

# Monday Morning, November 10, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+NS+PS+SS+TF-MoM

## 2D Materials Growth and Processing

Moderator: Thomas Greber, University of Zurich

8:20am **2D+EM+NS+PS+SS+TF-MoM1 Exploring the Flatlands: Synthesis, Characterization and Engineering of Two-Dimensional Materials, Jun Lou**, Rice University **INVITED**

In this talk, we report the controlled vapor phase synthesis of MoS<sub>2</sub> atomic layers and elucidate a fundamental mechanism for the nucleation, growth, and grain boundary formation in its crystalline monolayers. The atomic structure and morphology of the grains and their boundaries in the polycrystalline molybdenum disulfide atomic layers are examined and first-principles calculations are applied to investigate their energy landscape. The electrical properties of the atomic layers are examined and the role of grain boundaries is evaluated. More importantly, if precise two-dimensional domains of graphene, h-BN and MoS<sub>2</sub> atomic layers can be seamlessly stitched together, in-plane heterostructures with interesting electronic applications could potentially be created. Here, we show that planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically-patterned h-BN atomic layers. Our approach can create periodic arrangements of domains with size that ranging from tens of nanometers to millimeters. The resulting graphene/h-BN atomic layers can be peeled off from their growth substrate and transferred to various platforms including flexible substrate. Finally, we demonstrate how self-assembled monolayers with a variety of end termination chemistries can be utilized to tailor the physical properties of single-crystalline MoS<sub>2</sub> atomic-layers. Our data suggests that combined interface-related effects of charge transfer, built-in molecular polarities, varied densities of defects, and remote interfacial phonons strongly modify the electrical and optical properties of MoS<sub>2</sub>, illustrating an engineering approach for local and universal property modulations in two-dimensional atomic-layers.

9:00am **2D+EM+NS+PS+SS+TF-MoM3 Influence of Substrate Orientation on the Growth of Graphene on Cu Single Crystals, Tyler Mowll**, University at Albany-SUNY, Z.R. Robinson, U.S. Naval Research Laboratory, P. Tyagi, E.W. Ong, C.A. Ventrice, Jr., University at Albany-SUNY

A systematic study of graphene growth on on-axis Cu(100) and Cu(111) single crystals oriented within 0.1° from the surface normal and a vicinal Cu(111) crystal oriented 5° off-axis has been performed. Initial attempts to grow graphene by heating each crystal to 900°C in UHV, followed by backfilling the chamber with C<sub>2</sub>H<sub>4</sub> at pressures up to 5x10<sup>-3</sup> Torr did not result in graphene formation on either the on-axis Cu(100) or on-axis Cu(111) surfaces. For the vicinal Cu(111) surface, epitaxial graphene was formed under the same growth conditions. By backfilling the chamber with C<sub>2</sub>H<sub>4</sub> before heating to the growth temperature, epitaxial graphene was formed on both the on-axis Cu(100) and off-axis Cu(111) surfaces, but not the on-axis Cu(111) surface. By using an argon overpressure, epitaxial overlayers could be achieved on all three Cu substrates. These results indicate that the most catalytically active sites for the dissociation of ethylene are the step edges, followed by the Cu(100) terraces sites and the Cu(111) terrace sites. The need for an argon overpressure to form graphene the on-axis Cu(111) surface indicates that the Cu sublimation rate is higher than the graphene growth rate for this surface. This research was supported in part by the NSF (DMR-1006411).

9:20am **2D+EM+NS+PS+SS+TF-MoM4 Synthesis of Large Scale MoS<sub>2</sub>-Graphene Heterostructures, Kathleen McCreary, A.T. Hanbicki, J. Robinson, B.T. Jonker**, Naval Research Laboratory

A rapidly progressing field involves the stacking of multiple two-dimensional materials to form heterostructures. These heterostructures have exhibited unique and interesting properties. For the most part, heterostructure devices are produced via mechanical exfoliation requiring the careful aligning and stacking of the individual 2D layered components. This tedious and time consuming process typically limits lateral dimensions to micron-scale devices. Chemical vapor deposition (CVD) has proven to be a useful tool in the production of graphene and has very recently been investigated as a means for the growth of other 2D materials such as MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, and hexagonal boron nitride. Using a two-step CVD process we are able to synthesize MoS<sub>2</sub> on CVD grown graphene. AFM, Raman spectroscopy, and Photoluminescence spectroscopy of the MoS<sub>2</sub>-graphene heterostructure show a uniform and continuous film on the cm scale.

9:40am **2D+EM+NS+PS+SS+TF-MoM5 Growth of 2D MoS<sub>2</sub> Films by Magnetron Sputtering, Andrey Voevodin**, Air Force Research Laboratory, C. Muratore, University of Dayton, J.J. Hu, Air Force Research Laboratory/UDRI, B. Wang, M.A. Haque, Pennsylvania State University, J.E. Bultman, M.L. Jespersion, Air Force Research Laboratory/UDRI, P.J. Shamberger, Texas A&M University, R. Stevenson, Air Force Research Laboratory, A. Waite, Air Force Research Laboratory/UTC, M.E. McConney, R. Smith, Air Force Research Laboratory

Growth of two dimensional (2D) MoS<sub>2</sub> and similar materials over large areas is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. Typical preparation approaches with chemical or mechanical exfoliation lack scalability and uniformity over appreciable areas (>1 mm) and chemical vapor deposition processes require high substrate temperatures. We developed few-layer MoS<sub>2</sub> growth under non-equilibrium magnetron sputtering conditions selected to minimize the MoS<sub>2</sub> nucleation density and maximize 2D growth of individual crystals [1]. In this process, the thermodynamically driven tendency to form islands is accomplished by maximizing atomic mobility through the control of incident flux kinetic energies, densities, and arriving angle to the substrate while avoiding defect formation (i.e., vacancy creation by sputtering of S atoms). Amorphous SiO<sub>2</sub>, crystalline (0001) oriented Al<sub>2</sub>O<sub>3</sub>, and (002) oriented graphite substrates were used to grow few monolayer thick MoS<sub>2</sub> films. Continuous 2D MoS<sub>2</sub> films were produced over 4 cm<sup>2</sup> areas. They were composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements with contact separation on the order of centimeters. Their characteristics were similar to few-layer MoS<sub>2</sub> films produced by exfoliation with a direct band gap in thin samples of approximately 1.9 eV from photoluminescence spectra. The electron mobility measured for as-grown MoS<sub>2</sub> films was very strongly dependent on film thickness and substrate choice.

[1] "Continuous ultra-thin MoS<sub>2</sub> films grown by low-temperature physical vapor deposition", C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jespersion, P.J. Shamberger, A.A. Voevodin, Applied Physics Letters (2014) in press.

10:00am **2D+EM+NS+PS+SS+TF-MoM6 Formation of Graphene on the C-face of SiC{0001}: Experiment and Theory, Jun Li, G. He, M. Widom, R.M. Feenstra**, Carnegie Mellon University

There are two {0001} surfaces of SiC, the (0001) surface known as the "Si-face", and the (000-1) surface or "C-face". The formation of graphene (by heating the SiC to 1100 – 1600 °C in various gaseous environments) has been studied for both surfaces, although it is much better understood on the Si-face. In that case, an intermediate C-rich layer, or "buffer layer" forms between the graphene and the SiC crystal. This buffer layer has 6√3x6√3-R30° symmetry; its structure is well established,<sup>1</sup> and it acts as a template for the formation of subsequent graphene layers. In contrast, graphene formation on the C-face is much less well understood. More than one interface structure between the graphene and the SiC has been observed,<sup>2,3</sup> and, with one notable exception,<sup>4</sup> the quality of the graphene formed on the C-face is generally lower than that for the Si-face.

