature (RT) to 225°C – we have observed that the nominal ZnPc coverage required for the onset of nucleation has strong temperature dependence. The nucleation commences at about 0.2 ML at RT, while 0.7 ML is required at 190°C. At the same time the completion of 1st layer occurs at constant nominal coverage of ZnPc, independent of substrate temperature. Based on that observation, the delay in onset of nucleation could be understood as a result of increased equilibrium concentration of diffusing ZnPc molecules at higher temperatures. This is in contrast to a delay in nucleation and giant island growth observed during vacuum deposition of anisotropic molecules like pentacene (Pn), in which case the energy barrier for the reorientation of the molecule from diffusing state into its crystalline orientation plays a critical role [3]. Real-time tracking of the evolution of ZnPc island area at varying deposition conditions combined with DFT analysis revealed that the 5x5 structure has both, a detachment barrier with respect to attachment, and a pre-factor (or attempt frequency), lower than those for bulk-like structures, allowing for controlling of the resulting ZnPc structure.

[1] E. Bauer, Rep. Prog. Phys. **57**, 895 (1994).

[2] W. Dou et al, J. Chem. Phys. **133**, 144704 (2010).

[3] Al-Mahboob et al, Phys. Rev. **B 82**, 235421 (2010).

4:40pm IS+AS+BI+ET+GR+NS-TuA9 *In Situ* Sub-Micrometer Scale Chemical Imaging with Scanning Transmission X-ray Microscopy, S.T. Kelly, P. Nigge, Lawrence Berkeley National Laboratory, A. Laskin, B. Wang, Pacific Northwest National Laboratory, A. Tivanski, S. Ghorai, University of Iowa, T. Tyliszczak, M.K. Gilles, Lawrence Berkeley National Laboratory

Spatially resolved chemical information on length scales shorter than 50 nm has become crucial in many areas of science and engineering -- from analyzing the chemistry of geological and environmental samples to quantifying the detailed chemical structure of novel materials engineered on the nanoscale. Scanning transmission x-ray microscopy (STXM) allows collection of specific chemical speciation data on these length scales through the acquisition and analysis of near-edge x-ray absorption fine structure (NEXAFS) spectra at each image pixel. However, the full usefulness of the STXM instrument may ultimately be realized in the *in situ* analysis of chemical transformations by controlling the local sample environment.

In situ STXM/NEXAFS measurements have been made in several ways thus far, ranging from simple to very complex. Introducing gases directly into the microscope chamber is effective, yet the presence of the gas along the entire optical path of the x-rays reduces signal at the detector. Furthermore, gas choice with this configuration is limited to those compatible with the microscope components. Separate *in situ* reactor cells circumvent these limitations by confining the gaseous environment to a small region immediately around the sample. Several groups have used reactor cells to this end, with reactors ranging widely in complexity -- from simple cells with limited capability to complex systems which require substantial instrument reconfiguration.

Ideally, an *in situ* reactor for STXM should be capable, flexible, easy to install and configure, and easily fabricated. We have developed a gas phase

STXM reactor cell to meet many of these requirements. The reactor mounts directly to the standard STXM sample mount (making installation relatively simple) and contains an integrated sensor to actively measure relative humidity inside the cell for experiments using water vapor. We present here recent results using the reactor cell to examine two different systems. In the first system, we observed the hygroscopic properties of mixed organic/inorganic aerosol particles at increasing levels of relative humidity. In the second system, we monitored carbon dioxide sorption in metal organic framework materials. The advantages afforded by this reactor (and future improvements to it) will enable new scientific discoveries across a wide range of fields.

5:40pm IS+AS+BI+ET+GR+NS-TuA12 *In Situ* SEM and ToF-SIMS Imaging of Liquids for Biological Applications, L. Yang, X.-Y. Yu, Z. Zhu, S. Thevuthasan, Pacific Northwest National Laboratory, J. Cowin, Cowin In-Situ Science, L. L. C.

A vacuum compatible microfluidic interface was developed to enable surface analysis of liquids. The unique feature of the liquid flow cell is that the detection window is open to the vacuum allowing direct probing of the liquid surface. The flow cell is composed of a silicon nitride membrane and polydimethylsiloxane; and it is fully compatible with vacuum operations for surface analysis. The aperture can be drilled through the 100 nm silicon nitride membrane by using the focused ion beam/scanning electron microscope (FIB/SEM). Alternatively the primary Bi⁺ ions in ToF-SIMS can be used to fabricate the aperture window in real-time. New results using this vacuum interface and recent development will be presented in this paper. Several aqueous solutions containing conjugated IgG gold nanoparticles and representative biological solutions were studied *in situ* using scanning electron microscope (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Characteristic signals of the conjugated gold nanoparticles were successfully observed through the aperture by both energy-dispersive X-ray spectroscopy (EDX) in SEM and ToF-SIMS. Comparisons were also made among wet and dry samples and liquid sample in the flow cell using SEM/EDX. Stronger gold signal can be observed in our novel portable device by SEM/EDX compared with the wet or dry samples, respectively. Our results indicate that analyses of the nanoparticle conjugated antibodies are better made in their native liquid environment. Our unique microfluidic flow cell permits *in situ* liquid observations. In addition, a variety of aqueous solutions relevant to biological systems were analyzed. Our results indicate that chemical imaging by SEM and ToF-SIMS is applicable in analyzing more complicated aqueous solutions when coupled with our novel portable microfluidic platform.

**Nanometer-scale Science and Technology
Room: 12 - Session NS+EN+GR-TuA**

Nanomaterials in Two and Three Dimensions

Moderator: V.P. LaBella, University at Albany-SUNY

2:20pm NS+EN+GR-TuA2 Nanopatterning of SPRi Sensor Surfaces for Sub-Nanomolar Biomarker Detection, M.A. Parracino, M.J. Perez Roldan, J. Hanus, V. Spampinato, G. Ceccone, P. Colpo, F. Rossi, Nanobiosciences Unit, JRC, Italy

In this work we report the detection of low-molecular weight biomarkers on two kinds of nanostructured surfaces by using a SPRi sensor. Nanopatterned surfaces are fabricated by combining functionalization and patterning techniques. Two different methods were used for the surface nanopatterning: electro-beam lithography (EBL) and colloidal lithography (CL). Maltose binding protein (MBP) and transthyretin (TTR) are respectively immobilized on the two types of nanopatterns and used as biological recognition elements. Chemical contrast adhesive/non adhesive at nanoscale has been created in order to control protein binding at nanoscale. Plasma deposited (PEO)-like film was used as passivation layer to prevent non-specific binding of protein in between the protein adhesives nano-areas. All the fabrication steps of both surfaces have been carefully controlled and analyzed using several techniques such as AFM, XPS, and SEM. The gold nanostructures were 185 nm width lines, for the patterned created with EBL, and holes of 250 nm in diameters for the pattern fabricated using CL. The gold grating surface made using EBL was functionalized with sugar via a thiol-linker. Maltose Binding Protein (MBP) was bound on sugar modified surface in order to develop a competitive assay for maltose detection. In this competitive assay, the protein binding on the sugar functionalized surface depends on the concentration of his free competitor in solution: by measuring the protein binding, it is possible to evaluate the concentration of the small molecule in solution. In the second methods, NTA functionalized nanoholes in PEO like background were fabricated and subsequently activated with nickel (Ni II) for a selective immobilization of

histidines tagged TTR, which underlies to a direct detection of Thyroxine 4 (T4). In both case, the biological intermediates, MBP and TTR, are selectively immobilized onto nanopatterned surfaces. The ligand protein binding on the nanostructure is higher than on the flat surface. The better ligand orientation and immobilization on the nanostructures results in analyte detection at sub-nanomolar concentration. The combination of nanopatterning features with the two different methods of detection presented in this work provides a description for a more generalized approach for the development of stable and reliable biosensor platforms for the detection of different small molecules having an high impact in environmental, and biomedical field.

4:00pm NS+EN+GR-TuA7 Single Layer of MoS₂ on Close-Packed Metal Surfaces, D. Le, T.S. Rahman, University of Central Florida

We present results of first principles electronic structure calculations, using van der Waals density functional theory, of the adsorption of a single layer of Molybdenum disulfide (MoS₂) on several close-packed metal surfaces. On Cu(111) we find three energetically equivalent stacking types and a Moiré pattern whose periodicity is in agreement with experimental findings [1]. The layer is found not to be purely physisorbed on the surface, rather there exists a chemical interaction between it and the Cu surface atoms. We also find that the MoS₂ film is not appreciably buckled, while the top Cu layer gets reorganized and vertically disordered. The sizes of Moiré patterns for a single layer of MoS₂ adsorbed on other close-packed metal surfaces are also estimated by minimizing the lattice mismatch between the film and the substrate. The Moiré patterns on Ir(111), Pt(111), and Ru(0001) are particularly interesting as the MoS₂ layer is found to bind more strongly on them than on Cu(111). We compare the nature of the bond in these three substrates with that on Cu(111).

[1] D. Kim, D. Sun, W. Lu, Z. Cheng, Y. Zhu, D. Le, T. S. Rahman, and L. Bartels, *Langmuir* **27**, 11650 (2011).

* This work was supported in part by the U.S. Department of Energy under Grant No. DE-FG02-07ER15842.

4:20pm NS+EN+GR-TuA8 Chemically Exfoliated Two Dimensional Materials for Energy Applications, M. Chowalla, Rutgers University

INVITED

Chemical exfoliation of layered two-dimensional materials such as graphite and transition metal chalcogenides allow access to large quantities of atomically thin nanosheets that have properties that are distinctly different from their bulk counterparts. Although 2D materials have recently become popular, their fabrication via exfoliation of bulk crystals has been known for decades. For example, Brodie first exfoliated graphite into atomically thin oxidized form of graphene in 1859. In the case of layered transition metal dichalcogenides (LTMDs) such as MoS₂, WS₂, MoSe₂, WSe₂, etc., Frindt et al. performed seminal work in the '70s and '80s. We have revived these techniques to obtain a wide variety of chemically exfoliated two-dimensional nanosheets and utilized these materials in wide variety of electronic and energy applications. In this presentation, I will highlight some of our key contributions with graphene oxide (GO) and LTMD nanosheets. Specifically, I will present their implementation into large area electronics, strategic implementation into solar cells, and as catalyst for hydrogen evolution.

5:00pm NS+EN+GR-TuA10 Isolation and Surface Structure of Ultrathin Nanosheets formed by Atomic Layer Deposition, K.M. Lee, D.H. Kim, G.N. Parsons, North Carolina State University

Ultrathin nanosheets are two-dimensional structures that are often exfoliated from layered compounds. The nanosheets are flat with large surface area (100's of nm²) but with very small thickness in several nm scale. A common example of a nanosheet is graphene which is exfoliated from graphite. Other nanosheet materials that are chemically exfoliated from layered crystals include MoS₂, VS₂, and many oxide materials such as MnO₂, TiNbO₅, or LaNb₂O₇. These materials show unique capabilities for nanoelectronic devices, photocatalysts, and electrochemical sensor applications. For our work, we explore atomic layer deposition (ALD) as an effective technique to fabricate metal oxide nanosheets with precisely controlling thickness and chemical composition. To form nanosheets, we spin-coated a substrate with polymer such as polymethylmethacrylate (PMMA), polyvinyl alcohol (PVA), or polyacrylic acid (PAA) as a sacrificial layer, then deposited TiO₂, Al₂O₃ or ZnO on polymer layer by ALD. Dissolving the polymer in solvent releases nanosheets from the substrate. We successfully attained two dimensional TiO₂ nanosheets with several hundred μm in lateral size and less than 10 nm in thickness. Attaining nanosheets with thickness near 1nm proved to be rather challenging. For Al₂O₃ and TiO₂, nanosheets with thickness of ~ 1 nm can be isolated by two-immiscible liquid separation process. For ZnO, the thinnest nanosheet obtained to date is closer to 15 nm. We characterized nanosheets using AFM to confirm their thickness and found that the surface

structure and roughness depends on the materials and thickness. We also examined the functionality of TiO₂ nanosheets as an agent for photocatalytic degradation of organic dyes. This work demonstrates and defines the capabilities and limits for functional nanosheets fabrication by atomic layer deposition.

5:20pm NS+EN+GR-TuA11 All Solution Processed InGaO₃(ZnO)_m Thin Films with Layered Structure and their Thermoelectric Properties, J.H. Kim, H.K. Cho, Sungkyunkwan University, Republic of Korea

As the materials currently in use have been reached terminal and showed low productivity in a few field, the development of advanced materials are demanded. In the middle of atmosphere, low-dimensional nanostructures have been introduced in recent studies such as 1-D nanowire and 2-D superlattice. Among them, a multi-layered structure shows unique properties originating from the confinement of carriers in the two-dimensional layer. For example, LaFeO₃-LaCrO₃ superlattice structures fabricated by pulsed layer deposition (PLD) have shown enhanced ferromagnetism [1] and InGaO₃(ZnO)_m superlattice structure grown by sputtering method has improved thermoelectric properties [2].

These homologous series of RAO₃(MO)_m (R=In or rare earth elements; A=Ga, In, Al, or Fe ; M=Mg, Co, Cu, or Zn ; m=integer) comprise alternating stacks of RO₂⁻ and AO⁺(MO)_m layers and are candidate to exhibit the quantum effect due to its natural superlattice [3]. Despite these materials being widely investigated, the fabrication of RAO₃(MO)_m thin film with layered structure is limit due to their fabrication which requires expensive high-vacuum equipment and shows low productivity.

In this study, all solution process (an epitaxial ZnO buffer layer growth on sapphire substrate, amorphous IGZO layer on ZnO buffer layer by composition controlled solution process, and post-annealing at 900°C for 9hours) enables us to fabricate InGaO₃(ZnO)_m thin film with periodic superlattice structure. Crystallinity of thin film was analyzed by X-ray diffraction and TEM results. And also, TE properties such as Seebeck coefficient, electrical conductivity, thermal conductivity were evaluated to identify the degree of crystallization of superlattice with layered structure.

Reference

[1] K. Ueda, H. Tabata and T. Kawai, *Science*, 1998, **280**, 1064

[2] D. K. Seo, B. H. Kong and H. K. Cho, *Cryst. Growth Des.*, 2010, **10**, 4638

[3] J. L. F. Da Silva, Y. F. Yan and S. H. Wei, *Physical Review Letters*, 2008, **100**, 255501.

Wednesday Morning, October 31, 2012

Graphene and Related Materials Focus Topic

Room: 13 - Session GR+AS+BI+PS+SS-WeM

Graphene Surface Chemistry, Functionalization, Biological and Sensor Applications

Moderator: D.K. Gaskill, U.S. Naval Research Laboratory

8:00am **GR+AS+BI+PS+SS-WeM1 Structural Analysis of Chemically Functionalized Epitaxial Graphene with High-Resolution X-ray Reflectivity**, J.D. Emery, Q.H. Wang, M. Zarrouati, Northwestern University, P. Fenter, Argonne National Laboratory, M.C. Hersam, M.J. Bedzyk, Northwestern University

For graphene to realize its potential in next-generation electronics it must be incorporated with a variety of materials to form devices. Recently, the use of self-assembled organic monolayers deposited on epitaxial graphene (prepared by graphitization of the 6H-SiC(0001) surface) has been effective in the functionalization of the bare graphene sheet, enabling the additional chemistry necessary for device fabrication. In this work, we present high-resolution X-ray Reflectivity (XRR) studies of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on epitaxial graphene. Initially, a model-independent vertical electron density profile of the graphene/silicon carbide interface is retrieved with the use of Feinup-based error correction algorithms in order to minimize ambiguities that can arise from model-based methods. This retrieved structure is then used as the foundation for model-based analysis, from which the final structures are extracted. A series of structures comprising 0, 1, and 2MLs of PTCDA deposited on 1-2ML graphene are discussed. The interlayer spacing between the PTCDA and top graphene layer are revealed to be approximately 0.35 nm, which supports the view that the PTCDA molecules are interacting only weakly (van der Waals) with the graphene layer. In addition to the characterization of PTCDA-functionalized graphene, we will also demonstrate the efficacy of these molecules to form a weakly-interacting seeding layer for subsequent growth of high-k dielectrics via atomic layer deposition.

8:20am **GR+AS+BI+PS+SS-WeM2 In Situ FT-IR Study of Graphene Fluorination using XeF₂**, J.-F. Veyan, N. Shafiq, University of Texas at Dallas, K. Novoselov, University of Manchester, UK, Y.J. Chabal, University of Texas at Dallas

Graphene fluorination to obtain fluorographene has been successfully realized by exposing graphene flakes to molecular Xenon-Difluoride¹⁻³. To gain a mechanistic understanding of XeF₂ reaction with the graphene flakes, an all-aluminum custom-made two-stage reaction cell has been designed to fit into the main sample compartment of an FTIR Nicolet 6700 interferometer, for *in situ* infrared absorption spectroscopy. The first stage is a clean expansion chamber to isolate the pure XeF₂ in its gas phase, from solid XeF₂ (powder) stored in a storage vessel. The XeF₂ vapor is extracted by opening the valve V1 to the storage chamber and its pressure (up to ~4 Torr) is controlled by the valve V2. The second stage is a reactor equipped with two KBr windows, allowing the IR beam to penetrate and exit the enclosure. A pneumatic valve allows the transfer of gaseous XeF₂ from stage 1 into stage 2. Pressures in both storage and reactor chambers are measured with Baratron gauges (Ga1, Ga2). To avoid any contamination of the reactor and sample holders during sample preparation and loading, a N₂-purged glove bag is placed over the reactor to maintain a controlled environment. The graphene flakes in suspension in a NMP (N-Methylpyrrolidone) solution, are transferred onto three mechanically polished Aluminum plates at a temperature of 70°C. The plates are then mounted on the specially designed 3-reflection sample holder flange designed to fit stage 2.

By varying the sample temperature from 20 to 200°C as well as the XeF₂ pressure in the reactor stage from 0.1 to 4 Torr, the chemical attachment of fluorine on graphene is identified from a comprehensive FT-IR study performed under industrial conditions. Fluorine attached out of plane can be easily differentiated from fluorine attached at edges (i.e. remaining within the basal plane) and terminating the edge atoms.

¹ R. R. Nair, et al., *Small* **6**, 2877 (2010).

² J. T. Robinson, et al., *Nano Letters* **10**, 3001 (2010).

³ K.-J. Jeon, et al., *Acs Nano* **5**, 1042 (2011).

8:40am **GR+AS+BI+PS+SS-WeM3 Molecularly Resolved Chemical Functionalization of Graphene**, M.C. Hersam, Northwestern University
INVITED

Graphene has emerged as one of the leading materials in condensed matter physics due to its superlative electrical and mechanical properties. With an

eye towards expanding its functionality and applications, this talk will highlight our latest efforts to tailor the surface chemistry of graphene [1]. At the molecular scale, we employ ultra-high vacuum (UHV) scanning tunneling microscopy (STM) and conductive atomic force microscopy (cAFM) to characterize chemically modified epitaxial graphene on SiC(0001) [2,3]. For example, a suite of perylene-based molecules form highly ordered self-assembled monolayers (SAMs) on graphene via gas-phase deposition in UHV [4,5]. Due to their noncovalent bonding, these SAMs preserve the superlative electronic properties of the underlying graphene while providing uniform and tailorable chemical functionality [6]. In this manner, disparate materials (e.g., high-*k* gate dielectrics) can be seamlessly integrated with graphene, thus enabling the fabrication of capacitors, transistors, and related electronic/excitonic devices [7]. Alternatively, via aryl diazonium chemistry, functional polymers can be covalently grafted to graphene [8], while exposure to atomic oxygen in UHV enables chemically homogeneous and thermally reversible covalent epoxy functionalization [9]. Beyond UHV STM characterization, this talk will also delineate our most recent efforts to exploit chemically modified graphene in technologically significant applications including photovoltaics [10], transparent conductors [11-13], flexible GHz transistors [14], *in vivo* biomedical applications [15,16], and photocatalysts [17].

[1] Q. H. Wang and M. C. Hersam, *MRS Bull.*, **36**, 532 (2011).

[2] J. A. Kellar et al., *Appl. Phys. Lett.*, **96**, 143103 (2010).

[3] J. M. P. Alaboson et al., *Adv. Mater.*, **23**, 2181 (2011).

[4] Q. H. Wang and M. C. Hersam, *Nature Chemistry*, **1**, 206 (2009).

[5] Q. H. Wang and M. C. Hersam, *Nano Lett.*, **11**, 589 (2011).