In this work we provide new experimental and theoretical results that allow us to understand graphene formation on the C-face of SiC. Experimentally, by heating the SiC in a disilane environment, we map out the phase diagram of different surface and interface structures that form on the SiC as a function of disilane pressure and sample temperature. New surface structures that develop just prior to the graphene formation are observed. With additional heating, graphene forms on the surface, but some remnant of the surface structure prior to the graphene formation is believed to persist at the graphene/SiC interface. From first-principles theory, we find that the hydrogen in the disilane environment plays a critical role in the surface/interface structures that form. Experimentally, for disilane pressures below 5x10<sup>-5</sup> Torr, we find a 2x2 surface structure forming prior to graphene formation. From theory we identify this structure as consisting of a silicon adatom together with a carbon restatom on the surface, with H-termination of those atoms being possible but not necessary. At higher disilane pressures we observe a 4x4 structure, and we identify that as consisting of a lower density of Si adatoms than the 2x2, now with at least some of the adatoms and restatoms being H-terminated. With graphene formation, this structure converts to the observed √43x√43-R± 7.6° interface structure. At higher disilane pressures we theoretically predict the formation of a surface consisting simply of H-terminated carbon restatoms. Experiments are underway to observe that surface, along with subsequent graphene formation on the surface.

(1) Y. Qi et al., PRL **105**, 085502 (2010).

- (2) F. Hiebel et al., PRB **78**, 153412 (2008).  
(3) N. Srivastava et al., PRB **85**, 041404 (2012).  
(4) W. A. de Heer et al., PNAS **108**, 16900 (2011).

10:40am **2D+EM+NS+PS+SS+TF-MoM8 Graphene on Hexagonal Boron Nitride Heterostacks Grown by UHV-CVD on Metal Surfaces**, *Juerg Osterwalder, S. Roth, A. Hemmi*, University of Zurich, Switzerland, *F. Matsui*, Nara Institute of Science and Technology, Japan, *T. Greber*, University of Zurich, Switzerland **INVITED**

Chemical vapor deposition (CVD) performed under ultra-high vacuum conditions on single-crystal metal surfaces enables the growth of large-area and high-quality graphene and hexagonal boron nitride (h-BN) single layers. We explore the CVD parameter space of precursor pressure and temperature in order to go beyond the self-saturating single-layer growth, or to grow heterostacks of the two materials. Formed layers are characterized structurally by LEED, STM and x-ray photoelectron diffraction. On Cu(111) a graphene layer could be grown on a pre-deposited single layer of h-BN when using 3-pentanone as a precursor at a pressure of 2.2 mbar and a substrate temperature of 1100 K [1]. On Rh(111) the same procedure leads to incorporation of carbon into the metal surface layers, while a graphene layer is formed only upon a second high-pressure dose [2]. In both cases the heterostructures show clearly the stacking sequence and structural and ARPES signatures of graphene on h-BN but are far from defect-free.

[1] S. Roth et al., Nano Lett. 13, 2668 (2013).

[2] S. Roth, PhD Thesis, Department of Physics, University of Zurich (2013).

11:20am **2D+EM+NS+PS+SS+TF-MoM10 Kinetics of Monolayer Graphene Growth by Carbon Segregation on Pd(111)**, *Abbas Ebnonnasir, H.S. Mok, Y. Murata*, University of California at Los Angeles, *S. Nie, K.F. McCarty*, Sandia National Laboratories, *C.V. Ciobanu*, Colorado School of Mines, *S. Kodambaka*, University of California at Los Angeles

In this research, using in situ low-energy electron microscopy and density functional theory calculations, we elucidate the growth kinetics of monolayer graphene on single-crystalline Pd(111). In our experiments, carbon saturated Pd(111) samples were cooled down from 900 °C to segregate carbon on the surface in the form of graphene. Upon cooling the substrate, graphene nucleation begins on bare Pd surface and continues to occur during graphene growth. Measurements of graphene growth rates and Pd surface work functions along with DFT calculations establish that this continued nucleation is due to increasing C adatom concentration on the Pd surface with time. We attribute this anomalous phenomenon to a large barrier for attachment of C adatoms to graphene coupled with a strong binding of the non-graphitic C to the Pd surface.

## 2D Materials Focus Topic

Room: 310 - Session 2D+AS+EM+NS+SS-MoA

### Dopants, Defects, and Interfaces in 2D Materials

Moderator: Jun Lou, Rice University

2:00pm **2D+AS+EM+NS+SS-MoA1 Cutting and Assembling 2 Nanometer Voids in Single Layer Hexagonal Boron Nitride**, *Thomas Greber, H.Y. Cun, M. Iannuzzi, A. Hemmi, J. Osterwalder*, University of Zurich, Switzerland

INVITED

Argon implantation beneath hexagonal boron nitride nanomesh on Rh(111) [1] leads to the formation of vacancy and interstitial defects [2]. The nanomesh is a single layer of hexagonal boron nitride on Rh(111), where 13x13 h-BN units accommodate on 12x12 Rh unit cells. The resulting super-honeycomb has a lattice constant of 3.2 nm and consists in regions where the h-BN “wets” the Rh substrate (pores), and regions where h-BN is quasi freestanding (wires) [3].

The interstitial defects are called “nanotents”, where atoms are trapped beneath the ultimately thin “rainfly” made of a single layer of h-BN [2,4]. They are stable at room temperature and survive exposure to air.

The vacancy defects are sites where a boron or a nitrogen atom was kicked out by the Ar ion impact. If the implanted structures are annealed to 900 K the can-opener effect occurs: 2 nm h-BN-flakes or “lids” are cut out of the h-BN nanomesh and 2 nm voids form [2]. At higher temperatures the resulting voids may diffuse and assemble, due to their repulsive interaction, in a super-structure with some order, i.e., a nearest neighbor distance of about 15 nm. Near the disintegration temperature of the h-BN nanomesh we finally observe self-healing of the voids in the nanomesh, which we assign to their annihilation in larger holes in the structure.

The report bases on scanning tunneling microscopy, x-ray photoelectron spectroscopy, molecular dynamics and density functional theory calculations.

Financial support by the Swiss National Science Foundation and support by the EC under the Graphene Flagship (contract no. CNECT-ICT-604391) is gratefully acknowledged. We thank the Swiss National Supercomputer Centre (CSCS) for allocation of computer time.

[1] M. Corso et al. *Science*, 303 (2004) 217.

[2] H. Y. Cun et al. *Nano Letters* 13 (2013) 2098.

[3] S. Berner et al. *Angew. Chem. Int. Ed.* 46 (2007) 5115.

[4] H.Y. Cun et al. *ACS Nano* 8 (2014) 1014.

2:40pm **2D+AS+EM+NS+SS-MoA3 Engineering Structural Defects in Graphene Materials**, *Jeremy Robinson, M. Zhaludinov, J. Culbertson, C. Junkermier, P.E. Sheehan, T. Reinecke, A. Friedman*, Naval Research Laboratory

Graphene's atomic thinness makes it highly sensitive to surface adsorbates or defects within its carbon backbone. Aside from the known effects and impact on electronic properties, here we demonstrate the impact of defects on the mechanical properties and the response of mechanical resonators. In particular, once defects are formed in atomically-thin materials they can be quite mobile and form more complicated defect structures such as bi- or tetra-vacancy clusters. We execute experiments using mechanical drum resonators made from single- to multi- to many-layer graphene systems. We use both CVD grown graphene and reduced graphene oxide (rGO) films to capture a wide range of defect structures. By measuring the fundamental frequency response of the resonators (in the MHz range) we extract properties such as tension, quality factor, and modulus as a function of external manipulation [1]. For highly defective rGO films measuring 10-40nm thick, we can tune the frequency response by 500% and quality factor by 20x through laser annealing, which effectively rearranges defects throughout the film [1]. Alternatively, using graphene 1-4 layers thick, we find the resonator response is significantly more sensitive to the formation and annihilation of meta-stable defects, such as the tetra-vacancy structure. We will show how the defect mobility and resonator response changes with different energy photons and come to understand these differences based on calculated defect migration energies of different defects types in graphene.

[1] *Nano Letters* 12, 4212 (2012)

3:00pm **2D+AS+EM+NS+SS-MoA4 Graphene Cleaning using a Low Energy Ar Ion Beam**, *KiSeok Kim, G. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, graphene has been widely investigated due to the superior electrical, mechanical, thermal, and chemical properties. Especially, CVD graphene which was grown on Cu foil and transferred to various substrates using PMMA has been used most widely due to the possible large area applications such as electronic devices for displays, semiconductors, etc. However, in order to apply the transferred CVD graphene to the various electronic device fabrication, PMMA residue on the graphene surface formed during the transfer process and lithography process needs to be completely removed without damage. Various methods have been investigated to remove the residue on the graphene surface such as current cleaning, heat treatment, chemical cleaning, etc. However, it is reported that these methods are not effective in removing the residue on graphene or not applicable to industry.

In this study, a controlled Ar ion beam has been used to effectively remove the PMMA residue on graphene surface. By controlling the Ar ion beam condition, the residue on graphene surface could be removed while minimizing the damage on the graphene surface. Especially, by lowering the Ar beam energy less than 10 eV, it was possible to effectively remove the PMMA residue without damaging the graphene. The removal of PMMA residue on the graphene surface could be identified using Raman Spectroscopy showing the red shift of 2D peak ( $2670\text{ cm}^{-1}$ ) and blue shift of G peak ( $1580\text{ cm}^{-1}$ ) in addition to the decrease of RMS roughness from 1.3nm to 0.3 nm using an AFM (Atomic Force Microscopy). The effectiveness of graphene cleaning was also confirmed by XPS (X-ray Photoelectron Spectroscopy), by the uniform deposition of ALD  $\text{HfO}_2$  layer on the cleaned graphene surface, by measuring the electrical properties of deposited ALD  $\text{HfO}_2$ , etc.

3:40pm **2D+AS+EM+NS+SS-MoA6 Electronic Structure Modification in van der Waals Heterostructures: Interlayer Hybridization in the Case of Graphene/MoS<sub>2</sub>**, *Matthias Batzill, H. Coy-Diaz*, University of South Florida, *M.C. Asensio*, Synchrotron Soleil, France, *J. Avila*, Synchrotron Soleil

Artificial van der Waals heterostructures promise to combine materials with diverse properties. Simple mechanical stacking or conventional growth of molecular hetero-layers would enable fabrication of novel materials or device-structures with atomically precise interfaces. Because covalent bonding in these layered materials is limited to molecular-planes, interface interactions between dissimilar materials are expected to modify the properties of the individual layers only weakly. Here we prepare graphene/MoS<sub>2</sub> heterostructures by transferring CVD-grown graphene onto a MoS<sub>2</sub> substrate. It is shown that high quality interfaces between graphene and MoS<sub>2</sub> can be obtained by UHV annealing. The quality of the graphene is demonstrated by atomic resolution scanning tunneling microscopy of ultraflat graphene. The electronic structure of the interface between the polycrystalline graphene and a MoS<sub>2</sub> substrate is measured by angle resolved photoemission spectroscopy (ARPES) and nano-ARPES utilizing a focused photon beam at the SOLEIL synchrotron. We show that at the Fermi-level graphene exhibits a perfect, gapless and undoped Dirac-cone. However, in regions where the  $\pi$ -band of graphene overlaps with states of the MoS<sub>2</sub> substrate, opening of several band-gaps are observed. This demonstrates that the electronic properties in van der Waals heterostructures can be significantly modified by interlayer interaction and thus exemplifying opportunities for tuning materials properties of graphene and other 2D-materials by interfacing them with dissimilar van-der Waals materials.

4:00pm **2D+AS+EM+NS+SS-MoA7 Edge States and Exposure to Hydrogen of Silicon at the 2D Limit on Ag(111)**, *A.J. Mannix, B.T. Kiraly*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University, *Nathan Guisinger*, Argonne National Laboratory

Chemical functionalization of atomically thin materials results in significant modifications to their electronic properties, which can be exploited in device applications. Compared to the chemical inertness of graphene, 2D silicon is expected to exhibit greater reactivity, and thus a greater amenability to chemical functionalization. Among potential functionalization chemistries, hydrogen termination is favored for its relative simplicity and proven efficacy with graphene and bulk Si surfaces. Using ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have studied the temperature-dependent effects of exposing 2D silicon platelets grown on Ag(111) to molecular and atomic hydrogen. At low doses, atomic hydrogen results in limited adsorption and temperature dependent etching. In the bulk, the formation of vacancies and extended

etch pits is observed. In addition, edge states can play a critical role in the electronic properties of 2D materials. We have also examined at the atomic-scale the edges of 2D silicon platelets.

4:20pm **2D+AS+EM+NS+SS-MoA8 Chlorine Trap-Doping for Transparent, Conductive, Thermally Stable and Damage-Free Graphene.** *Pham Viet Phuong, K.N. Kim, M.H. Jeon, K.S. Kim, G. Yeom*, Sungkyunkwan University, Republic of Korea

We propose a novel doping method of graphene by cyclic trap-doping with low energy chlorine adsorption. Low energy chlorine adsorption for graphene chlorination avoided defect (D-band) formation during doping by maintaining the  $\pi$ -bonding of the graphene, which affects conductivity. In addition, by trapping chlorine dopants between the graphene layers, the proposed doping method dramatically decreased the sheet resistance by ~88% at an optimized condition. Among the reported doping methods including chemical, plasma, photochemical methods etc., the proposed doping method is believed to be the most promising for producing graphene of extremely high transmittance, low sheet resistance, high thermal stability, and high flexibility for use in various flexible electronic devices. Results of angle resolved X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron spectroscopy (HR-TEM), Raman spectroscopy, ultraviolet-Visible spectroscopy (UV-Vis) and sheet resistance, showed that this method is also non-destructive and controllable. The sheet resistance of the doped tri-layer graphene was  $70 \Omega/\text{sq}$  at 94% transmittance, which was maintained for more than 6.5 h at 230°C. Moreover, the defect intensity of graphene was not increased during the cyclic trap-doping.