[6] J. D. Emery et al., *Surf. Sci.*, **605**, 1685 (2011).

[7] J. M. P. Alaboson, et al., *ACS Nano*, **5**, 5223 (2011).

[8] Md. Z. Hossain et al., *J. Am. Chem. Soc.*, **132**, 15399 (2010).

[9] Md. Z. Hossain et al., *Nature Chemistry*, **4**, 305 (2012).

[10] I. P. Murray et al., *J. Phys. Chem. Lett.*, **2**, 3006 (2011).

[11] A. A. Green and M. C. Hersam, *J. Phys. Chem. Lett.*, **1**, 544 (2010).

[12] A. A. Green and M. C. Hersam, *Nano Lett.*, **9**, 4031 (2009).

[13] Y. T. Liang and M. C. Hersam, *J. Am. Chem. Soc.*, **132**, 17661 (2010).

[14] C. Sire et al., *Nano Lett.*, **12**, 1184 (2012).

[15] M. C. Duch et al., *Nano Lett.*, **11**, 5201 (2011).

[16] J.-W. T. Seo et al., *J. Phys. Chem. Lett.*, **2**, 1004 (2011).

[17] Y. T. Liang et al., *Nano Lett.*, **11**, 2865 (2011).

9:40am **GR+AS+BI+PS+SS-WeM6 Structure of a Peptide Adsorbed on Graphene and Graphite**, J. Katoch, University of Central Florida, S.N. Kim, Z. Kuang, B.L. Farmer, R.R. Naik, Air Force Research Laboratory, S.A. Tatulian, M. Ishigami, University of Central Florida

Non-covalent functionalization of graphene using peptides is a promising method for producing novel sensors with high sensitivity and selectivity. We have performed atomic force microscopy, Raman spectroscopy, infrared spectroscopy and molecular dynamics simulations to investigate peptide-binding behavior to graphene and graphite. We studied a dodecamer peptide, GAMHLPWHMGTL, identified by phage display to possess affinity for graphite.

Optical spectroscopy reveals that the peptide forms secondary structures both in powder form and in an aqueous medium. The dominant structure in the powder form is α -helix, which undergoes a transition to a distorted helical structure in aqueous solution. The peptide forms a complex reticular structure upon adsorption on graphene and graphite, having a helical conformation different from α -helix due to its interaction with the surface. Our observation is consistent with our molecular dynamics calculations and our study paves way for rational functionalization of graphene using biomolecules with defined structures and, therefore, functionalities. Our results have recently been published [1].

[1] J. Katoch, S.N. Kim, Z. Kuang, B. L. Farmer, R. R. Naik, S. A. Tatulian, and M. Ishigami, dx.doi.org/10.1021/nl300286k, *Nano Letters* (2012).

10:40am **GR+AS+BI+PS+SS-WeM9 Controlling the Spatial Distribution of Graphene Chemistry**, S.C. Hernández, E.H. Lock, S.G. Walton, C.J. Bennett, R. Stine, P.E. Sheehan, F.J. Bezares, L.O. Nyakiti, R.L. Myers-Ward, J.T. Robinson, J.D. Caldwell, C.R. Eddy, Jr., D.K. Gaskill, Naval Research Laboratory

Graphene has attracted a widespread of interest because of its unique structural and electronic properties however, manipulation of these properties is necessary before realizing its full potential as the next

generation material in a broad range of applications. Precise control of the surface chemistry of graphene can allow for subsequent surface procedures both for device fabrication (i.e. atomic layer deposition) and sensor applications. Chemical composition strongly impacts the electronic properties as well as chemical reactivity, both globally and locally. Electron-beam generated plasmas are capable of imparting a variety of functional group types over a range of coverages with minimal damage to the carbon back bone because of their inherently low ion energies and as such offer a unique approach for large area uniform processing of graphene films with controlled surface chemistry. The ability to manipulate the surface chemistry of this atomically thin material coupled with the capability to regulate the spatial distribution of functional will be discussed. Plasma processing conditions and characteristics, as well as the resulting chemical, structural, and electrical properties of the functionalized graphene will be demonstrated. This work is supported by the Naval Research Laboratory base program.

11:00am **GR+AS+BI+PS+SS-WeM10 Coverage-dependent Ordering of Adsorbed Iron Phthalocyanine on Epitaxial Graphene Grown on SiC(0001)-Si**, A.A. Sandin, D.B. Dougherty, J.E. Rowe, North Carolina State University

The crystallographic and electronic structure of monolayer and sub-monolayer Iron-Phthalocyanine (FePc) films are experimentally studied on graphene grown on SiC(0001) using Scanning Tunneling Microscopy and Spectroscopy (STM and STS) as well as Low Energy Electron Diffraction (LEED). At full monolayer coverage of FePc the STM images show that a nearly square overlayer lattice forms with flat-lying molecules and a densely-packed structure oriented 10° relative to the graphene principle lattice directions. This close-packed structure appears to be the same as that previously reported for FePc on graphite surfaces. For sub-monolayer coverage at room temperature, our STM images suggest that FePc forms a unique 2D molecular gas with images that have the hexagonal symmetry of the graphene honeycomb lattice. This is interpreted as suggesting that only a small diffusion barrier exists for molecular motion between neighboring sites in the 3-fold symmetry of the sub-monolayer overlayer lattice. The sub-monolayer gas condenses into islands at liquid Nitrogen temperatures with bare graphene regions and this implies that a weak attractive interaction exists between FePc molecules causing the close-packed ordering. Near defects in the graphene lattice we observe ring-like structures at room temperature that suggest an increased residence time of the mobile 2-D gas of FePc molecules. Our results using Scanning Tunneling Spectroscopy suggest the possibility of a hybrid molecule-graphene state in the unoccupied density of both states near the Fermi level which could possibly be useful in modifying the charge injection into graphene in future devices.

11:20am **GR+AS+BI+PS+SS-WeM11 A Molecular Route to Carbon Nanomembranes, Graphene and Their Hybrids with Tailored Physical and Chemical Properties**, A. Turchanin, University of Bielefeld, Germany **INVITED**

Bottom-up approaches via molecular self-assembly have high potential to facilitate the applications of two-dimensional (2D) carbon materials in nanotechnology. In this talk it will be demonstrated how self-assembled monolayers (SAMs) of aromatic molecules can be employed to this end. These monolayers are converted into *carbon nanomembranes* (CNMs) with a thickness of one molecule by electron or photon irradiation. CNMs can be separated from their original substrates and transferred onto various other substrates, fabricated as suspended nanomembranes or stacked into multilayer films with precise control over their thickness and composition. They possess two chemically distinct faces, which can be used for their selective functionalization, opening broad avenues for the engineering of novel materials with tailored on demand properties. High temperature annealing induces the transformation of CNMs into *graphene*, which allows large-area fabrication of the homogenous sheets with tunable electrical, optical and chemical properties. Integration of graphene sheets with CNMs into novel hybrids presents a promising route to flexibly functionalize graphene for applications as optical, electrical, chemical and biofunctional coating in nanoelectronics and sensors. Various physical and chemical properties of these novel materials, their nanopatterning and functional applications will be presented.

- 1) A. Turchanin and A. Götzhäuser, *Prog. Surf. Sci.* (2012) in press.
- 2) A. Turchanin, D. Weber, M. Bünenfeld, C. Kisielowski, M. Fistul, K. Efetov, R. Stosch, T. Weimann, J. Mayer, A. Götzhäuser, *ACS Nano* 5 (2011) 3896-3904.
- 3) C.T. Nottbohm, A. Turchanin, A. Beyer, R. Stosch, A. Götzhäuser, *Small* 7 (2011) 874-883.
- 4) Z. Zheng, C.T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Götzhäuser, *Angew. Chem. Int. Ed.* 49 (2010) 8493-8497.

5) A. Turchanin, A. Beyer, C.T. Nottbohm, X. H. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Götzhäuser, *Adv. Mater.* 21, 1233-1237 (2009).

Wednesday Afternoon, October 31, 2012

Graphene and Related Materials Focus Topic

Room: 13 - Session GR+AS+EM+NS+SS-WeA

Dopants and Defects in Graphene; Graphene Interfaces with Other Materials

Moderator: D. Gunlycke, Naval Research Laboratory

2:00pm **GR+AS+EM+NS+SS-WeA1 Increasing Interface Bonding and Tuning Doping Behavior at Metal-Graphene-Metal Sandwich Contact.** C. Gong, R.M. Wallace, K.J. Cho, Y.J. Chabal, The University of Texas at Dallas

Two types of interfaces can be formed between metals and graphene depending on the strength of the metal-graphene interaction: weak (metal physisorption) and strong (metal chemisorption) interfaces. "Physisorption" interfaces (e.g., with Al, Ag, Cu, Ir, Pt and Au) are characterized by a larger metal-carbon distance ($>3 \text{ \AA}$) with some charge transfer between metal and graphene (i.e. doping of graphene) that maintains its overall π -band dispersion. "Chemisorption" interfaces (e.g. with Ni, Co, Pd, and Ti) are characterized by a smaller metal-carbon distance ($<2.5 \text{ \AA}$) and strong orbital hybridization between metal- d and carbon- p_z orbitals, resulting in the destruction of the graphene's π -band dispersion around the Dirac point. Till now, only a small fraction of all available metals has been used as electrode materials for carbon-based devices due to metal-graphene interface debonding problems. The issue therefore is to keep graphene's intrinsic π bandstructure by using weakly interacting metals while enhancing the interface stability.

We report an enhancement of the bonding energy of weakly interacting metals by using a metal-graphene-metal sandwich geometry, without sacrificing the intrinsic π -electron dispersions of graphene that is usually undermined by strong metal-graphene interface hybridization. This sandwich structure further makes it possible to effectively tune the doping of graphene with an appropriate selection of metals. Density functional theory calculations reveal that the strengthening of the interface interaction is ascribed to an enhancement of interface dipole-dipole interactions. Raman scattering studies of metal-graphene-copper sandwiches are used to validate the theoretically predicted tuning of graphene doping through sandwich structures.

2:20pm **GR+AS+EM+NS+SS-WeA2 Defects in Two-Dimensional Materials and their Heterostructures.** L. Adamska, I.I. Oleynik, University of South Florida

Recent developments in graphene electronics have stimulated an interest in other two dimensional materials such as hexagonal boron nitride (BN) and molybdenum disulfide (MoS_2). In contrast to graphene, BN and MoS_2 possess appreciable band gap and may form good interfaces with graphene, which opens up exciting opportunities for development of novel nanoelectronic devices. For practical applications, it is important to understand the effect of defects, which appear during growth and processing, on resulting electronic properties. The defects in graphene, BN, MoS_2 and their heterostructures have been investigated by first-principles density functional theory. Their effect on electronic properties including density of states and simulated STM images will be discussed.

4:00pm **GR+AS+EM+NS+SS-WeA7 Metal Oxide Growth and Characterization on CVD Graphene.** A. Matsubayashi, College of Nanoscale Science and Engineering, University at Albany

Thin metal oxide layers deposited on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel. This is important for graphene based spintronic devices as dielectric layers between the ferromagnetic electrode and graphene have been shown to increase the spin relaxation time measured utilizing non-local detection and spin precession measurements^[1]. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier^[2]. In addition it is important to understand the stoichiometry of the resulting film. We will present a systematic study of aluminum oxide layers grown on CVD (chemical vapor deposition) graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS (X-ray photoelectron spectroscopy) will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium.

References:

(1) E. I. Rashba, Phys. Rev. B, **62**, 16267 (2000)

(2) W. Han *et al*, Phys. Rev. Lett., **105**, 167202 (2010)

4:20pm **GR+AS+EM+NS+SS-WeA8 Bi-layer Graphene Growth on Ni(111): The Role of Monolayer Graphene Rotation.** A. Dahal, A. Rafik, University of South Florida, P.W. Sutter, Brookhaven National Laboratory, M. Batzill, University of South Florida

Bi-layer graphene synthesis by chemical vapor deposition is of importance for field effect devices because the band gap can be tuned in bi-layer graphene by an applied electric field. Here, we demonstrate that bi-layer graphene can be synthesized above 650°C by chemical vapor deposition on thin Ni(111) films grown on YSZ(111) substrates in ultra high vacuum (UHV). We characterize the bi-layer graphene growth by low energy electron microscopy (LEEM), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Below 600°C graphene grows in registry with the Ni(111) lattice and no second layer graphene is formed upon cooling. At 650°C rotationally misaligned graphene domains are formed on Ni(111) and we observe second layer graphene to grow by carbon-segregation under those rotated monolayer graphene domains. The difference in second layer graphene nucleation and growth is explained by the graphene-Ni interaction, which is much stronger for graphene in registry with the substrate than for rotated graphene. The segregated second layer graphene sheet is in registry with the Ni(111) substrate and this suppresses further carbon-segregation, effectively self limiting graphene formation to two layers.

4:40pm **GR+AS+EM+NS+SS-WeA9 Energetic and Kinetic Factors of Graphene Nucleation on Cu.** N. Safron, M.S. Arnold, University of Wisconsin-Madison

Chemical Vapor Deposition (CVD) of graphene on Cu substrates uniquely allows for growth of uniform monolayer graphene and is a promising route for its scalable production for many industrial applications due to low cost. The growth is a purely surface driven process, due to carbon's low solubility in the Cu substrate, and relies on the Cu surface catalytically decomposing a carbon precursor (methane). As the growth of graphene proceeds across the surface, the reactivity of the Cu is passivated by the graphene, making the growth self-limiting to monolayer coverage. Research interest on the control of nucleation is intensifying, as the polycrystalline character of the graphene films can limit mobility, thermal conduction, and mechanical strength via grain boundaries.

In this paper, we study the nucleation dependencies of graphene at ambient pressure CVD in the context of surface nucleation theory. At low methane partial pressures, the concentration of carbon on the surface on the copper is low and carbon clusters cannot grow to a critical size for nucleation. As the partial pressure is increased, the methane partial pressure reaches a critical value and nucleation occurs. Tracking the critical pressure as a function of temperature from 880 to 1075°C , we have determined the formation energy of the critical graphene nucleus to be $\sim 1.5 \text{ eV/carbon atom}$, via the relation $c_{\text{muc}} \sim \exp(-E_{\text{form}}/k_{\text{B}}T)$. Additionally, we have found that the nucleation density of the graphene varies by 5 orders of magnitude over this temperature range at the critical methane concentration. The results are described under the desorption controlled regime of surface cluster nucleation.

Growths near the critical methane concentration yield hexagonal growing graphene domains characteristic of attachment limited kinetics, while at higher rates yield other growth shapes. Characterization by Raman Spectroscopy has been used to identify defects in the graphene layers. We find that the Raman defect band (D-Band) scales with the root of the nucleation density, indicating the majority of defects are located at the domain boundaries and the D-band intensity scales with the distance between them. Electrical mobility measurements show nearly constant values in samples across the range of temperatures indicating other limiting factors besides internal defects. Growths at 900°C yield $\mu > 1000 \text{ cm}^2/\text{Vs}$, ON/OFF ratio ~ 10 , and Raman D/G ratio < 1 , demonstrating high quality of growth even at relatively low temperatures.

5:00pm **GR+AS+EM+NS+SS-WeA10 Magnetic Spin Reorientation Transition in Graphene Covered Cobalt on Iridium(111).** A.T. N'Diaye, Lawrence Berkeley National Laboratory, J. Coraux, N. Rougemaille, C. Vo-Van, O. Fruchart, Institut NÉEL, CNRS & Université Joseph Fourier, France, A.K. Schmid, Lawrence Berkeley National Laboratory

One of graphene's promises is to be material for spintronic applications. While the influence of a magnet on graphene is under intense investigation by many groups little attention is given to the influence of graphene on a magnet.

With spin polarized low energy electron microscopy (SPLEEM) we studied thickness dependent spin reorientation transition on this system and

compare with Co/Ir(111) without graphene. Monitoring the spin orientation in three dimensions while increasing the film thickness by one ML at a time, we find that the presence of graphene on the film at least doubles the thickness at which the spin reorientation from out-of-plane to in-plane occurs from 6ML Co to transition to 12ML-13ML at 300°C and to between 14ML and 20ML at room temperature.

We attribute the significant contribution of the graphene/Cobalt interface to the magnetic anisotropy energy to a strong hybridization of graphene with Cobalt in directional bonds.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, by the French ANR contract ANR-2010-BLAN-1019-NMGEM and by the Alexander von Humboldt Foundation.

5:20pm **GR+AS+EM+NS+SS-WeA11 Nucleation and Growth of Rh and Au Clusters on Graphene Moiré/Ru(0001)**, *B. Habenicht*, Oak Ridge National Laboratory, *D. Teng*, Georgia Institute of Technology, *L. Semidey-Flecha*, Oak Ridge National Laboratory, *D. Sholl*, Georgia Institute of Technology, *Y. Xu*, Oak Ridge National Laboratory

Nanometer and sub-nanometer sized metal clusters may possess electronic and catalytic properties that differ greatly from those of the corresponding bulk metals. For potential applications, dense arrays of uniform metal clusters are desirable. However, the synthesis of such cluster materials remains a formidable challenge. Moiré superstructures that develop in graphene supported on certain metals have been shown to be viable templates for driving the formation of uniform metal clusters.[1] On graphene moiré (GM) on Ru(0001), dispersed clusters are obtained for Rh whereas Au coalesces into very large 2D islands.[2,3] We carry out a computational study to understand the disparate morphologies of Rh and Au clusters on GM/Ru(0001) via a multi-scale approach. DFT calculations are performed to study the adsorption and diffusion of the adatom and ad-clusters of Rh and Au on GM/Ru(0001) and the bonding mechanism between the metals, graphene, and Ru substrate. The potential energy landscape is then used to perform kinetic Monte Carlo simulations for the diffusion, nucleation, and growth of Rh and Au clusters. This approach allows us to predict the spatial and size distribution of the metal clusters and may be generally applicable to identifying the conditions necessary for obtaining desired cluster morphologies on GM.

(1) N'Diaye, A. T.; Bleikamp, S.; Feibelman, P. J.; Michely, T. *Phys. Rev. Lett.* **2006**, 97, 215501.

(2) Zhou, Z.; Gao, F.; Goodman, D. W. *Surf. Sci.* **2010**, 604, L31.

(3) Xu, Y.; Semidey-Flecha, L.; Liu, L.; Zhou, Z.; Goodman, D.W. *Faraday Discuss.*, **2011**, 152, 267.

5:40pm **GR+AS+EM+NS+SS-WeA12 Graphitic and Pyridinic N Species on N-doped HOPG Studied by STM, STS, PES and DFT**, *M. Sakurai*, *T. Shikano*, *D. Ushigome*, *T. Suzuki*, University of Tsukuba, Japan, *Y. Harada*, *M. Oshima*, University of Tokyo, Japan, *S. Casolo*, University of Milan, Italy, *M.I. Trioni*, ISTM, Italy, *G.F. Tantardini*, University of Milan, Italy, *T. Kondo*, *J. Nakamura*, University of Tsukuba, Japan

Nitrogen doped graphene and carbon nanotube have been reported to show superior catalytic activity or superior support effect in the fuel cell. However, effects of the dopant nitrogen on the modification of the electronic structure of such graphite-related materials have not been clarified because a wide variety of defects with different types of C-N bonding configurations can coexist in nitrogen doped graphite.

Here, we report comprehensive atomic-resolution characterization of the defects in a nitrogen-doped graphite surface by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), Photoemission spectroscopy (PES) and first-principles calculations based on the density functional theory (DFT). Nitrogen-doped graphite was produced by nitrogen ion bombardment of the HOPG (highly oriented pyrolytic graphite) followed by thermal annealing at about 900 K.

Two types of nitrogen species were identified at the atomic resolution. One is pyridinic N (N having two C nearest neighbors) with single-atom vacancy. The other is graphitic N (N having three C nearest neighbors). In the case of pyridinic N with single vacancy, the local electronic states of the non-bonding pz orbital of carbon are found to appear at occupied region near the Fermi level at the carbon atoms around pyridinic N. On the other hand, the local electronic states of the non-bonding pz orbital of carbon are found to appear at unoccupied region near the Fermi level at the carbon atoms around graphitic N.

These results indicate that in both cases more than 300 carbon atoms are found to be modified by the dopant N to show the non-bonding pz orbitals. Moreover, these results suggest that the graphitic-N and pyridinic-N as well as their surrounding carbon atoms may act as "acid" and "base", because their non-bonding pz orbitals appear at empty and occupied region, respectively.