4:40pm **2D+AS+EM+NS+SS-MoA9 Modification of Graphene by Neutral Beam Irradiation and Edge Structure Analysis.** *Takeru Okada, S. Samukawa*, Tohoku University, Japan

Since the discovery of single layer of Graphite, Graphene, a single layer of hexagonal carbon atoms, has attracted much attention and shown exciting specific properties. Graphene is a zero band gap semiconductor. Therefore band gap control is one of most important issue to apply for electronic device applications. In order to construct electronic devices with logic operation, both p- and n-type conduction and the control of the carrier density in an active channel are required. Doping with foreign atoms, such as N and B, has proven to be an effective way to modify the electronic properties of carbon related materials and extend their applications. In particular, nitrogen doping brings a carrier which could turn carbon nanotube into n-type semiconductors. It is also feasible to modify the electronic properties of Graphene. Although several doping methods have reported so far, process damages (defect generation) cause degradation of electronic properties.

In this paper, we introduce ultra-low damage neutral beam system which consists of a plasma and process chambers that are separated by a carbon aperture. Charged species and ultra-violet photon from the plasma can be effectively eliminated by the aperture. As a result, only the neutral beam arrives the surface of the sample at the substrate in the process chamber.

We used nitrogen gas for plasma generation and adopted multi-layer Graphene to investigate nitridation mechanism. Graphene multi-layer was irradiated by nitrogen neutral beam with controlled energy of 10 eV at room temperature. The surface modification was analyzed by x-ray photoelectron spectroscopy (XPS). XPS analysis indicated that the carbon atoms were substituted to nitrogen atom and atomic concentration of nitrogen reaches 15 %. Additionally, bonding state of C and N was found to depend on neutral beam irradiation time. Thus beam energy controlled neutral beam can selective nitridation of Graphene. Furthermore the doping density is estimated by Raman spectroscopy and result in  $10^{12} [\text{cm}^{-2}]$ , which is enough to n-type doping of Graphene.

5:00pm **2D+AS+EM+NS+SS-MoA10 Growth Mechanism of Metal Clusters on a Graphene/Ru(0001) Template.** *Shixuan Du, L.Z. Zhang*, Chinese Academy of Sciences, *W. Hofer*, University of Liverpool, UK, *H.-J. Gao*, Chinese Academy of Sciences

Metal nano-clusters have attracted considerable interest because of the potential applications in catalysis and information storage. Due to the soft nature of epitaxial graphene and the lattice mismatch between graphene and metal substrates periodic moiré patterns can be formed. A graphene/metal template, moiré template, can be used to grow dispersed metal nano-clusters with controllable size and shape, or metal clusters with large size and metal layers. However, how intrinsic properties of metal atoms and the moiré template influence the selective adsorption and the growth mode of metal clusters is still open to debate. A general rule, predicting the morphology of metal nano-clusters on a G/metal surface, important to guide experimenters, is still missing. Using first-principles calculations combined with scanning tunneling microscopy experiments, we investigated the adsorption configurations, electronic structures and the corresponding growth mechanism of several transition metal (TM) atoms (Pt, Ru, Ir, Ti, Pd, Au,

Ag, and Cu) on a graphene/Ru(0001) moiré template (G/Ru(0001)) at low coverage. We find that Pt, Ru, Ir, and Ti selectively adsorb on the fcc region of G/Ru(0001) and form ordered dispersed metal nano-clusters. This behavior is due to the unoccupied  $d$  orbital of the TM atoms and the strong  $sp^3$  hybridization of carbon atoms in the fcc region of G/Ru(0001). Pd, Au, Ag, and Cu form nonselective structures because of the fully occupied  $d$  orbital. This mechanism can be extended to metals on a graphene/Rh(111) template. By using Pt as an example, we provide a layer by layer growth path for Pt nano-clusters in the fcc region of the G/Ru(0001). The simulations agree well with the experimental observations. Moreover, they also provide guidance for the selection of suitable metal atoms to form ordered dispersed metal nano-clusters on similar templates.

References:

1. L.Z. Zhang *et al.* *Advanced Materials Interfaces*, accepted.
2. Y. Pan *et al.* *Applied Physics Letter*, 95, 093106 (2009)

## Materials Characterization in the Semiconductor Industry Focus Topic

Room: 313 - Session MC+2D+AP+AS-MoA

### Characterization of III-Vs (2:00-3:20 pm)/Photovoltaics, EUV masks, etc. (3:40-4:40 pm)

Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

2:00pm **MC+2D+AP+AS-MoA1 High Resolution SIMS Depth Profiling in III-V Compound Semiconductors.** *Marinus Hopstaken, M.S. Schamis, Y. Sun, A. Majumdar, C.-W. Cheng, B.A. Wacaser, G. Cohen, K.K. Chan, D.K. Sadana, D.-G. Park, E. Leobandung*, IBM T.J. Watson Research Center

Recently, there has been renewed technological interest for application of InGaAs and related III-V high-mobility materials as a potential replacement for the MOSFET Si-channel [1]. Successful integration of novel materials and processes requires accurate physical characterization of in-depth chemical distribution with nm-scale resolution. We will address some of the challenges regarding SIMS depth profiling of III-V materials and propose analytical solutions for the characterization of more complex multilayer substrates, impurities therein, and Ultra-Shallow Junction (USJ) doping profiles.

Ion beam based sputtering of III-V compounds is intrinsically more complex than in conventional Si substrates. One of the major issues with depth profiling of III-V materials is their higher sensitivity to formation of ion-beam induced topography, which has a detrimental impact on depth resolution [2]. We have previously reported anomalous sputtering behavior of (In)GaAs under low energy  $\text{O}_2^+$  sputtering, causing severe degradation of depth resolution [3].

In case of low energy  $\text{Cs}^+$  sputtering at oblique incidence, we have achieved uniform sputtering conditions on different III-V compounds with no significant topography formation. We have demonstrated constant depth resolution in III-V multilayer structures with decay lengths as low as 2 nm/decade at low  $\text{Cs}^+$  impact energy (down to 250 eV).

We will address some of the analytical challenges regarding the quantification of depth and concentration scales in III-V multilayer structures, grown by hetero-epitaxy. We employ explicit corrections for yield variations using appropriate standards in their respective matrices. A special case occurs for the group IV n-type dopants (*i.e.* Si, Ge), which are typically monitored as negative cluster ion attached to the group V element for reasons of sensitivity. We have developed a quantification scheme to determine [Si] doping profiles in hetero-epitaxial structures, composed from the negative cluster ions (e.g.  $\text{SiAs}^-$ ,  $\text{SiP}^-$ ) in the respective matrices.

In summary, this work has improved our fundamental understanding of low-energy ion beam interactions in III-V materials, which is essential for achieving sub-nm depth resolution in thin-film structures. In addition, this work has provided with an optimum window of analytical conditions for quantitative analysis of a wide variety of impurities and dopants with high sensitivity in different III-V materials.

1. Y. Sun *et al.*, *IEDM 2013 Conf. Proc.*, p. 48-51.
2. E.-H. Cirlin, J. J. Vajo, R. E. Doty, and T. C. Hasenberg, *J. Vac. Sci. Technol. A9*, 1395 (1991).
3. M. J. P. Hopstaken *et al.*, *J. Vac. Sci. Technol. B28*, 1287, (2012).

2:20pm **MC+2D+AP+AS-MoA2 Nitrogen Incorporation in Dilute Nitride III-V Semiconductors Measured by Resonant Nuclear Reaction Analysis and Ion Beam Channeling**, *John Demaree, S.P. Svensson, W.L. Sarney*, US Army Research Laboratory

The behavior of dilute nitride III-V semiconductors depends critically on the number of nitrogen atoms residing substitutionally on Group V sites, and this small nitrogen incorporation may be used to tailor the optical bandgap for detection of electromagnetic radiation in future low-cost near-infrared imaging systems. In this study, films of GaAsN and GaSbN were synthesized using molecular beam epitaxy at various temperatures and growth rates, with the assistance of a nitrogen plasma source isotopically enriched with  $^{15}\text{N}$ . The films were examined using x-ray diffraction, secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and resonant nuclear reaction analysis (RNRA) to assess the amount of nitrogen incorporation. Furthermore, RNRA measurements were combined with ion beam channeling methods to ascertain the fraction of incorporated nitrogen atoms residing on substitutional and interstitial lattice sites. The narrow energy resonance and corresponding high depth resolution of the nuclear reaction used (the 897 keV  $p,\gamma$  reaction with  $^{15}\text{N}$ ) also enabled an assessment of the substitutional incorporation of the nitrogen throughout the thickness of the 100-400 nm thick films.

2:40pm **MC+2D+AP+AS-MoA3 Determination of Growth Conditions for Highly Mismatched Alloys, Using In Situ Auger Electron Spectroscopy and Flux grading**, *Stefan Svensson, W.L. Sarney*, US Army Research Laboratory, *M. Ting, K.M. Yu*, Lawrence Berkeley National Laboratory, *L.W. Calley*, Staib Instruments, Inc.

The electronic band structures of GaN can be effectively modified by the incorporation of Sb. Because of the high electronegativity mismatch between Sb and N growth of GaNSb by molecular beam epitaxy (MBE) must be done at relatively low temperatures and under N-rich condition in order to control the bandgap of the material. The Sb-flux must also be chosen carefully in relation to the growth rate and N-overpressure to control composition and crystallinity. These growth conditions represent a vast parameter space, which is extremely time-consuming to explore in a systematic fashion.

The typical approach for attacking such a problem is to judiciously select a limited set of parameter combinations based on experience and literature data. However, if growth windows are narrow there is no guarantee for success. To more quickly cover a larger parameter range we have grown a very limited number of samples but continuously varied one parameter at a time while employing a combination of in situ and ex situ probes that can reveal critical parameter points. The most novel piece of equipment is the in situ *STAIB Auger Probe*, which allows uninterrupted chemical analysis during crystal growth. In all of the following experiments the substrate temperature was fixed at 325 °C.

In one experiment we determined the transition between Ga- and N-rich MBE growth conditions of GaN by setting a fixed N-flow that generated a steady-state background chamber pressure of  $1.5 \times 10^{-5}$  Torr, while the Ga-source was set up to generate a linear flux ramp from  $9.8 \times 10^{16}$  to  $3.9 \times 10^{18}$   $\text{at}/\text{m}^2/\text{s}$  over two hours. During this ramp, the Auger electron signals for N (375 eV), and Ga (1050 eV) were continuously monitored. As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N- and Ga-rich conditions and could thus determine the critical Ga-flux relative to the N gas-flow.

In a second experiment the previous information was used to set Ga- and N-fluxes to slight N-rich conditions, while the Sb-valve was slowly opened. In this case both the Auger signals and the reflection high-energy electron diffraction pattern were observed to find the transition between crystalline and amorphous growth conditions. The sample was subsequently analyzed with Rutherford backscattering, which verified the varying Sb-composition. With the data from these two test samples subsequent films were grown with the desired bandgap of 2.2 eV suitable as photoelectrodes for photoelectrochemical water splitting application.

3:00pm **MC+2D+AP+AS-MoA4 Electron Channeling Contrast Imaging: Examining Dislocation Effects in III-Ns**, *J.K. Hite*, U.S. Naval Research Laboratory, *P. Gaddipati*, American Society for Engineering Education, *Michael Mastro, C.R. Eddy, D.J. Meyer*, U.S. Naval Research Laboratory

III-N materials continue to play a significant role in a range of technologies from rf electronics to visible and UV emitters and detectors. This is true despite a heavy population of extended defects in the active regions of these devices, which degrade the operation, potential performance, and reliability of such devices. With such high dislocation densities when grown heteroepitaxially on sapphire or SiC ( $10^8$ - $10^{10}$   $\text{cm}^{-2}$ ), techniques to reliably,

rapidly, and non-destructively determine spatially defect density are necessary to determine the effects of these defects on device performance.

The most precise characterization tool for defect density has been transmission electron microscopy, but this is a destructive technique, as are other methods such as molten KOH or photo-electrochemical etching of the surface to reveal dislocation sites. Cathodoluminescence imaging only detects dislocations which change the optical emission of the material. X-ray diffraction can be used to extrapolate dislocation density, but not identify individual defects.

Electron channeling contrast imaging (ECCI), a non-destructive technique that has been used to examine defects in metals and ceramics, has recently seen use in III-nitride semiconductors. This technique allows for direct imaging of dislocations, grain boundaries, and topological information all at once. We will present an overview of the uses of ECCI in characterizing III-N materials, culminating in recent work applying the technique to AlGaIn/GaN HEMT structures. By imaging the active areas of van der Pauw structures on a single sample with varying mobility, we find a direct negative correlation between screw dislocation and electron mobility.

3:40pm **MC+2D+AP+AS-MoA6 EUV Lithography Mask Cleaning Applications of TOF SIMS Analysis**, *Thomas Laursen, S.W. Novak*, SUNY College of Nanoscale Science and Engineering, *A. Rastegar, SEMATECH, T. Nakayama*, SUNY College of Nanoscale Science and Engineering

Extreme-UV Lithography (EUVL) is the current R&D frontier for the semiconductor industry. Developing this new technology is generating new studies into a range of new materials issues. EUVL photomask is one important branch of this technology and serious issues have been identified related to the mask surfaces. Photomask performance is usually characterized in terms of EUV ( $\lambda = 13.5$  nm) Reflectivity (EUVR) and absorption. But when it comes to surface degradation by radiation exposure and mask cleaning of defects, it is valuable to complement EUVR with a surface analytical technique in order to elucidate the material changes taking place. TOF SIMS has proven to be a versatile analytical technique in this regard. While it may not be the optimal technique in each and every case, it does provide high sensitivity to compositional changes and high-resolution depth profiles. Furthermore, TOF-SIMS analysis on the IonToF V-300 can be done using full-size photomasks which allow analysis at the various stages of processing.