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. Lemaire*, A.F. Hebard, *B. Gila*, University of Florida, *A. Nadzeyka*, Raith GmbH, Germany, *F. Ren*, *X. Wang*, University of Florida, *D.K. Venkatchalam*, *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 laser².

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 MIBL³. 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. Lemaire, 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 Unripping 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 unripping 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 SiO₂. We obtained the latter system by using the recently developed transfer-free approach [2] based on the synthesis of SiO₂ 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 SiO₂). 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 $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ 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 H₂O₂.** *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 nanoclusters, nanoflakes 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 Institute 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: HfO₂, Hf_xZr_{1-x}O₂, Hf_xAl_{1-x}O₂ and Hf_xGd_{1-x}O₂. 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 GeO₂ layer (0.7 nm thick) followed by a thin (2 nm) ALD Al₂O₃ layer. The Al₂O₃ layer, which has high band offsets to Ge and GeO₂, was added since HfO₂, as many of the leading candidates for high-k dielectrics, are unstable on top of Ge or GeO₂. 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.

Graphene and Related Materials Focus Topic

Room: 13 - Session GR+AS+NS+SS-ThM

Graphene Nanostructures

Moderator: A. Kis, EPFL, Switzerland

8:00am **GR+AS+NS+SS-ThM1 Atomic and Electronic Structures of Graphene Nanoribbon made by MBE on Vicinal SiC Substrate.** F. Komori, K. Nakatsuji, T. Yoshimura, University of Tokyo, Japan, T. Kajiwara, K. Takagi, S. Tanaka, Kyushu University, Japan

Electronic states of graphene nanoribbon attract much interest because its intrinsic metallic band is modified to have a gap or a one-dimensional edge state at the Dirac energy E_D . Actually, microfabricated graphene [1] showed an energy gap at E_D , and the gap size increases with decreasing the width. Fabrication of well-controlled graphene nanoribbons on macroscopic area of a semiconductor substrate is, however, still one of the challenging issues in graphene research. Here, we report characterizations of graphene nanoribbon made by carbon molecular beam epitaxy (MBE) and a hydrogen treatment on a vicinal SiC(0001) substrate. Use of MBE is essential because graphene is made over the step edges of the SiC substrate in the case of graphene formation by widely-used thermal decomposition.

In the experiment, a $6\sqrt{3} \times 6\sqrt{3}$ structure was first made by MBE on the anisotropic terrace of the Si-terminated surface of a nitrogen-doped 6H-SiC(0001) substrate vicinal to the [1-100] direction. The tilting angle of the substrate was 4 degree, and a well-ordered step-and-terrace structure was made after cleaning the substrate by annealing in hydrogen as confirmed by atomic force microscopy. We optimized the substrate temperature and the carbon deposition rate to make a homogeneous $6\sqrt{3} \times 6\sqrt{3}$ structure on the terraces without thermal decomposition of the substrate. The surface structure was *in situ* monitored by reflection high energy electron diffraction, and the width of the $6\sqrt{3} \times 6\sqrt{3}$ area on the terrace was adjusted by monitoring the $6\sqrt{3} \times 6\sqrt{3}$ spots. After stopping the growth, the sample was exposed to hydrogen molecules at 600 °C to transform the surface $6\sqrt{3} \times 6\sqrt{3}$ layer to single-layer graphene by inserting hydrogen atoms at the interface. [2]

Graphene honeycomb lattice without the $6\sqrt{3} \times 6\sqrt{3}$ structure was confirmed by low energy electron diffraction and scanning tunneling microscopy (STM). Few point defects are seen at the graphene on the terrace in the STM images of atomic resolution. The width of graphene nanoribbon on the substrate terrace is 10-15 nm, depending on the growth condition. The electronic states of the graphene nanoribbon were studied using angle-resolved photoemission spectroscopy (ARPES) at 130 K as in the previous report. [3] The top of the π band of the graphene nanoribbon was 0.05 ~ 0.25 eV below the Fermi energy. No signal from the π^* band was detected by ARPES above the top of the π band, indicating the gap formation at E_D .

References

1. M. Y. Han *et al.*, Phys. Rev. Lett. **98**, 206805 (2007).
2. C. Riedl *et al.*, Phys. Rev. Lett. **103**, 246804 (2009).
3. K. Nakatsuji *et al.*, Phys. Rev. **B82** 045428 (2010).

8:20am **GR+AS+NS+SS-ThM2 Carrier Transport Behavior of Carbon Nanotube Transistors with Single Semiconducting and Metallic Tube.** P. Sakalas, M. Schroter, Technische Universität Dresden, Germany

The high interest in using carbon nanotube FETs in advanced electronics is based on their unique 1D transport properties such as quasi-ballistic transport. The high carrier velocity together with the quasi 1D tube geometry yield a very low intrinsic capacitance per tube of approximately 80 aF/mm in multitube structures. Those properties makes CNTFETs very interesting for high frequency and power applications.

CNTFETs with a single semiconducting tube yield too low current (25 μ A) for useful applications and thus the transistors with thousands tubes in parallel are being fabricated [1][2]. Unfortunately, following theory 1/3rd of all tubes are metallic. Carrier scattering is better understood for metallic tubes and it is believed that for semiconducting tubes, despite more complexity, the same scattering mechanisms are applicable: CNTs defect scattering, physical bends and phonon scattering are present. Investigation of CNTFETs with a single semiconducting (ST), single metallic (MT) and metallic+semiconducting (MST) tubes at different lattice temperature environment was never done before and enables a deeper insight of CNT transport properties to further improve the application-oriented device behavior. It was shown that multifinger CNTFETs exhibited a weak temperature dependence of IV, RF and NF indicating a very weak electron-

phonon interaction and the absence of charge-carrier freeze-out known for conventional doped semiconductors [3],[4].

In this work transistors with single ST, single MT and double MST were selected. Transistors have 800 nm channel length and features n-type behavior. IV characteristics were measured on wafer for manufacturable CNTFET process selected single CNTs at different lattice temperatures. The investigated structures have a fixed gate length of 0.35 μ m and gate width of 40 μ m. The source-drain spacing (channel length) is 800 nm. A 20 nm thick HfO₂ was used for the gate oxide. The devices were fabricated with the process technology described in [1][2]. The CNTFETs were embedded in DC pads for on-wafer measurements. Transfer characteristics of ST and MT transistor structures at ambient temperature $T_0 = 300$ K, are shown in Fig.1 and Fig.2, Fig.3, Fig.4. The drain current show saturation for ST device, typical for MOSFETs. Nevertheless the carrier transport is very different. The dependence of drain current over the temperature will enable the analysis of transport behavior of single ST and MT and coupled MST. As it is seen from Fig.3 and Fig.4 the MT transistor structure behaves as nonlinear resistor.

8:40am **GR+AS+NS+SS-ThM3 Fabrication of Chemically-isolated Graphene Nanoribbons (GNRs) by Scanning Probe Nanolithography using a Heated Probe.** W.K. Lee, J.T. Robinson, R. Stine, C.R. Tamanaha, D. Gunlycke, Naval Research Laboratory, M. Haydell, E. Cimpoiasu, U.S. Naval Academy, W. King, University of Illinois at Urbana Champaign, P.E. Sheehan, Naval Research Laboratory

One route to realizing graphene as a material for digital-type devices is through the lithographic patterning of graphene nanoribbons (GNRs). GNRs enable band gap engineering that is dependent on nanoribbon width and edge state. We employed two complementary AFM-based lithography techniques to pattern GNRs: (1) thermal dip-pen nanolithography (tDPN)¹ and (2) thermochemical nanolithography (TCNL)². Though inverse in approach, both techniques generate GNRs into a larger sheet of insulating chemically-modified graphene. Both lithographies were performed on CVD-grown single-layered graphene (SLG) on SiO₂/Si substrates using heated AFM probes. The first approach, tDPN, used the heated probe to deposit narrow polystyrene (PS) ribbons on pristine graphene. The areas of the graphene not protected by the polymer were then fluorinated, converting them to a highly insulating state, which leaves behind a chemically isolate GNR channel. We show that the PS protected ribbon was the only conductive pathway for active device. Secondly, we use the converse approach by using the heated AFM probe to locally reduce fluorographene back to graphene, leaving behind a conductive GNR channel. Both techniques can generate a wide range of nanoribbon widths while avoiding electron beams which can damage graphene. We discuss the relative merits of each strategy, as well as their impact on electrical properties (e.g., doping).

1. WK Lee *et al.*, *Nano Letters*, **11**, 5461, 2011

2. Z Wei *et al.*, *Science*, **328**, 1371, 2010

9:20am **GR+AS+NS+SS-ThM5 Growth of a Linear Topological Defect in Graphene as a Gate-tunable Valley Valve.** A. Zettl, J.-H. Chen, N. Alem, Univ. of California at Berkeley, Lawrence Berkeley Lab, G. Autes, F. Gargiulo, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, A. Gautam, M. Linck, Lawrence Berkeley National Lab, C. Kisielowski, Lawrence Livermore National Lab, O.V. Yazyev, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, S.G. Louie, Univ. of California at Berkeley, Lawrence Berkeley Lab

INVITED

The valleytronics, a zero-magnetic-field equivalent of spintronics, could be realized in graphene if a simple scheme can be conceived to generate and to detect valley polarization in the material. Here we provide the first direct experimental observation of the self-sustained, atomically controlled growth of a peculiar linear defect structure in suspended graphene. The structure consists in units of octagon and pentagon pairs (termed 5-5-8 defect) and can be grown from a single pentagon seed in graphene under electrical bias. First-principle simulations show that the 5-5-8 defect can act as a gate-tunable valley valve. The result represents a critical step towards realizing valleytronics in graphene.

10:40am **GR+AS+NS+SS-ThM9 Crystalline and Electrical Properties of Vertically-Laminated Carbon Nanowalls formed by Two-Step Growth Method.** H. Kondo, T. Kanda, Nagoya University, Japan, M. Hiramatsu, Meijo University, Japan, K. Ishikawa, M. Sekine, M. Hori, Nagoya University, Japan

Carbon nanowall (CNW) is one of carbon nanomaterials consisting of stacked graphene sheets, which are vertically standing on the substrate. Due to the unique properties of graphene sheets, such as high carrier mobility,

large current carrying capability, and so forth, it is expected that the CNW also have such the excellent electrical and physical properties. On the other hand, In the CNWs, the bending and branching graphene sheets take a maze-like form. Therefore, due to their unique morphology and properties, the CNWs are promising as channel and electrode materials in the various types of the future nanoelectrics devices. At the construction of the CNW devices, vertical lamination of different types of CNWs is one of the useful and important technique as basic elements of the devices.

In this study, we investigated sequential two-step growth of CNWs to form the vertically-laminated structures. In this experiment, two types of CNW growth processes with different conditions were sequentially performed on Si substrate by an electron beam excited plasma-enhanced chemical vapor deposition (EBEP-CVD) using CH₄/H₂ mixture gas. Firstly, the CNW was grown at 600°C and 2.67 Pa for 10 min. Then, the second-step growth process was performed at 480°C for 10 min. The CNW samples formed only by the single-step growth at 480°C or 600°C were also prepared for comparison. Morphology and crystalline structures of CNWs were analyzed by scanning electron microscopy and Raman spectroscopy.

In the case of the single-step growth, only after the growth at 600°C, about 600 nm-thick CNWs were formed, although CNWs hardly grew at 480°C. On the other hand, in the case of the step-growth, about 1200 nm-thick CNWs were formed after the second-step growth at 480°C, compared to the single-step growth at 600°C. No boundary was found between the lower and upper region. The stacks of graphene sheets formed seamless structures. According to the Raman spectra, the crystalline structures of the CNWs were hardly changed even after the first-step growth at 600°C and the second-step growth at 480°C. This result means that the nanographene can restart to grow easily and continuously at the edges of the previously-grown graphene even at 480°C without the nucleation. These results indicate the possibility to realize the vertical junction of different types of CNWs, such as a p-n junction. At the session, the interfacial structures and electrical properties of the vertically-laminated CNWs will also be discussed.

11:00am **GR+AS+NS+SS-ThM10 Surface Modification of Vertically Oriented Graphene Electrochemical Double-Layer Capacitors**, *R.A. Quinlan*, Naval Surface Warfare Center, Carderock Division, *M. Cai*, The College of William and Mary, *A.N. Mansour*, Naval Surface Warfare Center, Carderock Division, *R.A. Outlaw*, The College of William and Mary

Previously reported efforts have identified the potential of vertically oriented graphene nanosheets in electrochemical double-layer capacitors (Miller et. al, Science 2010) for efficient AC line-filtering performance. Continued investigations to improve performance suggest that the availability of a high edge and surface defect density could be the dominant mechanism. Furthermore, charge/discharge profiles over time show that performance can actually increase as the device ages. In an effort to understand these findings, X-ray photoelectron spectroscopy, Auger electron spectroscopy and near edge absorption fine structure spectroscopy have been utilized to study the interaction of the electrolytes and solvents with the graphene-based electrode materials. The EDL capacitance of graphene nanosheets has been measured before and after Ar plasma bombardment for various times and after exposure to water, isopropanol, methanol, NaOH and KOH. Graphene nanosheet electrochemical capacitors have been disassembled and analyzed following short term and long term operation.

11:20am **GR+AS+NS+SS-ThM11 Electronic Properties and Device Applications of Wafer-Scale Graphene Nanoribbons**, *D. Jena*, University of Notre Dame **INVITED**

Graphene boasts unique physical, electronic, and optical properties. For conventional electronic device applications, the zero band gap of 2-dimensional graphene is an impediment. Opening of effective band gaps can be achieved by field-effect in bilayer graphene, or by using Klein-tunneling properties of graphene p-n junctions. However, these methods appear not to effectively scale to small dimensions. Another way to open band gaps in graphene is to make graphene nano ribbons (GNRs) and use size quantization. Though many of the properties of 2D graphene are lost in the process, GNRs become similar to semiconducting carbon nanotubes, but with planar structures and compatibility with conventional lithographic processes. In this talk, I will present our group's research progress in making such wafer-scale GNR transistors. Band gaps ~0.15 eV appear in ~10 nm wide single GNRs, and band gaps are preserved in parallel arrays of GNRs. Based on these GNRs, we measure current drives as high as 10mA/micron, which far exceeds all other semiconductor materials and seems attractive for both logic and interconnect applications. The effects of edge roughness on scattering and mobility, and the progress towards making GNR-based tunneling transistors will also be presented.

Thursday Afternoon, November 1, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+SS+GR+SP-ThA

Electron Transport at the Nanoscale: Molecules and Defects

Moderator: S. Allen, The University of Nottingham, UK, J. Wendelken, Oak Ridge National Laboratory

2:00pm **ET+SS+GR+SP-ThA1 Molecule Substrate Interactions Probed by Scanning Tunneling Microscopy, H.-J. Gao**, Chinese Academy of Sciences **INVITED**

Molecule substrate interactions play an important role in constructing nanostructures of functionalities and controlling of the physical properties and thus have stimulated a great interest in the past decades. One of the challenges in this top is to make a single molecule or small quantum systems stably connected to a single metal atom on metal surfaces, and further to make the nanostructure create electric energy and optical/electro radiation. In the talk, I will present that by using Au adatoms of the Au(111) surface we have successfully formed a single molecule rotor array, isolated tetra-*tert*-butyl Zinc Phthalocyanine ((*t*-Bu)₄-ZnPc) molecules sticking to the Au adatoms of the Au(111) and rotating on the surface at 78 K. This kind of single molecular rotor was also found to be controlled by the different sites of the Au(111) surface using low temperature scanning tunneling microscopy (STM). Furthermore, by changing the molecular structure the same molecular family of the Pc, ZnPc and FePc can also modulate the rotation behavior of the molecular rotors. Given that the lateral structure of a molecule/substrate interface can be modified by the attachment of ligands, our results will be helpful for opening up the possibility to tailor physical properties of a single molecule or complex aggregates to the desired specifications.

2:40pm **ET+SS+GR+SP-ThA3 Electron Localization in Single Mixed-Valence Molecules, R.C. Quardokus, N.A. Wasio, Y. Lu, S.A. Kandel**, University of Notre Dame

Scanning tunneling microscopy (STM) is used to study two dinuclear organometallic molecules, meta-Fe₂ and para-Fe₂. These molecules share identical molecular formulas but differ in their positions of connectivity to the central phenyl ring. STM images of neutral meta-Fe₂ and para-Fe₂ show symmetrical distribution of electron density across the two metal centers. Chemical oxidation of these molecules leads to mixed-valence species. STM images of mixed-valence meta-Fe₂ show an asymmetric distribution of the electron density between the two metal centers. Despite the greater distance between the two metal centers, the electron density remains symmetric in mixed-valence para-Fe₂. Comparison with constrained density functional (CDFT) calculations leads to the conclusion that through-bond coupling of the two metal centers is more prevalent than through-space coupling. Further investigation of mixed-valence dinuclear organometallic molecules with asymmetric electron state density may open up the possibility for their use in molecularly based electronic devices.

3:00pm **ET+SS+GR+SP-ThA4 Rectification by a Single Molecular Diode, L. Adamska**, University of South Florida, *M. Kozhushner*, Institute of Chemical Physics, Russian Academy of Sciences, *I.I. Oleynik*, University of South Florida

Single-molecule rectification has been recently observed using the STM modulated break-junction technique in non-symmetric diblock dipyrimidinyl-diphenyl molecule covalently bound to metallic electrodes. To provide an insight to the nature of the rectification, first-principles calculations of atomic, electronic and transport properties of gold/molecule/gold junctions have been performed for both symmetrical tetraphenyl and asymmetrical dipyrimidinyl-diphenyl diblock molecules. The charge transport was found to occur by hole resonant tunneling mechanism via positively-charged hole states of the molecule, which are very susceptible to the external electric field and dispersive interactions with the metallic electrodes. It was found that the rectification effect in chemically-asymmetric dipyrimidinyl-diphenyl molecule is due to strong localization of the hole wave function at one end of the diblock under applied electric field. Such behavior is contrasted by symmetric I-V curves exhibited by symmetric tetraphenyl molecule.

3:40pm **ET+SS+GR+SP-ThA6 Electron Transport Study of Graphene Grain Boundaries Using Scanning Tunneling Potentiometry, K. Clark, X.-G. Zhang, I. Vlasiouk, A.-P. Li**, Oak Ridge National Laboratory

Graphene, due to its unique electronic structures, has quickly become one of the most notable "super-materials" poised to transform the electronics and nanotechnology landscape. The symmetry of the graphene honeycomb lattice is a key element for determining many of graphene's unique electronic properties, such as the linear energy-momentum dispersion and the reduced backscattering (i.e., high carrier mobility). However, topological lattice defects, such as grain boundaries and step edges, break the sublattice symmetry and can affect the electronic properties, especially in transport of graphene in unexpected ways. To utilize the full potential of graphene a complete understanding of the physical and electronic properties of defects in this system is needed. By using a scanning tunneling potentiometry method with a low temperature four-probe scanning tunneling microscope, two-dimensional maps of electrochemical potentials have been measured across individual grain boundaries on the graphene films grown on copper foil and transferred to SiO₂. An Atomic Force Microscope (AFM) is implemented to image the grain boundary that forms between individual graphene flakes that grow on the surface. The AFM imaging along with scanning tunneling potentiometry characterize the grain boundaries formed between coalesced grains on the SiO₂ surface. Results of the influence of the grain boundary on the electronic transport across this potentially revolutionary new electronic system will be presented. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

4:00pm **ET+SS+GR+SP-ThA7 Static and Dynamic Conductance in Topological Defects in Ferroelectrics, S.V. Kalinin**, Oak Ridge National Laboratory **INVITED**

Topological defects in ferroic materials are attracting much attention both as a playground of unique transport, magnetic, and ferroic phenomena and due potential applications in reconfigurable electronic devices. In this presentation, I will summarize recent studies of transport phenomena in 2D (domain walls) and 1D (vortexes and antivortexes) in ferroelectric materials by combination of piezoresponse force microscopy, phase-field modelling, and density functional theory. In particular, the observations such as memory effects and hysteresis in domain wall conductance, metallic conductivity of ferroelectric walls, and conductivity in vortex cores will be discussed. For domain walls, these observations are consistent with carrier accumulation due to presence of charged wall segments. We further demonstrate that a continuum of non-volatile metallic states across decades of conductance can be encoded in the size of ferroelectric nanodomains using electric field. For vortexes, modelling predicts that the core structure can undergo a reversible transformation into a metastable twist structure, extending charged domain walls segments through the film thickness. The vortex core is therefore a dynamic conductor controlled by the coupled response of polarization and electron/mobile vacancy subsystems with external bias. This controlled creation of conductive 1D channels opens a pathway for design and implementation of integrated oxide electronic devices based on domain patterning. Finally, recent insight on domain walls structure from combination of aberration corrected scanning transmission electron microscopy and phase-field theory will be discussed. Research supported (SVK) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and partially performed at the Center for Nanophase Materials Sciences, a DOE-BES user facility.