The surface structures on the EUV mask surface consist of a stack of thin films having thicknesses ranging from 1 to 50 nm. The reflective layer contains 40 bilayers of Mo-Si consisting of 2.7 nm Mo and 4.1 nm Si—ending with a Si layer. This multilayer is usually capped with either a 2.5 nm Ru or in some cases a 2 nm  $\text{TiO}_2$  surface film. Metallic films with high extinction coefficient with thicknesses in the range from 35 to 75 nm are deposited as an absorber layer and patterned on Ru-capped multilayer blanks.

The combination of EUVR and TOF-SIMS analysis of the Ru capped multilayer EUV masks and blanks provided detailed information on the effects of cleaning on contamination, materials degradation and oxidation. Whereas the EUVR measurements could be directly related to mask specifications, the TOF-SIMS analysis provided more detailed information on surface contamination and oxidation levels, as well as surface-film integrity.

The interactions of the various segments constituting a cleaning process have been characterized in terms of their effect on film etching and removals as well as film oxidation. In general sulfuric acid -  $\text{H}_2\text{O}_2$  -based treatments caused a severe deterioration of the film structures, whereas  $\text{NH}_4\text{OH}$  -  $\text{H}_2\text{O}_2$  -based treatments (SC1) caused a more manageable deterioration. Current mask cleaning processes are therefore primarily based on SC1 cleaning. Another concern for mask defectivity is progressive defects generated by sulfate and ammonium compounds. TOF-SIMS was also used to study the aggregation of these compounds during electron irradiation (simulating EUV-irradiation conditions), which was visualized by stage-scan imaging.

4:00pm **MC+2D+AP+AS-MoA7 Characterization of Ag/CuInSe<sub>2</sub> Thin-Film Photovoltaics by Photoelectron Spectroscopy**, *Pinar Aydoğan*, Bilkent University, Turkey, *N. Johnson, A. Rockett*, University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Photovoltaic power source technology is one of the most desirable ways to provide energy for the world of tomorrow. Hence, it is important to understand the surface, electrical and photo-induced properties of these materials in order to enhance their efficiencies. Currently used materials in photovoltaic manufacturing technology are mainly crystalline silicon, CdTe (cadmium telluride), amorphous and nanocrystalline silicon, CIS (copper indium diselenide) and CIGS (copper indium gallium selenide). In this study, we focused only on the silver/copper indium diselenide cells, which contain a CdS layer on top. X-ray photoelectron spectroscopy (XPS) that

we used for analysis was modified to apply both an external photo illumination and voltage bias during data acquisition. The first part of the research focuses on the result of photo induced variations in binding energies of elements and the main objective is to understand the different binding energy shifts of each element in the Ag/CuInSe<sub>2</sub> films in both wavelength- and intensity-sensitive fashion under illumination with three different continuous wave lasers. Furthermore, electrical charging properties of CIS/CdS thin film are studied with externally applied electrical square-wave pulses (SQW), so-called Dynamic XPS. Results will be presented with an ultimate aim of better understanding of the roles of defects affecting the performance of CIS devices. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

4:40pm **MC+2D+AP+AS-MoA9 Facile Synthesis of Composition Tuned Cu<sub>1-x</sub>Zn<sub>x</sub>O Nanoarchitecture on Alpha-Brass.** *Y. Myung, Sriya Banerjee*, Washington University, St. Louis, *H. Im, J. Park*, Korea University, *S. Raman*, Physical Electronics Inc., *P. Banerjee*, Washington University, St. Louis

Composition controlled Cu<sub>1-x</sub>Zn<sub>x</sub>O layers have been synthesized on pretreated a-brass followed by ambient oxidation. The pretreatment consists of a vacuum anneal step which effectively depletes the surface of Zn. The depleted Zn specimens were then oxidized at various temperatures ranging from 300°C – 600°C. SEM and XRD result shows the oxide consists of CuO/ZnO film/nanowire composite architecture. The analysis of electronic structure (XPS) and optical properties (PL) shows the formation of Zn containing alloy in the surface region of CuO films. The composition ratio of Cu and Zn were calculated based on XPS survey spectra. In particular, XPS fine spectra revealed that as the oxidation temperature increases, the binding energy of Zn 2p<sub>3/2</sub> shifts to higher energy, suggesting the possibility of hybridization between the Zn ions and Cu ions.

Photoelectrochemical properties of Cu<sub>1-x</sub>Zn<sub>x</sub>O cathodes exhibit robust photocurrent densities (~3 mA/cm<sup>2</sup>). We suggest the dezincification followed by thermal oxidation provides a better approach for composition tuned nanostructure design and fabrication. These semiconductor nanoarchitectures are excellent candidate materials for fabricating solar energy harvesting photoelectrodes as well as optoelectronic devices.

5:00pm **MC+2D+AP+AS-MoA10 In-line Dimensional Measurement via Simultaneous Small Spot XPS and XRF for Cu CMP Process Control.** *B. Lherron*, ST Microelectronics, *Wei Ti Lee*, Revera, *Motoyama, Chao, Deprosio, Kim*, IBM

As Cu lines used for CMOS devices interconnections become thinner and smaller, current metrology solutions reach their limits. XRay Photoelectron Spectroscopy (XPS) and XRay Fluorescence (XRF) are commonly used as Semiconductor manufacturing process control techniques to measure composition and/or film thickness. In this paper we are exploring the use of a combination of XPS and XRF collected simultaneously to measure the dimensions (line top CD, area and thickness) of Cu lines post Cu CMP on patterned structures. A set of structures with different Cu line width and pitch were used to demonstrate the capability of XPS/XRF on this new application. Results obtained showed good correlation with predicted CD measured by XPS and line section measured by XRF. The paper will also present the comparison with cross section as well as the performance in precision, sensitivity and accuracy of the newly developed technique.

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

5:20pm **MC+2D+AP+AS-MoA11 Imaging of the Native Inversion Layer on Silicon-on-Insulator via Scanning Surface Photovoltage; Implications for RF harmonic generation.** *Daminda Dahanayaka*, IBM, *A. Wong*, Dartmouth College, *P. Kaszuba, L. Moszkowicz, R. Wells, F. Alwine*, IBM, *L.A. Bumm*, University of Oklahoma, *R. Phelps, J. Slinkman*, IBM

**Imaging of the native inversion layer on Silicon-on-Insulator via Scanning Surface Photovoltage;**

**Implications for RF harmonic generation**

*Daminda Dahanayaka*<sup>1</sup>, *Andrew Wong*<sup>2</sup>, *Phil Kaszuba*<sup>1</sup>, *Leon Moszkowicz*<sup>1</sup>, *Randall Wells*<sup>1</sup>, *Frank Alwine*<sup>1</sup>, *Lloyd A. Bumm*<sup>3</sup>, *Richard Phelps*<sup>1</sup> and *James Slinkman*<sup>1</sup>

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One of the major challenges encountered during the development of IBM's state-of-the-art RF CMOS Technology on Silicon-on-Insulator (SOI) was to overcome the adverse effects on the harmonic performance of stacked switch devices and transmission lines due to the presence of trapped positive charge, Q<sup>+</sup>, at the interface of the buried oxide (BOX) and the underlying high-resistivity substrate (SX). Most commercially available standard SOI substrates for RF applications have specifications to maintain Q<sup>+</sup> less than 10<sup>11</sup> cm<sup>-2</sup>. The substrate resistivity for IBMs technology is specified to be greater than 1000 ohm-cm, (p-type), i.e. p<sub>0</sub> ≈ 5 x 10<sup>13</sup> cm<sup>-3</sup>. This combination induces a "built-in" n-type inversion layer just under the BOX/SX interface. Using "Scanning Surface Photovoltage" (SSPV) microscopy, we present the first data to show quantitatively the extent of this inversion layer into the substrate. The technique disclosed here quantifies the inversion layer, the degree to which it can be suppressed, and has led to further enhancements to the RF technology on SOI, such as substantial NFET off-state leakage reduction.

#### References

- [1] A. Botula et al., IEEE Topical Meeting on Silicon Monolithic Integrated Circuits in RF Systems, 2009. SiRF '09, 1-4 (2009).
- [2] L.A. Bumm et al., US Patent No. 7,944,550.
- [3] T. Ohno, IEDM Tech. Digest, 627-630 (1995).
- [4] J. Greco et al., US Patent No. 8299537 B2.

# Tuesday Morning, November 11, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+AS+BI+PS+SS-TuM

## 2D Materials: Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Richard Osgood, Columbia University

### 8:00am 2D+AS+BI+PS+SS-TuM1 Phase Engineering in 2D Transition Metal Dichalcogenides, *Manish Chhowalla*, Rutgers University INVITED

Two-dimensional transition metal dichalcogenides (2D TMDs) — whose generalized formula is  $\text{MX}_2$ , where M is a transition metal of groups 4–7 and X is a chalcogen — exhibit versatile chemistry and consist of a family of over 40 compounds that range from complex metals to semiconductors to insulator. Complex metal TMDs assume the 1T phase where the transition metal atom coordination is octahedral. The 2H phase is stable in semiconducting TMDs where the coordination of metal atoms is trigonal prismatic. Unlike mechanical exfoliation and chemical vapor deposition, chemical exfoliation of semiconducting layered TMDs yields monolayered nanosheets with heterogeneous atomic structure consisting of metallic (1T) and semiconducting (2H) phases. Metal (1T phase) to semiconductor (2H phase) transition can be achieved via mild annealing of exfoliated materials. Semiconductor to metal transitions can be achieved via chemistry. The 1T phase in semiconducting TMDs has scarcely been studied but it deserves urgent attention as it exhibits promise as a hydrogen evolution catalyst and as contact electrode in electronic devices. We will describe these phase transitions in semiconducting TMDs and provide examples of how we have learned to exploit them for covalent functionalization, enhanced catalytic and electronic performance.

### 8:40am 2D+AS+BI+PS+SS-TuM3 Transition Metal Nanoparticles on Single-Layer $\text{MoS}_2$ : Structural, Electronic and Catalytic Properties, *Takat B. Rawal, D.T. Le, T.S. Rahman*, University of Central Florida

We will present results of density functional theory based calculations of the geometric and electronic structure of several types of sub-nanometer sized transition metal nanoparticles (TMNPs) on pristine and defect-laden single-layer  $\text{MoS}_2$ . We will show that among the investigated TMNPs (Cu, Ag, Au), Cu nanoparticles bind strongest to pristine  $\text{MoS}_2$  while Au and Ag nanoparticles bind with similar, weaker strengths. The presence of the vacancy defect on  $\text{MoS}_2$  enhances significantly the binding strength of Cu nanoparticles, while it has very little effect on the binding strength of Au NPs. More interestingly, the amounts of charge transfer from TMNPs to  $\text{MoS}_2$  vary following the order of the binding energies of TMNPs on  $\text{MoS}_2$ . Additionally, the shape of the nanoparticles also has an impact on the binding characteristics. Of particular interest is the role of the substrate on the catalytic properties of the TMNP and conversely that of the TMNP on the defect-laden  $\text{MoS}_2$  single layer. In this regard we will examine in detail the reactivity of the atoms at the TMNP/ $\text{MoS}_2$  interface in reactions such as CO oxidation and methanol decomposition and compare them to that of similar nanoparticles when supported on titania.

Work supported in part by DOE Grant No. DE-FG02-07ER15842

### 9:00am 2D+AS+BI+PS+SS-TuM4 How Fluorination Enhances Friction Forces for Graphene, *Xin Liu, Q. Li*, University of Pennsylvania, *S.P. Kim*, Brown University, *V.B. Shenoy*, University of Pennsylvania, *P.E. Sheehan, J. Robinson*, Naval Research Laboratory, *R.W. Carpick*, University of Pennsylvania

The chemical functionalization of graphene can alter its electronic, chemical, mechanical, and tribological properties. Here we employ atomic force microscopy (AFM), Raman microscopy, and molecular dynamics (MD) simulations to show that friction can be fine-tuned by chemically modifying graphene. Although bulk fluorinated graphite has a very low surface energy, our experiments and simulations both show that friction between nanoscale tips and FG is up to 9 times higher than that for pristine graphene. The ability to resolve an ordered lattice in atomic stick-slip friction measurements also diminishes with greater fluorination, indicating that the fluorinated graphene is disordered. Our observation suggests that AFM friction measurements provide a sensitive local probe of the degree of fluorination of graphene. Motivated by MD simulations, we propose that the dramatic enhancement of friction results from increased corrugation of the interfacial potential due to the strong local charge concentrated at fluorine sites, consistent with the Prandtl-Tomlinson model.

### 9:20am 2D+AS+BI+PS+SS-TuM5 Chemical, Structural and Electrical Modification of Graphene, *Sandra Hernández, E.H. Lock, M. osofsky, S. Tsoi*, Naval Research Laboratory, *C. Junkermeier*, Penn State University, *R. Stine*, Nova Research, *J. Robinson*, Naval Research Laboratory, *A. Nath*, George Mason University, *V.D. Wheeler, R.L. Myers-Ward, J. Caldwell, C.R. Tamnaha, T. Reinecke, P.E. Sheehan, D.K. Gaskill, S.G. Walton*, Naval Research Laboratory

2D nanomaterials have been vigorously investigated due to their superlative mechanical, thermal, and electronic properties. Being composed entirely of surface atoms, they are incredibly amenable to surface modification thus providing the opportunity towards excellent control over their properties. Surface engineering of 2D materials composed of carbon materials, such as graphene, can be achieved by plasma modification. We will discuss our efforts in understanding the chemical, structural, and electrical properties of plasma functionalized graphene by introducing -oxygen, -fluorine, and -nitrogen chemical moieties, and discuss their impact on chemical reactivity, electrical transport, and enhanced sensing behavior. Demonstrating how precise nano-engineering of surface chemistry impacts contact engineering, biosensing and device based applications.

This work is supported by the Naval Research Laboratory Base Program.