4:40pm **ET+SS+GR+SP-ThA9 Transport and Mechanical Properties of Molecular Junctions formed by Acetophenon Deposited on Si (100) Surface, M. Setvin, Z. Majzik, O. Krejci, P. Hapala, P. Jelinek**, Institute of Physics of ASCR, Czech Republic

One of the main challenges of Molecular electronics is to understand and control charge transfer through a reproducible single molecule contact between electrodes. Most investigations of electron transport through molecules have been performed in "blind" junction experiments, where the molecular conformation and contact geometry cannot be probed. Therefore large gaps in our knowledge remains since in molecular electronics the atomic-scale structure of the entire junction including the leads is important for its conductance properties.

Our goal is to study electrical transport through well-defined molecular junction on semiconductor surfaces. Formation of molecular junctions using organic molecules on semiconductor surfaces might lead to interesting phenomena. For example, the presence of the band gap in electrodes can

lead to the negative differential resistance observed in transport through molecules bonded to dangling-bond sites[1].

In this contribution, we investigate formation of molecular junction consisting of a single acetophenone molecule deposited on Si(100) surface in upright position by means of simultaneous AFM/STM measurements and DFT calculations. We used a modified UHV VT STM/AFM Omicron machine allowing simultaneous acquisition of the current and forces with atomic resolution using a tuning fork sensor[2]. The simultaneous acquisition of the tunneling current and force during tip approach allows precise control of contact formation and its consequence on the charge transport through molecular junction[3]. On other hand, DFT simulations provide more insight into interaction mechanism between probe and molecule. It also helps to understand induced structural and electronic relaxations during tip approach.

References

- [1] T. Rakshit et al. Nanoletters 4, 1803–1807 (2004).
- [2] Z. Majzik et al, Beilstein J. Of Nanotech. 3, 249 (2012).
- [3] N. Fournier et al Phys. Rev. B 84, 035435 (2011).

5:00pm ET+SS+GR+SP-ThA10 Experimental Determination of the Charge Neutrality Level (CNL) of Conjugated Polymers, W. Wang, R. Schlaf, University of South Florida

The charge neutrality levels (CNL) of poly-(3-hexylthiophene) (P3HT) and poly-[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) were determined. This was achieved by investigating a number of interfaces between these conjugated polymers and metals with varying work function. The interfaces were fabricated using the electrospray deposition technique, which allows the direct deposition of polymers from solution into vacuum environment without interference of significant surface contamination. This enabled the measurement of the charge injection barriers at clean polymer interfaces without contamination interlayer with photoemission spectroscopy. The results of these measurements enabled the establishment of the correlation between barrier heights and substrate. The results indicate that conjugated polymer interfaces form in a similar fashion as small molecular materials interfaces to metals as described by the 'induced density of states' (IDIS) model. In contrast, the presented results also suggest that the 'integer charge transfer' (ICT) model, which was developed for polymer/metal interfaces, only describes interfaces prepared under atmosphere or inert environment, where the presence of contamination weakens the interaction between the materials in contact.

5:20pm ET+SS+GR+SP-ThA11 Investigation on the Electronic Structure of Arylthio (ArS)-functionalized CdSe Nanoparticle Hybrid Materials, Z. Li, University of South Florida, K. Mazzi, University of Washington, S. Gutmann, University of South Florida, C.K. Luscombe, University of Washington, R. Schlaf, University of South Florida

CdSe nanoparticles are a promising material for 3D heterojunction solar cells due to their tunable electronic and optical properties through size control. By covalently bonding these nanoparticles to organic ligands, a novel light absorption, charge separation and transportation system can be formed. This presentation will discuss efforts to measure the hybrid-internal orbital line-up at the nanoparticle/ligand junction. Photoemission spectroscopy was used to characterize a prototypical arylthio (ArS)-functionalized CdSe molecule nanoparticle/ligand hybrid. Generally, in such hybrid molecules, the highest occupied molecular orbital (HOMO) emission is a superposition of the emissions of the nanoparticles and that of the organic ligands. This superposition makes the direct study of the orbital line-up through PES measurements impossible. Hence, a new technique needed to be developed to delineate the orbital line-up at such inner-molecular contacts. This was achieved through the additional investigation of the isolated components, which yielded detailed information of their electronic structure. Combination of this data with measurements on the assembled hybrid molecules enabled the determination of the orbital line-up at the interface. The influence of the covalent bond on the orbital line-up was investigated by comparing the hybrid line-up with the electronic structure of a physisorbed interface formed between the hybrid components. This interface was prepared through in-vacuum electrospray deposition of a thin film sandwich of CdSe and ArSH films, while measuring the transition from the CdSe to the ArSH electronic structure.

Graphene and Related Materials Focus Topic Room: 13 - Session GR+EM+NS+SS+TF-ThA

Beyond Graphene: BN and Other 2D Electronic Materials; 2D Heterostructures

Moderator: I.I. Oleynik, University of South Florida

2:00pm GR+EM+NS+SS+TF-ThA1 X-ray Photoelectron Spectroscopy Investigation of the Valence and Conduction Band Offset at Hexagonal a-BN:H/Si Interfaces, S. King, M. French, J. Bielefeld, Intel Corporation, M. Jaehnig, Intel Corporation, M. Kuhn, B. French, Intel Corporation

Due to a wide band gap (~ 6 eV) and close lattice matching, hexagonal boron nitride (h-BN) is of interest as a potential gate dielectric in graphene channel transistor devices. A key property for the success of h-BN as a gate dielectric in such devices is the valence and conduction band offsets at the h-BN/graphene and h-BN/gate electrode interfaces. In many graphene channel devices, amorphous or poly-Si is a desirable gate electrode material for compatibility in standard CMOS processing. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the valence band offset present at the interface between plasma enhanced chemically vapor deposited hexagonal a-BN:H and a (100) Si substrate. Combined with Reflection Electron Energy Loss Spectroscopy measurements of the a-BN:H band gap, we have also been able to determine the conduction band offset at this interface. The combined measurements indicate a type I alignment with valence and conduction band offsets of 1.95 ± 0.1 and 2.15 ± 0.17 eV respectively.

2:20pm GR+EM+NS+SS+TF-ThA2 Monolayer Graphene-Boron Nitride 2D Heterostructures, R. Cortes, J. Lahiri, E. Sutter, P.W. Sutter, Brookhaven National Laboratory

Unusual electronic properties have been predicted for monolayer graphene-boron nitride heterostructures, but access to these properties depends on methods for controlling the formation of graphene-boron nitride interfaces [1]. Here we report on the growth and interface formation of monolayer graphene (MLG)-hexagonal boron nitride (h-BN) 2D heterostructures on Ru(0001), investigated by a combination of real-time low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM).

LEEM observations of sequential chemical vapor deposition growth show that h-BN attaches preferentially to the edges of existing MLG domains, while nucleation of h-BN on the Ru surface away from MLG is not observed at the conditions considered here. With increasing coverage, h-BN expands anisotropically and, ultimately, the substrate is covered by a continuous 2D membrane of MLG domains embedded in h-BN. The study of the 1D interface between MLG and h-BN in these membranes by STM demonstrates that, following sequential growth at high temperatures, the interface is not abrupt, but contains an intermixed zone consisting of h-BN with embedded carbon atoms. Using quantitative LEEM, we have identified processes that eliminate this intermixing and pave the way to atomically sharp graphene-boron nitride boundaries, as confirmed by STM. The application of a similar growth procedure to terminate the edges of atomically controlled graphene nanoribbons with h-BN, embedding them in a h-BN membrane, will be considered.

[1] P. Sutter, R. Cortes, J. Lahiri, and E. Sutter. *Submitted* (2012).

2:40pm GR+EM+NS+SS+TF-ThA3 Large Area Vapor Phase Growth and Characterization of MoS₂ Atomic Layers, J. Lou, S. Najmaei, Z. Liu, Y. Zhan, P. Ajayan, Rice University

INVITED

Monolayer Molybdenum disulfide (MoS₂), a two-dimensional crystal with a direct bandgap, is a promising candidate for 2D nanoelectronic devices complementing graphene. Unlike conductive graphene and insulating h-BN, atomic layered MoS₂ is a semiconductor material with a direct bandgap, offering possibilities of fabricating high performance devices with low power consumption in a more straight-forward manner.

In this talk, we will discuss our recent efforts on the large area growth of MoS₂ atomic layers by a scalable chemical vapor deposition (CVD) method. The as-prepared samples can either be readily utilized for further device fabrication or be easily released from the growth substrate and transferred to arbitrary substrates. High resolution transmission electron microscopy and Raman spectroscopy on the as grown films of MoS₂ indicate that the number of layers range from single layer to a few layers.

Our results on the direct growth of MoS₂ layers on dielectric leading to facile device fabrication possibilities show the expanding set of useful 2D atomic layers, on the heels of graphene, which can be controllably synthesized and manipulated for many applications.

3:40pm **GR+EM+NS+SS+TF-ThA6 Formation of Silicene and 2D Si Sheets on Ag(111): Growth Mode, Structural and Electronic Properties**, *P. Vogt*, Technical University of Berlin, Germany, *T. Bruhn, A. Resta, B. Ealet*, CNRS CiNaM, Marseille, France, *P. De Padova*, CNR-ISM, Rome, Italy, *G. Le Lay*, CNRS CiNaM, Marseille, France

Since the discovery of graphene enormous efforts have been invested to discover other similar 2-dimensional materials, like e.g. silicene. These 2D materials share similar structural, electronic and optical properties as graphene but are expected to differ in terms of their respective chemical reactivity and thus their applicability for electronic devices. In particular silicene could more easily be integrated into current Si-based electronics than graphene. Silicene has been predicted theoretically [1,2] but does not seem to exist in nature.

Recently, we could synthesize silicone layers grown epitaxially by depositing Si on Ag(111) surfaces. The electronic properties of these silicene layers were shown to behave as theoretically predicted [3] and the structural and electronic properties are very similar to graphene. In STM images the hexagonal 2D silicene sheet gives rise to triangular structures situated in a honeycomb arrangement with (4×4) symmetry with respect to the Ag(111) surface. A structural model derived from the STM measurements showed a very good agreement with DFT results and exhibited a downward conical electronic dispersion resembling that of relativistic Dirac fermions at the Si K-points [3]. Depending on the growth conditions the formation of different 2D silicon arrangements can be observed: 1) Si-clusters at low deposition temperatures, 2) the formation of less ordered 2D hexagonal Si-based structures at temperatures up to 180°C, 3) the formation of the (4×4) silicene sheet around 220°C and 4) a 2D Si structure with a ($\sqrt{13}\times\sqrt{13}$)-like periodicity at higher growth temperatures exhibiting a very regular, wide range ordered Moiré-like surface pattern in STM.

Here, we will discuss the formation and epitaxial growth mode of these different 2D Si structures and the dependence on the growth parameters. We will also investigate whether these different 2D Si layers all refer to similar silicene sheets which give rise to different appearances in STM due to a varying rotation with respect to each other.

Keywords: silicene, 2D materials, graphene, Dirac fermions

References:

- [1] S. Cahangirov et al., Phys. Rev. Lett. **102**, 236804 (2009)
- [2] G. G. Guzman-Verri and L. C. Lew Yan Voon, Phys. Rev. B **76**, 75131 (2007)
- [3] P. Vogt et al., Phys. Rev. Lett. **108**, 155501 (2012)

4:00pm **GR+EM+NS+SS+TF-ThA7 Yttria-monolayer on Pt(111) Supported Graphene: A Novel Two Dimensional Heterostructure and its Affect on Charge Doping of Graphene**, *R. Addou, A. Dahal, M. Batzill*, University of South Florida

Yttrium oxide (Y₂O₃) is a high-k dielectric material, with promising wetting behavior of graphene [1]. In our study we grew yttria by reactive MBE on Pt(111) supported graphene to investigate the structural and electronic properties of the graphene/yttria interface. Photoemission measurements indicate that the graphene layer is covered by yttria. Scanning tunneling microscopy (STM) and low energy electron diffraction reveal that at annealing temperatures higher than 600 °C yttria forms an ordered monolayer on top of graphene. In STM, a moiré pattern is observed that is a consequence of super-positioning of a hexagonal yttria monolayer lattice with that of graphene. X-ray photoemission indicates a shift of the C1s peak by 1 eV to higher binding energy upon depositing of the yttria film. This peak shift is explained by charge doping of graphene by the underlying Pt substrate due to the change in the work function of the yttria coated graphene.

[1] Z. Wang et al. Nano Lett. **2010**, 10, 2024–2030; L. Ding et al. Nano Lett. **2009**, 9, 4209–4214.

4:20pm **GR+EM+NS+SS+TF-ThA8 Probing the BCN-triangle by Computations—Outside the Carbon Corner**, *Yakobson*, Rice University
INVITED

We will discuss recent work on modeling 2D-materials “beyond graphene” [1-2]: two dimensional hexagonal h-BN, pure B polymorphs, MoS₂, etc. Lessons from graphene studies remain invaluable as they offer general approach and views on the edges [3] and interface structures and energies, and especially organization of the grain boundaries [4,5]. New dislocation

cores in BN (both 5/7 and 4/8 types) lead to accordingly new physical properties of emerging polar GB [6]. Similarly, we identify the dislocation cores and the grain boundary structure for more complex polar layer-material, MoS₂ (X. Zou, unpublished). Our analysis of edge and cleavage energies helps to explain fracture patterns emerging in the course of synthesis. In principle, computations suggest possibility of metastable 2D-layers of GaN or ZnO or even their hybrids. Finally, it is important to mention clear opportunities of designing 2D-circuits by combining 2D-materials in specific functional patterns like proposed nanoroads and quantum dots [7-8] which now become a subject of experimental laboratory work.

- [1] Y. Liu et al. Nano Lett. **11**, 3113 (2011).
- [2] E. Penev, et al, Nano Lett. **12**,2441 (2012).
- [3] Y. Liu et al. Phys. Rev. Lett. **105**, 235502 (2010).
- [4] BIY and F. Ding, ACS Nano **5**, 1569 (2011).
- [5] Ajayan and BIY, Nature Mater. **10**, 415 (2011).
- [6] Y. Liu et al. ACS Nano (2012).
- [7] A. Singh and BIY, Nano Lett., **9**, 1540 (2009).
- [8] A. Singh, E. Penev, and BIY, ACS Nano, **4**, 3510 (2010).

5:00pm **GR+EM+NS+SS+TF-ThA10 Single-layer MoS₂ Devices and Circuits**, *A. Kis*, EPFL, Switzerland
INVITED

Single layer MoS₂ is a recent addition to the family of 2D materials and is reminiscent of graphene except that it is an intrinsic direct band gap semiconductor with a 1.8 eV gap. We have exfoliated single layers 6.5 Angstrom thick from bulk crystals of semiconducting MoS₂, using the micromechanical cleavage technique commonly used for the production of graphene. Our nanolayers are mechanically and chemically stable under ambient conditions. We have fabricated transistors based on single-layer MoS₂ which demonstrate that this material has several advantages over silicon for potential applications in electronics. Our transistors have room-temperature current on/off ratios higher than 10⁸, mobility higher than 780 cm²/Vs and leakage currents in the fA range. Integrated circuits based on MoS₂ have the capability to amplify signals and perform logic operations. Finally, I will show our work on suspended MoS₂ membranes that show ripples similar to those observed in graphene. MoS₂ also has superior mechanical properties: higher stiffness than steel and 30 times its breaking strength which makes it suitable for integration in flexible electronics.

References

1. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis. Single-layer MoS₂ transistors. Nature Nanotechnology **6**, 147, 2011. doi: 10.1038/nnano.2010.279
2. M.M. Benameur, B. Radisavljevic, J.S. Heron, S. Sahoo, H. Berger, and A. Kis. Visibility of dichalcogenide nanolayers. Nanotechnology **22**, 125706, 2011. doi: 10.1088/0957-4484/22/12/125706
3. B. Radisavljevic, M.B. Whitwick, and A. Kis. Integrated circuits and logic operations based on single-layer MoS₂. ACS Nano **5**, 9934, 2011. doi: 10.1021/nn203715c
4. J. Brivio, D.T.L. Alexander, and A. Kis. Ripples and Layers in Ultrathin MoS₂ Membranes. Nano Letters **11**, 5148, 2011. doi: 10.1021/nl2022288
5. S. Bertolazzi, J. Brivio, and A. Kis. Stretching and Breaking of Ultrathin MoS₂. ACS Nano **5**, 9703, 2011. doi: 10.1021/nn203879f

Thursday Afternoon Poster Sessions

Graphene and Related Materials Focus Topic

Room: Central Hall - Session GR-ThP

Graphene and Related Materials Poster Session

GR-ThP1 Using Raman Spectroscopy and X-ray Photoelectron Spectroscopy to Guide the Development of Graphene-Based Materials. *T.S. Nunney, M.H. Wall*, Thermo Fisher Scientific, UK

The potential uses of graphene are currently being explored by the materials science community. Its immediate potential as a transparent conductive electrode for the microelectronics industry is already being exploited; the unique combination of electronic, chemical and structural properties exhibited by graphene are already having a significant impact on the development of thin film transistors and touch-screen devices. Further applications for the development of graphene-based catalytic systems and molecular sensors are also underway. Good materials characterization is required at all steps in the creation of new graphene devices, from guiding the initial graphene synthesis and transfer to the desired substrate, to chemical modification and analysis of the finished device. In this presentation we will show how a multi-technique approach using both Raman spectroscopy and XPS can address the challenges posed at these steps. Raman microscopy is an analytical technique that is well suited for the characterization of graphene. It is a vibrational spectroscopy that is very sensitive to small changes in the geometric structure of a molecule and its environment. This sensitivity allows Raman to be used as a probe for a number of properties important to a specific graphene samples, such as layer thickness. X-ray photoelectron spectroscopy (XPS) is ideally suited to the determination of the surface chemistry and the way in which that chemistry changes in the surface and near-surface region. The technique provides quantitative elemental and chemical information with extremely high surface specificity and is ideal for comprehensively and quantitatively characterising the elemental composition and chemical bonding states at surfaces and interfaces. This approach will be illustrated by examples from graphene samples created by mechanical exfoliation, chemical reduction and CVD methods.

GR-ThP2 Ionic Strength Effects on Graphene Oxide Nanosheets and Fluorescence Quenching of ssDNA Aptamers. *M.Y. Lin, Y.P. Lu*, National Applied Research Laboratories, Taiwan, Republic of China

Recently, graphene has attracted considerable attention because of its remarkable electronics, its mechanical and optical properties, and its unique single-atom thickness and two-dimensional sp² carbon networking material [1]. Graphene oxide (GO) presents excellent properties in high water dispersibility, capabilities of bridging biomolecules on the surface, and acts as a highly efficient fluorescent quencher material [2]. Single-stranded DNA (ssDNA) has been reported to bind on a graphene surface through non-covalent π - π interactions, whereas double-stranded DNA (dsDNA) cannot bind on graphene surfaces. Aptamers are synthetic, single-stranded DNA or RNA molecules that fold into unique 3D structures, and bind specifically to a wide range of molecules such as chemicals, proteins, and drugs. Therefore, aptamer-based GO biosensors have been developed for detecting various targets [3-5]. Ionic strength and pH are closely related to biochemical reactions and interactions between aptamer and targets. However, less studies have been reported to the ionic strength and pH effects on GO and interaction between GO and DNA [6]. Phosphate buffer saline (PBS) was commonly used as isotonic reagent for protein solution. In this study, the fluorescence intensity of GO significantly decreasing with increasing concentration of PBS. In addition, increasing quenching effect was found in the group with PBS as solvent for GO-aptamer interaction. The reported report are of importance in further applications of GO in biosensors and biochemical reactions.

GR-ThP3 Isotope Effect in the Graphene Deuteration Kinetics. *A. Nefedov*, Karlsruhe Institute of Technology, Germany, *A. Paris*, Interdisciplinary Laboratory for Computational Science, FBK-CMM, Italy, *N. Verbitsky*, Moscow State University, Russia, *Y. Wang*, Nagoya University, Japan, *A. Fedorov*, *D. Haberer*, IFW Dresden, Germany, *M. Oehzelt*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, *L. Petaccia*, ELETTRA Synchrotron Light Laboratory, Italy, *D. Usachov*, St. Petersburg State University, Russia, *D. Vyalikh*, Technical University Dresden, Germany, *H. Sachdev*, Max-Planck-Institute for Polymer Research, Germany, *Ch. Wöll*, Karlsruhe Institute of Technology, Germany, *M. Knüpfer*, *B. Buechner*, IFW Dresden, Germany, *L. Calliari*, Interdisciplinary Laboratory for Computational Science, FBK-CMM, Italy, *L. Yashina*, Moscow State University, Russia, *S. Irle*, Nagoya University, Japan, *A. Grueneis*, University of Vienna, Austria

Kinetic isotope effects (KIE) are important phenomena in physical chemistry and have been investigated for a long time in relation to activation and rate of chemical reactions. KIE are easily observable for the hydrogen isotopes due to the large relative mass difference and have been studied for example in hydrogen transfer in organic chemistry such as acid and base catalysis, enzyme reactions and catalytic decomposition.

Here we present results of time-dependent x-ray photoemission spectroscopy (XPS) in order to investigate the kinetics of the hydrogenation/deuteration reaction of graphene. A pristine monolayer graphene was prepared under ultrahigh vacuum conditions by chemical vapor deposition on Ni(111) thin films epitaxial grown on W(110). Then a monolayer of Au was intercalated into the interface between Ni and graphene, making the latter quasi free-standing. The graphene layer was then exposed to hydrogen or deuterium atomic gas beams, obtained by thermal cracking in a tungsten capillary at T=3000 K. The maximum surface coverage was obtained after several hydrogenation or deuteration steps of different time. After each step XPS of the C1s line was performed in order to measure H/C and D/C ratios. After reaching saturation, the electronic structure of the hydrogenated and deuterated layer was analyzed by near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy at the carbon K-edge.

We have observed a strong inverse KIE for the hydrogenation/deuteration reaction leading to substantially faster adsorption and higher maximum D/C ratios as compared to H/C (D/C~35% vs. H/C~25%). These results can be understood by the fact that atomic D has a lower chemisorption barrier and a higher desorption barrier. Quantum chemical calculations and molecular dynamics simulations can reproduce the experimental trends and reveal the contribution of the constituent chemisorption, reaction and associative desorption processes of H(D) atoms onto graphene. The reported case of a strong inverse KIE is an extremely unusual case and is important for isotope specific chemical reactivity in organic molecules and functionalized graphene.

GR-ThP4 Graphene Nanoribbons Electronic Structure Modulations. *N.B. Le, L.M. Woods*, University of South Florida

Graphene nanoribbons are studied using density functional theory methods. Various factors are considered as different ways to tailor their electronic structure properties. These include folding, types of edges, and extended defects. Of particular importance is the van der Waals interaction in the folded structures with closed edges. These are taken into account via a DFT-D2 method, which is a pragmatic approach based on a semi-empirical pairwise correction to the conventional Kohn-Sham energy. Equilibrium distances, stacking patterns, and geometry configurations upon folding are determined. The energy gaps, band structure changes, and characteristic energies are also obtained for nanoribbons with armchair and zigzag edges when folded and/or extended defects present. Our results attest to the many possible methods that can be explored to modify the properties of these graphitic nanostructures.

GR-ThP5 Effects of an Interfacial Water Layer on Protein Adsorption to Graphene Sheets on Solid Substrates. *K. Yamazaki, T. Ogino*, Yokohama National University, Japan

Graphene is two-dimensional honeycomb lattice of carbon atoms. It is well known that the graphene sheets are strongly affected by their environment because of its extremely small thickness and large specific surface area. There are many reports about the chemical doping into graphene films induced by the support substrate and charge transfer. In this paper, we studied control of chemical doping to graphene flakes through the substrate engineering and using raman spectroscopy. We also demonstrate the selective adsorption of biomolecules toward the unique sensors.

We used sapphire surfaces for support substrates of graphene. After the acid treatment, the sapphire surfaces are terminated with hydroxyl groups, which work as adsorption sites of water molecules. We deposited graphene flakes on sapphire (0001) and (1-102) surfaces by mechanical exfoliation method. To reveal influence of a water layer at the interface between the sapphire surface and graphene, we annealed the sapphire surfaces at 700°C for 1h just before graphene deposition and compared the G-peak and 2D-peak positions on Raman spectra.

We observed shift of G-peak and 2D-peak positions to wave numbers lower than those on the hydrophilic sapphire (0001) substrate. But, in the case of (1-102) surfaces, the G-peak and 2D-peak positions did not shift upon annealing. The peak positions are almost same among the annealed (0001), the annealed (1-102), and the on-annealed (1-102) surfaces. It is well known that formation of water layers on sapphire surfaces depends on plane directions¹⁾. A (0001) surface has more bound water molecules than the other faces. Therefore, the peak shifts were induced by the amount of water layer that existed at the interfaces between the sapphire surfaces and the graphene flakes. We demonstrated the adsorption of protein molecules on these surfaces. We used ferritin molecules, which are negatively charged for adsorption on the graphene flakes. We observed well-correlated adsorption pattern with the G-peak and the 2D-peak positions of Raman spectra. Ferritin molecules were preferentially adsorbed to the graphene flakes that were supported by hydrophilic (0001) surfaces. Amount of adsorbed ferritin molecules to the other surfaces were dramatically small. These different adsorption behaviors directly show the effect of chemical doping from the interfacial water molecules to the graphene flakes.

In summary, we demonstrated control of protein adsorption to the graphene surfaces by using the suitable support substrates for graphene towards the biosensors without any labeling to substrates and targets.

1) T. Tsukamoto et al. *J. Phys. Chem. C* (2012) 116, 4732-4737.

GR-ThP6 Layer Dependent Growth of Pentacene on Epitaxial Graphene. *W. Jung, D.-H. Oh, J. Lee, B.G. Shin, C.-Y. Park, J.R. Ahn, Sungkyunkwan University, Republic of Korea*

Graphene have showed promising performance as electrodes of organic devices such as organic transistors, light-emitting diodes, and photovoltaic solar cells. In particular, among various organic materials of graphene-based organic devices, pentacene has been regarded as one of promising organic materials because of its high mobility, chemical stability, and compatibility with a low-temperature silicon processing. In the development of graphene-based organic devices, it is thus important to understand an interaction of pentacene with graphene. In this study, we focused on how the growth of pentacene depends on an interaction between graphene and a substrate. Epitaxial graphene grown on a 6H-SiC(0001) surface was used as a pristine graphene because zeroth-layer graphene, called a buffer layer, and monolayer graphene have the same graphene structure but zeroth-layer graphene, which bonds strongly to a SiC substrate, has different electronic properties from monolayer graphene. We have studied how graphene grows differently at room temperature on monolayer graphene in comparison to zeroth-layer graphene using scanning tunneling microscopy and first principles calculations. On the zeroth-layer graphene, pentacene was adsorbed on specific sites with three different orientations but did not show a long-range order. In contrast to zeroth-layer graphene, pentacene forms a two dimensional ordered structure on monolayer graphene. The orientation of pentacene in the ordered structure was determined by the zigzag direction of the edge structure of monolayer graphene. The short-range and long-range ordering on zeroth-layer and monolayer graphene, respectively, was understood by different energetics of pentacene on zeroth-layer from monolayer graphene, where a total energy of pentacene on graphene was calculated by first principles calculations.

GR-ThP7 Optical Properties and Surface Radicals Content of Graphene Decorated with Metal Nanoparticles. *M.A. Bratescu, T. Ueno, O. Takai, N. Saito, Nagoya University, Japan*

Recently the increased interest of carbon-based materials decorated with metal nanoparticles (NPs) for sensors and energy applications has generated a huge development of the research in this field. Unfortunately, the immediate use of graphene in sensors or fuel cells applications is not yet possible since more effort must be performed to understand how NPs decorated graphene affect the selectivity and the sensitivity of the sensor and how surface radicals content influences the fuel cell performance.

In the present research, we developed a simple synthesis method of metal NPs on graphene layer and we investigated the optical properties and the surface radicals content of this system. Graphene layer have been produced on Cu foils by CVD method and transferred on different substrates to be characterized.¹ The metal NPs were synthesized on the graphene layer using a well-established method used in our laboratory, based on a solution plasma process (SPP) system^{2,3}, directly on the Cu foil covered with the graphene layer. The metal NPs were synthesized on the graphene surface

through the reduction of the metal ion from the salt to the neutral form, or by the erosion of the electrode material. The graphene layer decorated with metal NPs was transferred on glass, Si/SiO₂ substrate, Kapton scotch and carbon/Cu(Mo) grid surfaces to be analyzed by UV-vis spectroscopy, micro-Raman mapping spectroscopy, electron spin resonance (ESR), and transmission electron microscope (TEM) techniques, respectively. Micro-Raman mapping of 2D band at 2700 cm⁻¹ (two photon double resonance band) which has higher intensity than G band at 1583 cm⁻¹ (interlayer vibrations band of sp²-hybridized carbon) shows the quality and the uniformity of graphene layer on substrates. An enhanced Raman spectrum of graphene was detected when gold or silver NPs were adsorbed on the surface. The UV-vis spectra of graphene layer decorated with gold NPs which was transferred on a glass substrate, shows a weak absorption band of surface plasmon resonance, at 520 nm, due to the thin layer of NPs on surface. The adsorbed metal NPs on graphene layers was observed by high resolution TEM analysis. The surface radicals content will be examined using ESR through calibration with stable free radicals compounds. The dependence of the surface radicals content of the graphene decorated with NPs on the size and shape of NPs will be discussed.

1 Xuesong Li, et al., *Science* **2009**, 324, 1312.

2 Takai, O. *Pure Appl. Chem.* **2008**, 80, 2003 – 2011.

3 M.A. Bratescu, et al., *J. Phys. Chem.*, **2011**, 115, 24569.

GR-ThP8 Electronic Structure of MoS₂ Monolayers on Copper. *Q. Ma, D.Z. Sun, W.H. Lu, University of California Riverside, D. Le, M. Amanpour, University of Central Florida, J. Mann, S. Bobek, University of California Riverside, T. Raman, University of Central Florida, L. Bartels, University of California Riverside*

MoS₂ is a very promising material for photocatalysis and it has many current applications in catalytic hydrodesulfurization. Similar to graphene, it is a layered material. Recently, it has been shown that it transitions from an 1.6 eV indirect bandgap to a 1.9 eV direct bandgap semiconductor when reduced to a monolayer. Important for its usefulness e.g. in catalytic hydrogen splitting, is not only its bandgap but also its band alignment when deposited on different substrates. Using CVD grown MoS₂ on a copper surface, we use XPS to ascertain the identity of the material and the nature of its internal bonding when on this metallic substrate. Spectroscopy also shows a metal induced reduction of the bandgap to 1.5 eV and a strong signature of n-type doping through the underlayer. Density Functional Theory calculation corroborate this finding and provide a microscopic understanding of the bandgap and alignment depending on the number of MoS₂ layers and the presence of any substrate.

GR-ThP9 Dry Transfer of Graphene to Organic and Inorganic Substrates. *E.H. Lock, S. Hernandez, S.G. Walton, M. Laskoski, S.P. Mulvaney, P.E. Sheehan, W.K. Lee, T.J. Anderson, F.J. Bezares, V.D. Wheeler, F.J. Kub, J.D. Caldwell, K.D. Hobart, B.N. Feygelson, L.O. Nyakiti, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill, Naval Research Laboratory*

High quality graphene transfer is critical for preserving the extraordinary graphene properties. In this paper we report our progress on transferring graphene from different growth substrates. Our method is a dry transfer approach which exploits an azide linker molecule to establish a covalent bond to graphene. Successful transfer is observed when the adhesion between the graphene and the transfer substrate is higher than the graphene/growth substrate adhesion. Thus, this transfer technique provides a novel alternative route of graphene transfer. This work was supported by the Naval Research Laboratory Base Program.

GR-ThP10 Controllable Assembly of Aromatic Molecules on a Surface via Diels-Alder Reaction: A Carbon Source for Graphene. *C.L. Henderson, J. Baltazar, H. Sojoudi, J. Kowalik, S. Graham, L. Tolbert, Georgia Institute of Technology*

Graphene is of tremendous interest based on its electronic properties, such as mobilities $\geq 200,000$ cm²/V-s, as well as a very high thermal conductivity. Furthermore, graphene is one atom thick, making it a perfect substitute for silicon in small high performance devices. Graphene formation by directed chemical synthesis, utilizing intelligently designed precursors that can be converted thermally or chemically to graphene and graphene nanostructures with interesting electronic properties are of great interest. We successfully synthesized a silyl derivative of a maleimide that allows: (1) self-assembly to produce a controllable aromatic monolayer on a CMOS compatible surface, and (2) the ability to perform a reverse Diels-Alder reaction that allows us to obtain the carbonaceous starting material of interest in the surface for further thermal or chemical consolidation. Graphene so produced was analyzed and identified by Raman spectroscopy and other methods.

GR-ThP11 Unique Electronic Mixing between Iron Phthalocyanine and Graphene*, *D.B. Dougherty, A.A. Sandin*, North Carolina State University, *A. Calzolari*, CNR-NANO, Istituto Nanoscienze, Italy, *M. Buongiorno-Nardelli*, North Carolina State University, *A. Al-Mahboob, J.T. Sadowski*, Brookhaven National Laboratory, *J.E. Rowe*, North Carolina State University

Graphene is an ideal material for long-range spin transport due to its very high carrier mobilities and long spin lifetimes due to minimal spin-orbit scattering effects [1]. Direct spin injection into graphene has been demonstrated, but is inefficient due to the well-known bulk conductivity mismatch between graphene and a magnetic metal electrode. The standard approach to overcome this effect is to engineer a tunneling barrier at the interface to provide an effectively large spin-dependent interface resistance. However, for insulating tunnel barrier growth on graphene, great care must be taken to avoid 3D islanding due to the typically weak interactions between the substrate and deposited species [1].

An alternate approach is to consider the use of planar organic materials as interfacial layers to enhance spin injection into graphene. Since weak intermolecular interactions can be comparable in size to molecule-substrate interactions for planar aromatics on graphene, high quality film growth is more likely. We have studied the growth of iron phthalocyanine (FePc), a chemically-robust paramagnet, on epitaxial graphene on SiC(0001) by a combination of STM, STS, LEED, UPS, and density functional theory calculations. Our calculations predict an energetically weak interaction between graphene and FePc that nevertheless leads to a unique spin-dependent electronic mixing. A non-dispersive hybrid interface state is created along with a small gap in one spin sub-band while the graphene band structure is essentially unchanged in the other sub-band. STM and LEED indicate a highly-ordered, flat-lying monolayer film of FePc on epitaxial graphene and UPS measurements compare favorably with the calculated occupied density of states. STS studies of the ordered monolayer show an unoccupied state for FePc on graphene that is *not present* for FePc on graphite. We interpret this unique state as evidence for the predicted spin-polarized interface state.

*This work was funded by the NSF Phase I Center for Chemical Innovation: Center for Molecular Spintronics (CHE-0943975).

[1] Han et al., *J. Magn. Mag. Mat.* 324, 369 (2012).

GR-ThP13 Raman Spectroscopy of Double Layer Graphene FETs: Mapping the Misorientation Angle, *Z. Razavi Hesabi, C. Joiner, T. Roy, E.M. Vogel*, Georgia Institute of Technology

Double layer graphene, a stacked two dimensional honeycomb lattice of carbon atoms, is a very promising candidate for nanoelectronic applications. The electrical properties, such as high carrier mobility and tunable band gap, have been theoretically predicted to be highly dependent on the misorientation angle between the two layers. For industrial applications, the ability to map and control the misorientation angle between layers will be necessary to achieve the desirable electrical properties of the graphene devices. This work presents a method for systematically determining the misorientation between two layers on a wafer scale through the use of Raman spectroscopy.

Friday Morning, November 2, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+SS+GR+SP-FrM

Electron Transport at the Nanoscale: Development of Theories and Techniques

Moderator: C. Su, Bruker Nano

8:20am **ET+SS+GR+SP-FrM1 What is Missing in the Space Charge Limited Current Theory?**, X.-G. Zhang, Oak Ridge National Laboratory, S.T. Pantelides, Vanderbilt University **INVITED**

Space-charge-limited currents are important in energy devices such as solar cells and light-emitting diodes, but the available theory from the 1950's finds it necessary to postulate defect states that are distributed in energy in order to match data. This has prevented the theory to be used in extracting reliable defect information such as energy level and trap density from measurements. Here we revisit the theory and show that this postulate is not warranted. Instead, we demonstrate that dopants and the concomitant Frenkel effect, which have been neglected, control the shape of measured current-voltage characteristics. For highly disordered material, there is a significant inter-trap tunnelling current in the Ohmic regime, which accounts for the observed peak in the noise power. The new theory can anchor efforts to develop experimental techniques to measure deep-trap levels.

This research was conducted at the Center for Nanophase Materials Sciences, sponsored at ORNL by the Division of Scientific User Facilities (XGZ), and by Division of Material Science and Engineering, Basic Energy Sciences, U.S. Department of Energy (STP), and the McMinn Endowment at Vanderbilt University (STP).

9:00am **ET+SS+GR+SP-FrM3 Mapping Solar Cell Internal Fields and Band Offsets**, H. Cohen, Y. Izhaik, G. Hodes, Weizmann Institute of Science, Israel

The internal fields and band offsets across device interfaces are key features in various applications and, yet, this information is generally inaccessible by standard electrical tools. A systematic approach addressing this problem is demonstrated here, based on chemically resolved electrical measurements (CREM). Studying nanoporous photovoltaic cells, we resolve the internal details layer-by-layer and, thus, extract a realistic band diagram for the multi-interfacial structure. We show the spontaneous evolution of two p-n-like junctions and quantify the associated band bending at corresponding domains. An account for the 'real' working conditions of the device is attempted by exposing the cell to optical and electrical stimuli, revealing the charge trapping at each specific layer and showing how certain sample treatments affect the trapping mechanisms. Our methodology overcomes a critical missing link in device characterization and in fundamental studies of nanoscale solid-state devices.

9:20am **ET+SS+GR+SP-FrM4 Quantum Degeneracy Revealed by the Relation between the Tunneling Current and the Chemical Force**, P. Jelinek, M. Ondracek, Institute of Physics of ASCR, Czech Republic, F. Flores, Universidad Autonoma de Madrid, Spain

Recent progress has allowed merging AFM and STM into a new experimental setup where tunneling current and atomic forces are recorded simultaneously. The possibility to collect both quantities simultaneously opens new horizons not only in advanced characterization at the atomic scale but also in understanding fundamental relations between the electron transfer and formation of the chemical bond between two bodies.

Actually, there is a long-standing debate in the scientific community about the relation between the chemical force and the tunneling current (see e.g. [1]) on the atomic scale. Both the tunneling current and the short-range component of the force, induced by the formation of the chemical bond, exhibit in atomic contacts an exponential decay with increasing distance in the range of several angstroms. As the quantities depend directly on the wave-function overlap between outermost atoms of tip and surface, the corresponding exponential functions should have similar characteristic decay length. In particular, the relation between the chemical force F and the tunneling current I follows the law $F^n \sim I$, where n is an integer number. Over the last 10 years, several different scaling factors n , varying from 1 to 4, have been proposed by different groups based on both theoretical analysis and experimental measurements (see reference in [2]); still there is no consensus on the relation between the chemical force and the tunneling current.

In this contribution, we explain the relation between the tunneling current and the interaction force at the atomic scale using a simple analytical model

[2]. The model unveils the existence of two characteristic scaling regimes, where the tunneling current is either proportional to the chemical force $I \sim F$ or to the square of the chemical force, i.e. $I \sim F^2$. We show that the existence of a given regime is basically controlled by two parameters: (i) the electronic level degeneracy and (ii) the hopping between electronic levels involved in the interaction process. Finally, we will collate our theoretical prediction with experimental AFM/STM measurements of single-atom point contacts and complex DFT simulations [3] to confirm the existence of these two characteristic regimes.

[1] W. Hofer and A.J. Fisher, *Phys. Rev. Lett.* 91, 036803 (2003) and the reply in by C.J. Chen

[2] P. Jelinek et al, *J. Cond. Mat. Phys.* 24, 084001 (2012).

[3] M. Ternes et al *Phys. Rev. Lett.* 106, 016802 (2011).

9:40am **ET+SS+GR+SP-FrM5 Understanding the Influence of the Tunneling Current and the Chemical Force on the Contrast Formation in KPFM**, Z. Majzik, M. Ondráček, M. Švec, J. Berger, P. Jelinek, Institute of Physics of ASCR, Czech Republic

Kelvin Probe Force Microscopy (KPFM) [1] senses the variation in the electrostatic force. The electrostatic force is $F_{el} = -dCTS/dz(V_{bias} - V_{lcpd})^2$, where V_{lcpd} denotes to the local contact potential difference (LCPD). Atomic scale resolution was achieved by KPFM on the prototypical Si(111)- 7×7 surface [2]. It was shown that the formation of a chemical bond between the closest tip-surface atoms induces significant variation in the LCPD [2]. Lately it was observed that the tunneling current leads to the raise of an additional electrostatic (phantom) force [3]. Consequently, the total electrostatic force must be the combination of several components where the contribution of each component is defined by the tip-sample separation.

Recent progress in Scanning Probe Microscopy opens the possibility of simultaneous acquisition of the tunneling current, atomic forces and local potential difference with atomic resolution [4]. The aim of this contribution is to discuss the origin of electrostatic force contribution at different tip-sample separations. In particular, we performed simultaneous site-specific AFM/STM measurements on Si(111)- 7×7 using a modified Omicron qPlus (tuning fork based) system [5]. We found that along the tip approach three characteristic regions can be well distinguished. At large tip-sample separations, the capacitance is a function of tip geometry and the tip-sample distance. Approaching the tip closer towards the surface, quantum effects become to play important role. The overlap between the tip and sample wave functions produces electron tunneling, which induces additional electrostatic force. Formation of the chemical interaction between the tip apex atom and the adatoms of the 7×7 surface induces changes in the electron charge distribution reflected in variation of the LCPD [2] and the permittivity in the tunneling gap. Hence the capacitance is modified accordingly. In order to have better understanding of the impact of the chemical interaction, atomic hydrogen was deposited to saturate the dangling bonds of adatoms. Over the hydrogenated adatoms, nor strong shift in the LCPD or sudden change in the capacitance was observed. Further to gain more insight into ongoing processes we carried out DFT calculations for tip-sample interaction to understand affect of the formation of covalent bond between tip apex and surface adatoms on the Si 7×7 surface.

References

[1] M. Nonnenmacher et. al, *App. Phys. Lett.* 58, 2921 (1991)

[2] S. Sadewasser et. al, *Phys. Rev. Lett.* 103, 266103 (2009)

[3] A. J. Weymouth et. al, *Phys. Rev. Lett.* 106, 226801 (2011)

[4] F.J. Giessibl, *Appl. Phys. Lett.* 73, 3956 (1998)

[5] Z. Majzik et. al. *B. J. Nano* 249, 3 (2012)

10:00am **ET+SS+GR+SP-FrM6 An In Situ Technique for Using Ballistic Electron Emission Microscopy to Measure Hot Electron Transport at Metal Semiconductor Interfaces**, R. Ralsano, V.P. LaBella, University at Albany-SUNY

Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) technique that can measure transport of hot electrons through materials and interfaces with high spatial and energetic resolution. BEEM requires an additional contact to ground the metal base layer of a metal semiconductor junction. Performing BEEM *in situ* with the sample fabrication requires a custom built STM or modifying a commercial one to facilitate the extra contact, which leaves the technique to highly trained experts. This presentation will describe our work to develop a special silicon substrate that has the extra contact and oxide hard mask built in to enable *in situ* BEEM without modifications to the STM. Electrically

isolated contact traces are lithographically patterned *ex situ* onto the silicon substrate. Then a hard mask is grown and lithographically patterned and connected to the BEEM sample plate which is then inserted into the ultra-high vacuum chamber. The metal is then deposited on top of the hard mask and then mounted *in situ* onto the STM for BEEM measurements. BEEM measurements comparing both *in situ* and *ex situ* deposited films will be presented.

10:20am **ET+SS+GR+SP-FrM7 Electronic Transport on the Nanoscale, R. Moeller**, University of Duisburg-Essen, Germany **INVITED**

To study the transport through objects at the nanoscale a scanning tunneling microscope with several tips is used. Two different configurations will be discussed. The lateral transport of electrons may be studied by using two tips to drive a current parallel to the surface. A third tip enables to map the corresponding electrochemical potential. Measurements for a 2D conducting layer will be discussed. To analyze the transport perpendicular to the surface, a thin metallic layer is placed on a semiconducting surface. At the interface a Schottky barrier is formed, which can only be overcome by electrons of sufficient energy. This may be used to split the current of electrons coming from the tip of the microscope into two parts, the ballistic electrons and the electrons which have been scattered. This technique has been applied to study the ballistic transport of electrons through individual molecules. On the other hand inelastic processes may be revealed by analyzing the fluctuations in the tunneling current observed at different positions of the tunneling tip above an adsorbed molecule.

Graphene and Related Materials Focus Topic

Room: 13 - Session GR+EM+ET+MS+NS-FrM

Graphene Device Physics and Applications

Moderator: A. Turchanin, University of Bielefeld, Germany

8:20am **GR+EM+ET+MS+NS-FrM1 Heterointegration of Graphene with Nano and Molecular Scale Structures for High Performance Devices, X. Duan**, University of California, Los Angeles **INVITED**

Nanoscale integration of dissimilar materials with distinct compositions, structures and properties has the potential to create a new generation of integrated systems with unique functions and/or unprecedented performance to break the boundaries of traditional technologies. In this talk, I will focus my discussion on the heterointegration of graphene with a variety of nano and molecular scale structures of designed architectures to open up exciting opportunities for nanoscale device engineering. In particular, I will discuss our recent effort in integrating graphene with a self-aligned nanowire gate to create the highest speed graphene transistors, integrating graphene with plasmonic nanostructures to create multi-color high speed photodetectors, integrating graphene with nanoscale templates for the creation of graphene nanostructures, and integrating graphene with various π -conjugating molecular systems for band gap engineering and molecular sensing.

9:00am **GR+EM+ET+MS+NS-FrM3 Graphene RF: From Fundamentals to Opportunities, J.S. Moon, H.-C. Seo, M. Antcliffe, S. Lin, A. Schmitz, D. Le, C. McGuire, D. Zehnder**, HRL Laboratories LLC, L.O. Nyakiti, V.D. Wheeler, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill, P.M. Campbell, Naval Research Laboratory, K.-M. Lee, P. Asbeck, UC San Diego **INVITED**

Graphene is a topic of very active research from basic science to potential applications. Various RF circuit applications are under evaluation, which include low-noise amplifiers, frequency multipliers, mixers and high-speed radiometers. Potential integration of graphene on Silicon substrates with CMOS compatibility would also benefit future RF systems. The future success of the RF circuit applications depends on vertical and lateral scaling of graphene MOSFETs to minimize parasitics and improve gate modulation efficiency in the channel. In this presentation, we highlight recent progress in graphene materials and devices. For example, with hydrogen intercalation, a graphene wafer showed an electron mobility of 2500 cm²/Vs at 6.8 x 10¹²/cm² carrier density, and sheet resistance of 230 ohm/square. The Ti-based ohmic contact resistance is below 100 ohm* μ m and hysteresis in HfO₂/Graphene MOSFET transfer curves are no longer concerns in RF applications. We will show graphene MOSFETs in mixer and detector applications with performances comparable to and better than the current state-of-the-art technologies. Also, we will present recent progress in graphene heterostructure based diodes with on/off ratio greater than 10⁶. In summary, while graphene is relatively new material, it shows a strong potential to become disruptive in RF applications.

This work was partially supported by DARPA, monitored by Dr. J. Albrecht, under SPAWAR contract number N66001-08-C-2048.

The views, opinions, and/or findings contained in this article/presentation are those of the author/presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense.

[1] J. S. Moon and D. K. Gaskill, IEEE Trans. Microwave Theory and Techniques, p. 2702, 2011

9:40am **GR+EM+ET+MS+NS-FrM5 Graphene and Dielectric Integration: A Sticky Situation?, V.D. Wheeler, N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, D.J. Meyer**, U.S. Naval Research Laboratory, A. Nath, George Mason University, C.R. Eddy, Jr., D.K. Gaskill, U.S. Naval Research Laboratory **INVITED**

Scalable high- κ dielectric integration is needed to realize graphene-based THz transistors. Yet, the inert nature of graphene inhibits direct application of high-quality uniform atomic layer deposition (ALD) dielectrics. While several methods have rendered the surface more susceptible to ALD[1], they often degrade mobility and/or shift the Dirac voltage due to charges within the gate stack. Recently, we developed a dry chemical functionalization approach using XeF₂ that results in conformal, thin high- κ ALD oxide films with a 10-25% improvement in graphene mobility[2], high dielectric constants (HfO₂=18.5, Al₂O₃=8.9), and small Dirac voltage shifts (HfO₂=2V, Al₂O₃=0.1V), indicating the effectiveness of F functionalization. We will present in-depth details of our fluorination process, discuss its advantages and limitations with respect to other methods used to enhance ALD reactivity with graphene, and provide future directions for this field of study.

Fluorination of EG surfaces was performed in a Xactix X3 XeF₂ etcher operating in pulse mode. Results show that 15 nm pinhole-free Al₂O₃ and HfO₂ films are obtained with an optimized XeF₂ surface treatment prior to ALD consisting of six, 20s pulses (XeF₂=1 torr, N₂=35 torr). This optimal treatment resulted in ~6% fluorine surface coverage, as semi-ionic C-F bonds (F1s ~687eV) only, which provided additional ALD reaction sites needed to obtain uniform oxide films. This unique semi-ionic nature of the C-F bond allows the graphene lattice to maintain planarity and minimize degradation to transport properties.

Theoretical studies suggest that the semi-ionic nature of the C-F bond is related to the graphene electron sheet carrier density (n_e), requiring at least 10¹³ cm⁻² to form[3]. To test this, EG samples with similar thickness but varying n_e (2x10¹²-1.3x10¹³ cm⁻²) were fluorinated simultaneously using the optimal conditions above. Samples with $n_e > 1 \times 10^{13}$ cm⁻² had only semi-ionic C-F bonding, but those with $n_e < 1 \times 10^{13}$ cm⁻² had both covalent and semi-ionic bonding – verifying the theoretical calculations. The amount of covalent bonding increased as n_e decreased, and an increased pinhole density was seen in subsequent Al₂O₃ films. This implies that the underlying EG properties can impact the effectiveness of this fluorination method. Yet, by adjusting the pulse conditions one can tailor this method to still obtain uniform ALD oxides on low carrier density and even p-type EG. To this end, results of our XeF₂ approach on p-type H₂ intercalated EG samples will be shown.

1. Garces, et.al. *JVST B* **30(3)** 03D104 (2012)
2. Wheeler, et.al. *Carbon* **50** 2307 (2012)
3. Sofo, et.al. *Phys Rev B* **83(8)** 081411(R) (2011)

10:20am **GR+EM+ET+MS+NS-FrM7 Achieving Scaled Dielectrics on Graphene Using Atomic Layer Deposition, S. Jandhyala, G. Mordi, R.M. Wallace, J. Kim**, University of Texas at Dallas

In order to realize high-performance graphene-based field-effect-devices, local gating of graphene channel is one of the foremost requirements [1]. Therefore, deposition of high-quality, scalable dielectrics on graphene is required. The ability to precisely control thickness and conformally deposit materials makes atomic layer deposition (ALD) an ideal technique for achieving such dielectrics [2]. However, ALD is a surface-reaction limited process [2] and graphene, being sp² bonded, has no *out-of-plane* covalent functional groups [3] and this can cause difficulties in initiating the ALD reaction [4]. In previous studies we have shown that using a reversibly physisorbed ozone (O₃) functionalization approach, we can deposit high quality ALD oxides (such as Al₂O₃) on graphene with thicknesses below 5 nm [5]. Further understanding regarding the interaction of O₃ and metal precursors with graphene is required for successfully applying the ozone process to deposit different oxides.

In this study, we will use *in-situ* electrical measurements of graphene devices inside an ALD chamber as a characterization technique in order to understand the adhesion mechanisms of oxidants (such as O₃ and H₂O) and

metal precursors (such as trimethylaluminum-TMA, titanium tetrachloride-TiCl₄) on graphene surfaces. The characterization scheme used is packaged back-gated graphene-FETs which can detect the molecules adsorbed on the graphene surface. We will compare exfoliated graphene and chemical vapor deposited (CVD) graphene (which tends to have a higher number of defect sites). Using such *real-time* electrical measurements, the observed charge scattering mechanisms and the effect on mobility and doping due to the interaction of these molecules with graphene will be presented.

Acknowledgement

This work was funded through the South West Academy of Nanoelectronics (SWAN) program of NRI under SRC.

References

- [1] S. K. Banerjee, et al., *Pro. of the IEEE* 98 (12), pp. 2032-2046 (2010).
- [2] R. L. Puurunen, *J. Appl. Phys.* 97 (12), pp. 121301-121352, (2005)
- [3] A. H. Castro Neto, et al., *Rev. Mod. Phys.* 81 (1), pp. 109-162 (2009)
- [4] L. Liao, X. Duan, *Mat. Sci. Eng. R* 70 (3-6), pp. 354-370, (2010)
- [5] S. Jandhyala, et al., *ACS Nano*, 6 (3), pp. 2722-2730 (2012)

10:40am **GR+EM+ET+MS+NS-FrM8 Atomically-Smooth MgO Films Grown on Epitaxial Graphene by Pulsed Laser Deposition.** *S.C. Stuart, A.A. Sandin*, North Carolina State University, *O. Nayfeh, M.D. Dubey*, Army Research Laboratory, *J.E. Rowe, D.B. Dougherty*, North Carolina State University, *M.D. Ulrich*, Army Research Office

The growth of high quality insulating films on graphene is a crucial materials science task for the development of graphene-based spintronics because graphene is a potentially revolutionary material for electronic and spintronic applications. For efficient spin-injection, graphene is expected to suffer from the well known “conductivity mismatch” problem at metal-semiconductor spin electrode interfaces. The standard approach to mitigating this problem has been to grow thin, insulating tunnel barriers between the graphene and the magnetic metallic electrode to provide a spin-dependent resistance via the tunneling magnetoresistance effect. It has been demonstrated by several experiments that direct spin injection from a magnetic electrode to graphene is possible but using aluminum oxide or MgO tunnel barriers to assist injection in graphene spin-valve devices is more efficient if suitable oxide-graphene interfaces can be formed. To address this problem we have used pulsed laser deposition (PLD) to grow thin (1-1000 nm) magnesium oxide films directly on epitaxial graphene on SiC(0001). We observe very smooth film morphologies (typical rms roughness of ~0.4 nm) that are nearly independent of film thickness and conform to the substrate surface which had ~0.2 nm rms roughness. Surface roughness is less than 0.5 nm for thicknesses up to 1000 nm and is independent of deposition laser pulse energy within the range 300-700 mJ/pulse at rates of 1-50 Hz. X-ray diffraction shows predominant (111) and (100) orientations, indicating the possibility of doping the graphene by the polar (111) interface. Raman spectroscopy indicates that the graphene is not measurably damaged by magnesium oxide growth. This work shows that PLD is a good technique to produce graphene-oxide interfaces without pre-deposition of an adhesion layer. The films are free of defects or pinholes (that can be observed by atomic force microscopy) and can be grown at arbitrary thicknesses without increasing the roughness or damaging the graphene. The details and kinetics of the deposition process will be described with comparisons being made to other dielectric-on-graphene deposition approaches.

11:00am **GR+EM+ET+MS+NS-FrM9 Facile, Controllable Graphene-based P-N Junctions Using Self-Assembled Monolayers.** *J. Baltazar, H. Sojoudi, J. Kowalik, L. Tolbert, S. Graham, C.L. Henderson*, Georgia Institute of Technology

In this study we investigate the use of a self-assembled monolayer (SAM) to create a p-n junction in graphene films. Previous techniques rely on charge transfer from adsorbants or electrostatic gate/potentials. Here we demonstrate that, by successfully modifying the SiO₂ surface with an aminopropyltriethoxysilane (APTES) layer, and using intrinsically p-doped transferred CVD graphene films, a well-defined junction can be achieved. Field-effect transistors and p-n junction regions are fabricated prior to graphene film transfer, in order to preserve the pristine properties of the graphene. The I-V characteristic curve indicates the presence of two thermally-controllable neutrality points. This method allows a facile, controllable and low temperature fabrication of graphene p-n junctions.

11:20am **GR+EM+ET+MS+NS-FrM10 Impact of Cleaning Procedures on the Performance of Graphene-Based Field Effect Transistors.** *M. Lodge, M. Ishigami*, University of Central Florida

It is now widely accepted that surface contaminants have large effects on the performance of graphene-based field effect transistors. Various techniques are now available to clean processing residues from graphene, yet some of these techniques are chemically aggressive leaving concerns that they may damage graphene and affect the device performance. In addition, there are no consensus on the best method to produce the cleanest and, therefore, the best graphene devices.

Here, we have performed a study on the impact of various chemical treatments on the performance of field effect transistors fabricated from graphene grown using chemical vapor deposition. By measuring the impact of hydrogen-annealing, oxygen-annealing, and various solvent-based cleaning on 50 graphene field effect transistors, we generate a statistically-significant conclusion on the best cleaning technique for producing the highest performance. We will present our results along with our scanning tunneling microscopy images and Raman spectra to shed a light on the mechanism involved in each cleaning technique.

11:40am **GR+EM+ET+MS+NS-FrM11 High Efficiency Graphene Solar Cells by Chemical Doping.** *X. Miao, S. Tongay, M.K. Petterson, K. Berke, A.G. Rinzler, B.R. Appleton, A.F. Hebard*, University of Florida

We demonstrate single layer graphene/n-Si Schottky junction solar cells that under AM1.5 illumination exhibit a power conversion efficiency (PCE) of 8.6%. This performance, achieved by doping the graphene with bis(trifluoromethanesulfonyl)amide, exceeds the native (undoped) device performance by a factor of 4.5 and is the **highest PCE** reported for graphene-based solar cells to date. Current-voltage, capacitance-voltage, and external quantum efficiency measurements show the enhancement to be due to the doping-induced shift in the graphene chemical potential that increases the graphene carrier density (decreasing the cell series resistance) and increases the cell's built-in potential (increasing the open circuit voltage) both of which improve the solar cell fill factor.

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Caldwell, J.D.: GR+AS+BI+PS+SS-WeM9, 15;
GR+EM+ET+NS+TF-MoA1, 7; GR-ThP9, 27

Calliari, L.: GR-ThP3, 26
Calzolari, A.: GR-ThP11, 28
Campbell, P.M.: GR+EM+ET+MS+NS-FrM3, 30
Cantor, M.: EM+TF+OX+GR-MoA1, 5
Cartier, E.A.: EM+TF+OX+GR-MoA7, 6
Casolo, S.: GR+AS+EM+NS+SS-WeA12, 18
Castner, D.G.: IS+AS+BI+ET+GR+NS-TuA1, 12
Caymax, M.: EM+TF+OX+GR-MoA1, 5;
LB+EM+GR+MN+TR-WeA12, 20
Ceballos-Sanchez, O.: EM+TF+OX+GR-MoA9, 6
Ceccone, G.: NS+EN+GR-TuA2, 13
Chabal, Y.J.: EM+TF+OX+GR-MoA6, 5;
GR+AS+BI+PS+SS-WeM2, 15;
GR+AS+EM+NS+SS-WeA1, 17
Chae, J.: GR+EM+ET+NS+TF-MoA10, **8**
Champlain, J.: EM+TF+OX+GR-MoA10, 6
Chang, C.S.: GR+EM+ET+NS+TF-MoA6, 7
Chao, Y.C.: LB+EM+GR+MN+TR-WeA8, 19
Chen, J.: GR+AS+NS+SP+SS-TuA2, 10
Chen, J.-H.: GR+AS+NS+SS-ThM5, 21
Chen, S.: GR+AS+NS+SP+SS-TuA11, 11
Cheng, S.-F.: GR+AS+EM+MI+MN-TuM1, 9
Chhowalla, M.: NS+EN+GR-TuA8, **14**
Cho, H.K.: NS+EN+GR-TuA11, 14
Cho, K.J.: GR+AS+EM+NS+SS-WeA1, 17
Choi, J.: GR+EM+ET+NS+TF-MoA7, 7
Choi, J.Y.: GR+EM+NS+PS+SS+TF-MoM11, 3
Choi, K.: EM+TF+OX+GR-MoA7, 6
Cimpoiasu, E.: GR+AS+NS+SS-ThM3, 21
Clark, K.: ET+SS+GR+SP-ThA6, **23**;
GR+EM+NS+PS+SS+TF-MoM2, 2
Cleveland, E.: EM+TF+OX+GR-MoA10, **6**
Cohen, H.: ET+SS+GR+SP-FrM3, **29**
Colón Santana, J.: GR+EM+ET+NS+TF-MoA7, 7
Colpo, P.: NS+EN+GR-TuA2, 13
Conrad, E.: GR+AS+NS+SP+SS-TuA1, 10
Copel, M.W.: GR+EM+NS+PS+SS+TF-MoM8, 3
Coraux, J.: GR+AS+EM+NS+SS-WeA10, 17
Cortes, R.: GR+EM+NS+SS+TF-ThA2, **24**
Cowin, J.: IS+AS+BI+ET+GR+NS-TuA12, 13
Cui, S.: GR+AS+NS+SP+SS-TuA2, 10
Culbertson, J.C.: GR+EM+NS+PS+SS+TF-
MoM3, 2

— D —

Dahal, A.: GR+AS+EM+NS+SS-WeA8, **17**;
GR+EM+NS+SS+TF-ThA7, 25
Davis, R.C.: LB+EM+GR+MN+TR-WeA3, 18
De Padova, P.: GR+EM+NS+SS+TF-ThA6, 25
Dean, C.: GR+EM+ET+NS+TF-MoA10, 8
Dekoster, J.: EM+TF+OX+GR-MoA1, 5
Desai, T.V.: IS+AS+BI+ET+GR+NS-TuA2, 12
Desplats, O.: EM+TF+OX+GR-MoA9, 6
Detslefs, B.: GR+AS+NS+SP+SS-TuA9, 11
Diebold, A.C.: GR+AS+NS+SP+SS-TuA11, 11
Dimitrakopoulos, C.: GR+AS+NS+SP+SS-TuA11,
11
Dong, H.: EM+TF+OX+GR-MoM5, 1
Doudin, B.: GR+EM+ET+NS+TF-MoA7, 7
Dougherty, D.B.: GR+AS+BI+PS+SS-WeM10,
16; GR+AS+NS+SP+SS-TuA11, 11;
GR+EM+ET+MS+NS-FrM8, 31; GR-ThP11,
28
Dowben, P.A.: GR+EM+ET+NS+TF-MoA7, 7
Duan, X.: GR+EM+ET+MS+NS-FrM1, **30**
Dubey, M.D.: GR+EM+ET+MS+NS-FrM8, 31
Dugger, M.T.: LB+EM+GR+MN+TR-WeA1, 18

— E —

Ealet, B.: GR+EM+NS+SS+TF-ThA6, 25
Eddy, Jr., C.R.: EM+TF+OX+GR-MoM9, 1;
GR+AS+BI+PS+SS-WeM9, 15;
GR+AS+EM+MI+MN-TuM1, 9;
GR+AS+NS+SP+SS-TuA9, 11;
GR+EM+ET+MS+NS-FrM3, 30;
GR+EM+ET+MS+NS-FrM5, 30;
GR+EM+ET+NS+TF-MoA1, 7;

GR+EM+NS+PS+SS+TF-MoM1, 2;
GR+EM+NS+PS+SS+TF-MoM3, 2; GR-ThP9,
27
Edgar, J.H.: EM+TF+OX+GR-MoM9, 1
Eizenberg, M.: LB+EM+GR+MN+TR-WeA12, **20**
Elliman, R.G.: LB+EM+GR+MN+TR-WeA7, 19
Elmquist, R.: LB+EM+GR+MN+TR-WeA10, 19
Emery, J.D.: GR+AS+BI+PS+SS-WeM1, 15;
GR+AS+NS+SP+SS-TuA9, **11**
Engstrom, J.R.: IS+AS+BI+ET+GR+NS-TuA2, **12**
Enta, Y.: GR+EM+NS+PS+SS+TF-MoM10, 3
Esquinazi, P.: GR+AS+EM+MI+MN-TuM9, 9
Exarhos, A.L.: GR+AS+EM+MI+MN-TuM2, 9

— F —

Fadida, S.: LB+EM+GR+MN+TR-WeA12, 20
Farmer, B.L.: GR+AS+BI+PS+SS-WeM6, 15
Fedorov, A.: GR-ThP3, 26
Feenstra, R.: GR+AS+NS+SP+SS-TuA10, 11
Feigelson, B.: GR+AS+EM+MI+MN-TuM1, 9
Fenter, P.: GR+AS+BI+PS+SS-WeM1, 15
Feygelson, B.N.: GR-ThP9, 27
Firrinelli, A.: EM+TF+OX+GR-MoA1, 5
First, P.N.: GR+AS+NS+SP+SS-TuA3, **10**
Flores, F.: ET+SS+GR+SP-FrM4, 29
Frank, M.M.: EM+TF+OX+GR-MoA7, 6
French, B.: GR+EM+NS+SS+TF-ThA1, 24
French, M.: GR+EM+NS+SS+TF-ThA1, 24
Fridmann, J.: LB+EM+GR+MN+TR-WeA7, **19**
Fromm, F.: GR+EM+NS+PS+SS+TF-MoM10, 3
Fruchart, O.: GR+AS+EM+NS+SS-WeA10, 17
Fukidome, H.: GR+EM+NS+PS+SS+TF-MoM10,
3

— G —

Gajdardziska-Josifovska, M.:
GR+AS+NS+SP+SS-TuA2, 10
Gao, H.-J.: ET+SS+GR+SP-ThA1, **23**
Gao, Y.: GR+EM+ET+NS+TF-MoA10, 8
Garces, N.Y.: EM+TF+OX+GR-MoM9, 1;
GR+AS+EM+MI+MN-TuM1, 9;
GR+EM+ET+MS+NS-FrM5, 30;
GR+EM+NS+PS+SS+TF-MoM1, 2;
GR+EM+NS+PS+SS+TF-MoM3, 2
Gargiulo, F.: GR+AS+NS+SS-ThM5, 21
Gaskill, D.K.: GR+AS+BI+PS+SS-WeM9, 15;
GR+AS+NS+SP+SS-TuA9, 11;
GR+EM+ET+MS+NS-FrM3, 30;
GR+EM+ET+MS+NS-FrM5, 30;
GR+EM+ET+NS+TF-MoA1, 7;
GR+EM+NS+PS+SS+TF-MoM1, 2;
GR+EM+NS+PS+SS+TF-MoM3, 2; GR-ThP9,
27
Gautam, A.: GR+AS+NS+SS-ThM5, 21
Gerber, T.: GR+AS+NS+SP+SS-TuA7, 10
Ghorai, S.: IS+AS+BI+ET+GR+NS-TuA9, 13
Gila, B.: LB+EM+GR+MN+TR-WeA7, 19
Gilles, M.K.: IS+AS+BI+ET+GR+NS-TuA9, 13
Gong, C.: GR+AS+EM+NS+SS-WeA1, **17**
Gowda, M.H.: GR+AS+EM+MI+MN-TuM1, 9
Graham, S.: GR+EM+ET+MS+NS-FrM9, 31; GR-
ThP10, 27
Grampeix, H.: EM+TF+OX+GR-MoA9, 6
Grånäs, E.: GR+AS+NS+SP+SS-TuA7, **10**
Greene, A.: EM+TF+OX+GR-MoM3, 1
Grill, A.: GR+AS+NS+SP+SS-TuA11, 11
Grueneis, A.: GR-ThP3, 26
Guallar-Hoyas, C.: IS+AS+BI+ET+GR+NS-TuA3,
12

— H —

Guerrero, J.: EM+TF+OX+GR-MoA9, 6
Gunlycke, D.: GR+AS+NS+SS-ThM3, 21
Guo, J.H.: GR+EM+ET+NS+TF-MoA11, 8
Gutmann, S.: ET+SS+GR+SP-ThA11, 24

Handa, H.: GR+EM+NS+PS+SS+TF-MoM10, 3
Hannon, J.B.: GR+EM+NS+PS+SS+TF-MoM8, 3
Hanus, J.: NS+EN+GR-TuA2, 13
Hao, Y.: GR+AS+NS+SP+SS-TuA11, 11
Hapala, P.: ET+SS+GR+SP-ThA9, 23
Harada, Y.: GR+AS+EM+NS+SS-WeA12, 18
Harker, M.: LB+EM+GR+MN+TR-WeA3, 18
Haydell, M.: GR+AS+NS+SS-ThM3, 21
He, G.: GR+AS+NS+SP+SS-TuA10, 11
Hebard, A.F.: GR+EM+ET+MS+NS-FrM11, 31;
LB+EM+GR+MN+TR-WeA7, 19
Henderson, C.L.: GR+EM+ET+MS+NS-FrM9, 31;
GR-ThP10, 27
Hernandez, S.: GR-ThP9, 27
Hernández, S.C.: GR+AS+BI+PS+SS-WeM9, 15;
GR+EM+NS+PS+SS+TF-MoM1, 2
Herrera-Gomez, A.: EM+TF+OX+GR-MoA9, 6
Hersam, M.C.: GR+AS+BI+PS+SS-WeM1, 15;
GR+AS+BI+PS+SS-WeM3, 15;
GR+AS+NS+SP+SS-TuA9, 11
Heyns, M.: EM+TF+OX+GR-MoA1, 5
Hinkle, C.L.: EM+TF+OX+GR-MoA4, 5
Hiramatsu, M.: GR+AS+NS+SS-ThM9, 21
Hirschmugl, C.: GR+AS+NS+SP+SS-TuA2, 10
Hobart, K.D.: GR-ThP9, 27
Hodes, G.: ET+SS+GR+SP-FrM3, 29
Hoehne, R.: GR+AS+EM+MI+MN-TuM9, 9
Hofmann, T.: LB+EM+GR+MN+TR-WeA10, 19
Hone, J.C.: GR+EM+ET+NS+TF-MoA10, 8
Hori, M.: GR+AS+NS+SS-ThM9, 21
Horn, K.: GR+EM+ET+NS+TF-MoA8, 8
Horsfall, A.B.: GR+EM+NS+PS+SS+TF-MoM1, 2
Hossain, T.: EM+TF+OX+GR-MoM9, 1
Howe, J.: GR+EM+NS+PS+SS+TF-MoM3, 2
Hu, Y.C.: LB+EM+GR+MN+TR-WeA8, 19
Huang, L.W.: GR+EM+ET+NS+TF-MoA6, 7

— I —

Ide, T.: GR+EM+NS+PS+SS+TF-MoM10, 3
Irlle, S.: GR-ThP3, 26
Ishigami, M.: GR+AS+BI+PS+SS-WeM6, 15;
GR+EM+ET+MS+NS-FrM10, 31;
GR+EM+ET+NS+TF-MoA2, 7
Ishikawa, K.: GR+AS+NS+SS-ThM9, 21
Itzhaik, Y.: ET+SS+GR+SP-FrM3, 29

— J —

Jaehnig, M.: GR+EM+NS+SS+TF-ThA1, 24
Jandhyala, S.: GR+EM+ET+MS+NS-FrM7, 30
Jelinek, P.: ET+SS+GR+SP-FrM4, 29;
ET+SS+GR+SP-ThA9, 23
Jelinek, P.: ET+SS+GR+SP-FrM5, 29
Jena, D.: GR+AS+NS+SS-ThM11, 22
Jensen, B.D.: LB+EM+GR+MN+TR-WeA3, 18
Ji, S.-H.: GR+EM+NS+PS+SS+TF-MoM8, 3
Jiang, S.: EM+TF+OX+GR-MoA1, 5
Johnson, C.E.: IS+AS+BI+ET+GR+NS-TuA7, 12
Johnson, J.A.: IS+AS+BI+ET+GR+NS-TuA7, 12
Johnson, S.D.: GR+AS+EM+MI+MN-TuM1, 9
Joiner, C.: GR-ThP13, 28
Jones, K.: LB+EM+GR+MN+TR-WeA3, 18
Jung, S.: GR+EM+ET+NS+TF-MoA10, 8
Jung, W.: GR-ThP6, 27

— K —

Kajiwara, T.: GR+AS+NS+SS-ThM1, 21
Kalinin, S.V.: ET+SS+GR+SP-ThA7, 23
Kanda, T.: GR+AS+NS+SS-ThM9, 21
Kandel, S.A.: ET+SS+GR+SP-ThA3, 23
Karmel, H.J.: GR+AS+NS+SP+SS-TuA9, 11
Katoch, J.: GR+AS+BI+PS+SS-WeM6, 15;
GR+EM+ET+NS+TF-MoA2, 7
Kaufman Osborn, T.: LB+EM+GR+MN+TR-
WeA11, 20
Kaufman-Osborn, T.: EM+TF+OX+GR-MoA3, 5
Kawai, Y.: GR+EM+NS+PS+SS+TF-MoM10, 3
Kawakami, R.: GR+AS+EM+MI+MN-TuM3, 9
Kellogg, G.L.: GR+AS+NS+SP+SS-TuA8, 10
Kelly, S.T.: IS+AS+BI+ET+GR+NS-TuA9, 13
Kent, T.J.: LB+EM+GR+MN+TR-WeA11, 20

Kiantaj, K.: EM+TF+OX+GR-MoA3, 5;
LB+EM+GR+MN+TR-WeA11, 20
Kikkawa, J.M.: GR+AS+EM+MI+MN-TuM2, 9
Kim, D.H.: NS+EN+GR-TuA10, 14
Kim, J.: EM+TF+OX+GR-MoM6, 1;
GR+EM+ET+MS+NS-FrM7, 30
Kim, J.H.: NS+EN+GR-TuA11, 14
Kim, M.J.: EM+TF+OX+GR-MoA4, 5
Kim, P.: GR+EM+ET+NS+TF-MoA10, 8
Kim, S.N.: GR+AS+BI+PS+SS-WeM6, 15
King, S.: GR+EM+NS+SS+TF-ThA1, 24
King, W.: GR+AS+NS+SS-ThM3, 21
Kinoshita, T.: GR+EM+NS+PS+SS+TF-MoM10,
3
Kinross, J.: IS+AS+BI+ET+GR+NS-TuA3, 12
Kis, A.: GR+EM+NS+SS+TF-ThA10, 25
Kisielowski, C.: GR+AS+NS+SS-ThM5, 21
Knudsen, J.: GR+AS+NS+SP+SS-TuA7, 10
Knupfer, M.: GR-ThP3, 26
Komori, F.: GR+AS+NS+SS-ThM1, 21
Kondo, H.: GR+AS+NS+SS-ThM9, 21
Kondo, T.: GR+AS+EM+NS+SS-WeA12, 18
Kong, L.: GR+EM+ET+NS+TF-MoA7, 7
Kostov, K.: LB+EM+GR+MN+TR-WeA9, 19
Kotsugi, M.: GR+EM+NS+PS+SS+TF-MoM10, 3
Kowalik, J.: GR+EM+ET+MS+NS-FrM9, 31; GR-
ThP10, 27
Kozhushner, M.: ET+SS+GR+SP-ThA4, 23
Krejci, O.: ET+SS+GR+SP-ThA9, 23
Kroemker, B.: GR+AS+NS+SP+SS-TuA1, 10
Kuang, Z.: GR+AS+BI+PS+SS-WeM6, 15
Kub, F.J.: GR+AS+EM+MI+MN-TuM1, 9; GR-
ThP9, 27
Kuhn, M.: GR+EM+NS+SS+TF-ThA1, 24
Kummel, A.C.: EM+TF+OX+GR-MoA3, 5;
LB+EM+GR+MN+TR-WeA11, 20

— L —

LaBella, V.P.: ET+SS+GR+SP-FrM6, 29;
GR+AS+NS+SP+SS-TuA11, 11
Lacovig, P.: LB+EM+GR+MN+TR-WeA9, 19
Lahiri, J.: GR+EM+NS+SS+TF-ThA2, 24
Larciprete, R.: LB+EM+GR+MN+TR-WeA9, 19
Laskin, A.: IS+AS+BI+ET+GR+NS-TuA9, 13
Laskoski, M.: GR-ThP9, 27
Le Lay, G.: GR+EM+NS+SS+TF-ThA6, 25
Le, D.: GR+EM+ET+MS+NS-FrM3, 30;
GR+EM+ET+NS+TF-MoA2, 7; GR-ThP8, 27;
NS+EN+GR-TuA7, 14
Le, N.B.: GR-ThP4, 26
Lee, C.-M.: GR+EM+ET+NS+TF-MoA7, 7
Lee, J.: GR-ThP6, 27
Lee, J.S.: EM+TF+OX+GR-MoA3, 5
Lee, K.M.: NS+EN+GR-TuA10, 14
Lee, K.-M.: GR+EM+ET+MS+NS-FrM3, 30
Lee, W.K.: GR+AS+NS+SS-ThM3, 21; GR-ThP9,
27
Lemaitre, M.: LB+EM+GR+MN+TR-WeA7, 19
Li, A.-P.: ET+SS+GR+SP-ThA6, 23;
GR+EM+NS+PS+SS+TF-MoM2, 2
Li, L.J.: LB+EM+GR+MN+TR-WeA8, 19
Li, Z.: ET+SS+GR+SP-ThA11, 24
Liddiard, S.: LB+EM+GR+MN+TR-WeA3, 18
Lin, D.: LB+EM+GR+MN+TR-WeA12, 20
Lin, K.C.: LB+EM+GR+MN+TR-WeA8, 19
Lin, M.Y.: GR-ThP2, 26
Lin, S.: GR+EM+ET+MS+NS-FrM3, 30
Linck, M.: GR+AS+NS+SS-ThM5, 21
Linder, B.P.: EM+TF+OX+GR-MoA7, 6
Liu, Z.: GR+EM+NS+SS+TF-ThA3, 24
Lizzit, S.: LB+EM+GR+MN+TR-WeA9, 19
Lo, E.: IS+AS+BI+ET+GR+NS-TuA1, 12
Lock, E.H.: GR+AS+BI+PS+SS-WeM9, 15; GR-
ThP9, 27
Lodge, M.: GR+EM+ET+MS+NS-FrM10, 31
Lou, J.: GR+EM+NS+SS+TF-ThA3, 24
Louie, S.G.: GR+AS+NS+SS-ThM5, 21
Lu, G.: GR+AS+NS+SP+SS-TuA2, 10
Lu, N.: EM+TF+OX+GR-MoA4, 5
Lu, W.H.: GR-ThP8, 27

Lu, Y.: ET+SS+GR+SP-ThA3, 23
Lu, Y.P.: GR-ThP2, 26
Lucero, A.T.: EM+TF+OX+GR-MoM6, 1
Lui, Y.: IS+AS+BI+ET+GR+NS-TuA7, 12
Lund, J.: LB+EM+GR+MN+TR-WeA3, 18
Luscombe, C.K.: ET+SS+GR+SP-ThA11, 24
— M —
Ma, Q.: GR-ThP8, 27
Madisetti, S.: EM+TF+OX+GR-MoM3, 1
Magnuson, C.W.: GR+AS+NS+SP+SS-TuA11, 11
Majzik, Z.: ET+SS+GR+SP-FrM5, 29;
ET+SS+GR+SP-ThA9, 23
Mann, J.: GR-ThP8, 27
Mansour, A.N.: GR+AS+NS+SS-ThM10, 22
Martin, F.: EM+TF+OX+GR-MoA9, 6
Martinez, E.: EM+TF+OX+GR-MoA9, 6
Matsubayashi, A.: GR+AS+EM+NS+SS-WeA7,
17
Mattson, E.: GR+AS+NS+SP+SS-TuA2, 10
Mazzio, K.: ET+SS+GR+SP-ThA11, 24
McGuire, C.: GR+EM+ET+MS+NS-FrM3, 30
McNeilan, J.D.: GR+AS+NS+SP+SS-TuA11, 11
Menzel, D.: LB+EM+GR+MN+TR-WeA9, 19
Merckling, C.: EM+TF+OX+GR-MoA1, 5
Meyer III, H.M.: EM+TF+OX+GR-MoM9, 1
Meyer, D.J.: GR+EM+ET+MS+NS-FrM5, 30
Miao, X.: GR+EM+ET+MS+NS-FrM11, 31
Michely, T.W.: GR+AS+NS+SP+SS-TuA7, 10;
GR+EM+NS+PS+SS+TF-MoM5, 3
Miyamoto, J.: LB+EM+GR+MN+TR-WeA2, 18
Miyashita, H.: GR+EM+NS+PS+SS+TF-MoM10,
3
Moeller, R.: ET+SS+GR+SP-FrM7, 30
Moon, J.S.: GR+EM+ET+MS+NS-FrM3, 30;
GR+EM+NS+PS+SS+TF-MoM1, 2
Moore, R.: EM+TF+OX+GR-MoM3, 1;
GR+AS+NS+SP+SS-TuA11, 11
Mordi, G.: GR+EM+ET+MS+NS-FrM7, 30
Mowll, T.: GR+EM+NS+PS+SS+TF-MoM2, 2
Muirhead, L.: IS+AS+BI+ET+GR+NS-TuA3, 12
Mulvaney, S.P.: GR-ThP9, 27
Munson, A.: GR+AS+NS+SP+SS-TuA11, 11
Myers-Ward, R.L.: GR+AS+BI+PS+SS-WeM9,
15; GR+AS+NS+SP+SS-TuA9, 11;
GR+EM+ET+MS+NS-FrM3, 30;
GR+EM+ET+MS+NS-FrM5, 30;
GR+EM+ET+NS+TF-MoA1, 7;
GR+EM+NS+PS+SS+TF-MoM1, 2;
GR+EM+NS+PS+SS+TF-MoM3, 2; GR-ThP9,
27

— N —

Nadzeyka, A.: LB+EM+GR+MN+TR-WeA7, 19
Nagaiah, P.: EM+TF+OX+GR-MoM3, 1
Nagareddy, V.K.: GR+EM+NS+PS+SS+TF-
MoM1, 2
Naik, R.R.: GR+AS+BI+PS+SS-WeM6, 15
Najmaei, S.: GR+EM+NS+SS+TF-ThA3, 24
Nakamura, J.: GR+AS+EM+NS+SS-WeA12, 18
Nakatsuji, K.: GR+AS+NS+SS-ThM1, 21
Narayanan, V.: EM+TF+OX+GR-MoA7, 6
Nasse, M.: GR+AS+NS+SP+SS-TuA2, 10
Nath, A.: GR+EM+ET+MS+NS-FrM5, 30;
GR+EM+ET+NS+TF-MoA1, 7;
GR+EM+NS+PS+SS+TF-MoM1, 2;
GR+EM+NS+PS+SS+TF-MoM3, 2
Nayfeh, O.: GR+EM+ET+MS+NS-FrM8, 31
N'Diaye, A.T.: GR+AS+EM+NS+SS-WeA10, 17
Nefedov, A.: GR-ThP3, 26
Nelson, F.J.: GR+AS+NS+SP+SS-TuA11, 11
Nepal, N.: EM+TF+OX+GR-MoM9, 1;
GR+EM+ET+NS+TF-MoA1, 7
Nigge, P.: IS+AS+BI+ET+GR+NS-TuA9, 13
Novak, S.: EM+TF+OX+GR-MoM3, 1
Novoselov, K.: GR+AS+BI+PS+SS-WeM2, 15
Nunney, T.S.: GR-ThP1, 26
Nyakiti, L.O.: GR+AS+BI+PS+SS-WeM9, 15;
GR+AS+NS+SP+SS-TuA9, 11;
GR+EM+ET+MS+NS-FrM3, 30;

GR+EM+ET+MS+NS-FrM5, 30;
 GR+EM+ET+NS+TF-MoA1, 7;
 GR+EM+NS+PS+SS+TF-MoM1, 2;
 GR+EM+NS+PS+SS+TF-MoM3, 2; GR-ThP9,
 27
 Nyns, L.: LB+EM+GR+MN+TR-WeA12, 20
 — **O** —
 Oehzelt, M.: GR-ThP3, 26
 Ogino, T.: GR-ThP5, 26
 Oh, D.-H.: GR-ThP6, 27
 Ohkouchi, T.: GR+EM+NS+PS+SS+TF-MoM10,
 3
 Ohldag, H.: GR+AS+EM+MI+MN-TuM9, 9
 Ohta, T.: GR+AS+NS+SP+SS-TuA8, 10
 Oktyabrsky, S.: EM+TF+OX+GR-MoM3, 1
 Oleynik, I.I.: ET+SS+GR+SP-ThA4, 23;
 GR+AS+EM+MI+MN-TuM10, 9;
 GR+AS+EM+NS+SS-WeA2, 17
 Ondracek, M.: ET+SS+GR+SP-FrM4, 29
 Ondráček, M.: ET+SS+GR+SP-FrM5, 29
 Oshima, M.: GR+AS+EM+NS+SS-WeA12, 18
 Outlaw, R.A.: GR+AS+NS+SS-ThM10, 22
 — **P** —
 Pai, W.W.: LB+EM+GR+MN+TR-WeA8, 19
 Pantelides, S.T.: ET+SS+GR+SP-FrM1, 29
 Paris, A.: GR-ThP3, 26
 Park, C.-Y.: GR+EM+NS+PS+SS+TF-MoM4, 3;
 GR-ThP6, 27
 Park, J.-H.: GR+EM+NS+PS+SS+TF-MoM11, 3
 Parracino, M.A.: NS+EN+GR-TuA2, 13
 Parsons, G.N.: NS+EN+GR-TuA10, 14
 Pei, L.: LB+EM+GR+MN+TR-WeA3, 18
 Perez Medina, G.J.: GR+EM+ET+NS+TF-MoA7,
 7
 Perez Roldan, M.J.: NS+EN+GR-TuA2, 13
 Perriot, R.: GR+AS+EM+MI+MN-TuM10, 9
 Petaccia, L.: GR-ThP3, 26
 Petford-Long, A.: IS+AS+BI+ET+GR+NS-TuA7,
 12
 Petterson, M.K.: GR+EM+ET+MS+NS-FrM11, 31
 Povey, I.M.: EM+TF+OX+GR-MoA6, 5
 Prasad, S.V.: LB+EM+GR+MN+TR-WeA1, 18
 Prokes, S.M.: EM+TF+OX+GR-MoA10, 6
 Pu, H.: GR+AS+NS+SP+SS-TuA2, 10
 — **Q** —
 Qin, X.: EM+TF+OX+GR-MoM5, 1
 Quardokus, R.C.: ET+SS+GR+SP-ThA3, 23
 Quinlan, R.A.: GR+AS+NS+SS-ThM10, 22
 — **R** —
 Rafik, A.: GR+AS+EM+NS+SS-WeA8, 17
 Rahman, T.S.: GR+EM+ET+NS+TF-MoA2, 7;
 NS+EN+GR-TuA7, 14
 Ralsano, R.: ET+SS+GR+SP-FrM6, 29
 Raman, T.: GR-ThP8, 27
 Rao, M.V.: GR+EM+NS+PS+SS+TF-MoM1, 2
 Ratner, B.D.: IS+AS+BI+ET+GR+NS-TuA1, 12
 Razavi Hesabi, Z.: GR-ThP13, 28
 Real, M.: LB+EM+GR+MN+TR-WeA10, 19
 Ren, F.: LB+EM+GR+MN+TR-WeA7, 19
 Resta, A.: GR+EM+NS+SS+TF-ThA6, 25
 Rhim, S.: GR+AS+NS+SP+SS-TuA2, 10
 Rinzler, A.G.: GR+EM+ET+MS+NS-FrM11, 31
 Robertson, J.: EM+TF+OX+GR-MoM10, 2
 Robinson, J.T.: GR+AS+BI+PS+SS-WeM9, 15;
 GR+AS+NS+SP+SS-TuA8, 10;
 GR+AS+NS+SS-ThM3, 21
 Robinson, Z.R.: GR+AS+NS+SP+SS-TuA11, 11;
 GR+EM+NS+PS+SS+TF-MoM2, 2
 Rosa, L.: GR+EM+ET+NS+TF-MoA7, 7
 Ross, F.M.: GR+EM+NS+PS+SS+TF-MoM8, 3
 Rossi, F.: NS+EN+GR-TuA2, 13
 Rotenberg, E.: GR+EM+ET+NS+TF-MoA8, 8
 Rougemaille, N.: GR+AS+EM+NS+SS-WeA10,
 17
 Routaboul, L.: GR+EM+ET+NS+TF-MoA7, 7
 Rowe, J.E.: GR+AS+BI+PS+SS-WeM10, 16;
 GR+AS+NS+SP+SS-TuA11, 11;

GR+EM+ET+MS+NS-FrM8, 31; GR-ThP11,
 28
 Roy, T.: GR-ThP13, 28
 Rozen, J.: EM+TF+OX+GR-MoA7, 6
 Ruoff, R.S.: GR+AS+NS+SP+SS-TuA11, 11;
 GR+AS+NS+SP+SS-TuA2, 10
 Ruppalt, L.: EM+TF+OX+GR-MoA10, 6
 — **S** —
 Sachdev, H.: GR-ThP3, 26
 Sadowski, J.T.: GR-ThP11, 28;
 IS+AS+BI+ET+GR+NS-TuA8, 13
 Safran, N.: GR+AS+EM+NS+SS-WeA9, 17
 Saito, N.: GR-ThP7, 27
 Sakalas, P.: GR+AS+NS+SS-ThM2, 21
 Sakurai, M.: GR+AS+EM+NS+SS-WeA12, 18
 Sandin, A.A.: GR+AS+BI+PS+SS-WeM10, 16;
 GR+AS+NS+SP+SS-TuA11, 11;
 GR+EM+ET+MS+NS-FrM8, 31; GR-ThP11,
 28
 Sasi-Szabo, L.A.: IS+AS+BI+ET+GR+NS-TuA3,
 12
 Schafer, K.C.: IS+AS+BI+ET+GR+NS-TuA3, 12
 Schlaf, R.: ET+SS+GR+SP-ThA10, 24;
 ET+SS+GR+SP-ThA11, 24
 Schmid, A.K.: GR+AS+EM+NS+SS-WeA10, 17
 Schmitz, A.: GR+EM+ET+MS+NS-FrM3, 30
 Schofield, M.: GR+AS+NS+SP+SS-TuA2, 10
 Schröder, U.: GR+AS+NS+SP+SS-TuA7, 10
 Schroter, M.: GR+AS+NS+SS-ThM2, 21
 Schubert, M.: LB+EM+GR+MN+TR-WeA10, 19
 Schulte, K.: GR+AS+NS+SP+SS-TuA7, 10
 Sekine, M.: GR+AS+NS+SS-ThM9, 21
 Semidey-Flecha, L.: GR+AS+EM+NS+SS-
 WeA11, 18
 Seo, H.-C.: GR+EM+ET+MS+NS-FrM3, 30
 Setvin, M.: ET+SS+GR+SP-ThA9, 23
 Seyller, Th.: GR+EM+ET+NS+TF-MoA8, 8;
 GR+EM+NS+PS+SS+TF-MoM10, 3
 Shafiq, N.: GR+AS+BI+PS+SS-WeM2, 15
 Sheehan, P.E.: GR+AS+BI+PS+SS-WeM9, 15;
 GR+AS+NS+SS-ThM3, 21; GR-ThP9, 27
 Shepard, K.L.: GR+EM+ET+NS+TF-MoA10, 8
 Shikano, T.: GR+AS+EM+NS+SS-WeA12, 18
 Shin, B.G.: GR-ThP6, 27
 Shin, H.: GR+EM+NS+PS+SS+TF-MoM4, 3
 Shin, H.-J.: GR+EM+NS+PS+SS+TF-MoM11, 3
 Sholl, D.: GR+AS+EM+NS+SS-WeA11, 18
 Sojoudi, H.: GR+EM+ET+MS+NS-FrM9, 31; GR-
 ThP10, 27
 Song, I.: GR+EM+NS+PS+SS+TF-MoM4, 3
 Spampinato, V.: NS+EN+GR-TuA2, 13
 Spemann, D.: GR+AS+EM+MI+MN-TuM9, 9
 Srivastava, N.: GR+AS+NS+SP+SS-TuA10, 11
 Steele, B.: GR+AS+EM+MI+MN-TuM10, 9
 Stein, M.J.: IS+AS+BI+ET+GR+NS-TuA1, 12
 Stine, R.: GR+AS+BI+PS+SS-WeM9, 15;
 GR+AS+NS+SS-ThM3, 21
 Strocio, J.A.: GR+EM+ET+NS+TF-MoA10, 8
 Stuart, S.C.: GR+EM+ET+MS+NS-FrM8, 31
 Suemitsu, M.: GR+EM+NS+PS+SS+TF-MoM10,
 3
 Sun, D.Z.: GR-ThP8, 27
 Sung, C.Y.: GR+AS+NS+SP+SS-TuA11, 11
 Sutter, E.: GR+EM+NS+SS+TF-ThA2, 24
 Sutter, P.W.: GR+AS+EM+NS+SS-WeA8, 17;
 GR+EM+NS+SS+TF-ThA2, 24
 Suzuki, T.: GR+AS+EM+NS+SS-WeA12, 18
 Švec, M.: ET+SS+GR+SP-FrM5, 29
 — **T** —
 Takagi, K.: GR+AS+NS+SS-ThM1, 21
 Takai, O.: GR-ThP7, 27
 Takats, Z.: IS+AS+BI+ET+GR+NS-TuA3, 12
 Tamañana, C.R.: GR+AS+NS+SS-ThM3, 21
 Tanaka, S.: GR+AS+NS+SS-ThM1, 21
 Tantarini, G.F.: GR+AS+EM+NS+SS-WeA12,
 18
 Tatulian, S.A.: GR+AS+BI+PS+SS-WeM6, 15
 Teng, D.: GR+AS+EM+NS+SS-WeA11, 18

Thevuthasan, S.: IS+AS+BI+ET+GR+NS-TuA12,
 13
 Tivanski, A.: IS+AS+BI+ET+GR+NS-TuA9, 13
 Tokranov, V.: EM+TF+OX+GR-MoM3, 1
 Tolbert, L.: GR+EM+ET+MS+NS-FrM9, 31; GR-
 ThP10, 27
 Tongay, S.: GR+EM+ET+MS+NS-FrM11, 31;
 LB+EM+GR+MN+TR-WeA7, 19
 Trioni, M.I.: GR+AS+EM+NS+SS-WeA12, 18
 Tromp, R.M.: GR+EM+NS+PS+SS+TF-MoM8, 3
 Turchanin, A.: GR+AS+BI+PS+SS-WeM11, 16
 Turk, M.E.: GR+AS+EM+MI+MN-TuM2, 9
 Tyagi, P.: GR+AS+NS+SP+SS-TuA11, 11;
 GR+EM+NS+PS+SS+TF-MoM2, 2
 Tyliczszak, T.: GR+AS+EM+MI+MN-TuM9, 9;
 IS+AS+BI+ET+GR+NS-TuA9, 13
 Tzeng, Y.R.: LB+EM+GR+MN+TR-WeA8, 19
 — **U** —
 Ueno, T.: GR-ThP7, 27
 Ulrich, M.D.: GR+EM+ET+MS+NS-FrM8, 31
 Ungureanu, M.: GR+AS+EM+MI+MN-TuM9, 9
 Usachov, D.: GR-ThP3, 26
 Ushigome, D.: GR+AS+EM+NS+SS-WeA12, 18
 — **V** —
 Van Elshocht, S.: LB+EM+GR+MN+TR-WeA12,
 20
 VanFleet, R.: LB+EM+GR+MN+TR-WeA3, 18
 Venkatachalam, D.K.: LB+EM+GR+MN+TR-
 WeA7, 19
 Ventrice, Jr., C.A.: GR+AS+NS+SP+SS-TuA11,
 11; GR+EM+NS+PS+SS+TF-MoM2, 2
 Verbitsky, N.: GR-ThP3, 26
 Veyan, J.-F.: GR+AS+BI+PS+SS-WeM2, 15
 Vlasiouk, I.: ET+SS+GR+SP-ThA6, 23
 Vogel, E.M.: GR-ThP13, 28
 Vogt, P.: GR+EM+NS+SS+TF-ThA6, 25
 Vora, P.M.: GR+AS+EM+MI+MN-TuM2, 9
 Vo-Van, C.: GR+AS+EM+NS+SS-WeA10, 17
 Vyalikh, D.: GR-ThP3, 26
 — **W** —
 Wall, M.H.: GR-ThP1, 26
 Wallace, R.M.: EM+TF+OX+GR-MoM1, 1;
 EM+TF+OX+GR-MoM5, 1;
 GR+AS+EM+NS+SS-WeA1, 17;
 GR+EM+ET+MS+NS-FrM7, 30
 Walter, A.: GR+EM+ET+NS+TF-MoA8, 8
 Walton, S.G.: GR+AS+BI+PS+SS-WeM9, 15;
 GR+EM+NS+PS+SS+TF-MoM1, 2; GR-ThP9,
 27
 Wang, B.: IS+AS+BI+ET+GR+NS-TuA9, 13
 Wang, L.: GR+EM+ET+NS+TF-MoA10, 8
 Wang, Q.H.: GR+AS+BI+PS+SS-WeM1, 15
 Wang, W.: ET+SS+GR+SP-ThA10, 24
 Wang, X.: LB+EM+GR+MN+TR-WeA7, 19
 Wang, Y.: GR-ThP3, 26
 Wasio, N.A.: ET+SS+GR+SP-ThA3, 23
 Waterton, C.: IS+AS+BI+ET+GR+NS-TuA1, 12
 Wei, D.: EM+TF+OX+GR-MoM9, 1
 Weinert, M.: GR+AS+NS+SP+SS-TuA2, 10
 Wheeler, V.D.: GR+AS+NS+SP+SS-TuA9, 11;
 GR+EM+ET+MS+NS-FrM3, 30;
 GR+EM+ET+MS+NS-FrM5, 30;
 GR+EM+ET+NS+TF-MoA1, 7;
 GR+EM+NS+PS+SS+TF-MoM1, 2;
 GR+EM+NS+PS+SS+TF-MoM3, 2; GR-ThP9,
 27
 Winkler, K.: GR+AS+NS+SP+SS-TuA1, 10
 Woll, A.R.: IS+AS+BI+ET+GR+NS-TuA2, 12
 Wöll, Ch.: GR-ThP3, 26
 Woods, L.M.: GR-ThP4, 26
 Wu, S.: GR+AS+NS+SP+SS-TuA12, 11
 — **X** —
 Xu, Y.: GR+AS+EM+NS+SS-WeA11, 18
 — **Y** —
 Yakimov, M.: EM+TF+OX+GR-MoM3, 1
 Yakobson, GR+EM+NS+SS+TF-ThA8, 25
 Yamazaki, K.: GR-ThP5, 26

Yang, L.: IS+AS+BI+ET+GR+NS-TuA12, **13**
Yashina, L.: GR-ThP3, 26
Yazyev, O.V.: GR+AS+NS+SS-ThM5, 21
Yckache, K.: EM+TF+OX+GR-MoA9, 6
Yoshimura, T.: GR+AS+NS+SS-ThM1, 21
Young, A.: GR+EM+ET+NS+TF-MoA10, 8
Yu, J.: GR+AS+NS+SP+SS-TuA12, **11**
Yu, X.-Y.: IS+AS+BI+ET+GR+NS-TuA12, 13

— **Z** —

Zappe, M.: LB+EM+GR+MN+TR-WeA3, 18
Zarrouati, M.: GR+AS+BI+PS+SS-WeM1, 15
Zegenhagen, J.: GR+AS+NS+SP+SS-TuA9, 11
Zehnder, D.: GR+EM+ET+MS+NS-FrM3, 30
Zettl, A.: GR+AS+NS+SS-ThM5, **21**
Zhakhovsky, V.: GR+AS+EM+MI+MN-TuM10, 9
Zhan, Y.: GR+EM+NS+SS+TF-ThA3, 24

Zhang, L.: GR+EM+ET+NS+TF-MoA11, **8**
Zhang, X.-G.: ET+SS+GR+SP-FrM1, **29**;
ET+SS+GR+SP-ThA6, 23
Zhao, Y.: GR+EM+ET+NS+TF-MoA10, 8
Zhitenev, N.B.: GR+EM+ET+NS+TF-MoA10, 8
Zhu, J.F.: GR+EM+ET+NS+TF-MoA11, 8
Zhu, Z.: IS+AS+BI+ET+GR+NS-TuA12, 13
Zufelt, K.: LB+EM+GR+MN+TR-WeA3, 18