### 9:40am 2D+AS+BI+PS+SS-TuM6 The Mechanochemistry of Chemically Modified Graphene, *Jonathan Felts, S.C. Hernandez, A.J. Oyer, J. Robinson, S.G. Walton, P.E. Sheehan*, Naval Research Laboratory

Defining the optoelectronic properties of graphene through controlled chemical functionalization provides a route to fabricating a wide range of graphene based devices. In prior work, we showed that heat supplied by a scanning probe removed functional groups from chemically modified graphene (CMG) thereby restoring it to graphene [1]. Here we show that mechanical stress alone effectively removes functional groups. We measured the degree of surface functionalization by monitoring both normal load and friction between the sliding tip and a plasma processed CMG sheet. For oxygenated graphene, friction decayed exponentially with sliding distance, dropping to ~15% of the starting value. These measurements revealed an initial drop in friction that was independent of applied stress, suggesting the presence of an adsorbed water layer on the surface. More importantly, they reveal an Arrhenius-like relationship between contact stress and degree of surface reduction. The reduction in friction persisted, precluding the presence of the adsorbed contaminants as the source of the friction change. Conductive AFM and Raman measurements provide further evidence for chemical reduction. Conductive diamond AFM tips measure the current through the surface during the reduction process, revealing a 5x increase in conductivity corresponding to the friction force reduction. Additionally, Raman measurements on a 5 mm<sup>2</sup> reduced area showed a relative increase in both the G and 2D peaks, consistent with a reduction in functionalization. These experiments enabled detailed comparison of tribochemical reactions without the complications of transfer films or the initial run-in of the film. They also enable experiments difficult by other means. For instance we could directly compare the mechanical barrier to functional group removal by monitoring friction while slowly ramping the applied stress between the tip and a graphene surface functionalized with either oxygen or fluorine groups. For oxygenated graphene, the contact stress at the maximum reduction rate was  $\sim 0.47 \pm 0.14$  GPa; for fluorinated graphene it was  $\sim 0.85 \pm 0.27$  GPa. Thus, by using the same tip and same supporting substrate we could directly compare the bond strengths between different functional groups and the graphene lattice. This work demonstrates the ability to measure and control the chemistry of single-layer functionalized surfaces at the nanometer scale, and has wide application in tribochemical wear, mechanochemistry, and nanoelectronic device fabrication with chemically tuned optoelectronic properties.

[1] Z. Wei, et al, *Science* **328**, 1373-1376 (2010)

### 11:00am 2D+AS+BI+PS+SS-TuM10 Fe-catalyzed Etching of Graphene, Few-Layer Graphene, and Graphite, *Guangjun Cheng, A.R. Hight Walker*, National Institute of Standards and Technology

Mechanically exfoliating graphite onto a substrate provides a family of layered materials with adjustable thickness, including monolayer graphene, few-layer graphene (FLG), and graphite. In this work, we investigated the Fe-catalyzed etching of graphene, FLG, and graphite in forming gas (10%  $\text{H}_2$ /90%  $\text{N}_2$ ) or  $\text{N}_2$  using low-voltage scanning electron microscopy and Raman spectroscopy. Fe thin films were deposited by sputtering onto mechanically exfoliated graphene, FLG, and graphite flakes on a Si/SiO<sub>2</sub> substrate. When the sample is rapidly annealed in either gas environment, particles are produced due to the dewetting of the Fe thin film and expected to catalyze the etching of graphene, FLG, and graphite. The combined microscopic and spectroscopic evidence reveals a thickness-dependent,

catalytic etching behavior in these two gas environments and provides insights into the catalytic mechanisms involving carbon hydrogenation and carbon dissolution.

11:20am **2D+AS+BI+PS+SS-TuM11 Tunable Graphene/Si Schottky Diode Sensor: Before and After Functionalization for Wide Range of Molecular Sensing**, *MdAhsan Uddin, A. Singh, T. Sudarshan, M.V.S. Chandrashekar, G. Koley*, University of South Carolina

Graphene/Semiconductor Schottky devices attracted significant research attention due to wide range of applications from transistor to IR detector [1-2]. Such heterojunctions are also promising for sensing applications due to the molecular adsorption induced Schottky barrier height (SBH) change at the interface, affecting the junction current exponentially in reverse bias, which leads to ultrahigh sensitivity. Graphene/p-Si diode sensor [Device image, Raman spectra and I-V characteristics shown in fig. 1(a), (b) and (c)] has been developed with high bias-dependent sensitivity and low operating power.

Performance enhancement has been demonstrated by fabricating graphene chemiresistor and diode sensor on the same chip. The diode sensor exhibited 13 times higher sensitivity for NO<sub>2</sub> [Fig. 2(a)] and 3 times higher for NH<sub>3</sub> [Fig. 2(b)] in ambient condition, while consuming ~500 times less power for same applied voltage. Sensing tunability is achieved by operating the device in reverse bias, tuning the graphene work function and hence the SBH by the applied bias. The sensitivity varied from 268 to 574% for NO<sub>2</sub> as the bias magnitude varied from -1 to -8V [Fig. 3(a)]. Optimized sensor design to detect particular analyte is also possible by careful selection of graphene/Si heterojunction SBH. For example, graphene/p-Si with larger SBH is better NO<sub>2</sub> sensor while smaller SBH device has better NH<sub>3</sub> sensitivity. The sensing mechanism based on SBH change has been confirmed by capacitance-voltage measurements [Fig. 3(b)]. The SBH decreased by 0.23eV for NO<sub>2</sub> exposure while increased by 0.16eV for NH<sub>3</sub>. Variation in sensitivity with NO<sub>2</sub> and NH<sub>3</sub> concentration has also been demonstrated (Fig. 4).

Pd and Pt functionalization has been carried out to make the graphene/Si diode [Fig 5] sensitive to H<sub>2</sub>. Extrapolated SBH from the I-V characteristics, before and after few nm metal decoration, and H<sub>2</sub> exposure showed initial SBH decrease after functionalization and subsequent increase in presence of H<sub>2</sub>, respectively [Fig. 6(a) and (b)]. Compared to graphene chemiresistor, the chemi-diode sensor offers more than one order of magnitude higher H<sub>2</sub> sensitivity for both types of functionalization. Similarly, the reverse bias operation also enables low power consumption, tunable sensitivity and detection of H<sub>2</sub> down to 1 ppm [Fig. 7(a)] in air which is close to the atmospheric background of 0.6 ppm [3]. Among the two metals, Pd-functionalization always exhibited better sensing response irrespective of the bias voltage [Fig. 7(b)]. Remarkably, for Pd-functionalization, the sensor response showed absolute exponential change with varying H<sub>2</sub> concentration ranging from 2 to 1000 ppm [Fig. 7(c)].

12:00pm **2D+AS+BI+PS+SS-TuM13 Dielectrics Layer Deposition on Graphene Surface by Functionalization with Polar Titanyl Phthalocyanine**, *Jun Hong Park, I.J. Kwak, K. Sardashti, A.C. Kummel*, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a monolayer low-k dielectric or as a nucleation layer for growth of high-k insulators. This study demonstrates the molecular scale observation of formation of O-TiPc mono and bilayers on graphene with UHV scanning tunneling microscopy (STM). O-TiPc monolayers were deposited on HOPG surfaces by organic molecular beam epitaxy. After deposition, O-TiPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.4 x 1.4 nm grid. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. STS shows the band gap of the monolayer is 1.7 eV and the band gap of the bilayer is 2.3 eV. The monolayer or bilayer can directly be employed for sub-nanometer insulators on 2D semiconductors at low bias. Multiple cycles of TMA and water were dosed onto O-TiPc/HOPG to investigate nucleation of Al<sub>2</sub>O<sub>3</sub> on the O-TiPc layers. The first cycle of TMA was observed to chemisorb on a 1.4 x 1.4 nm grid on the TiOPc monolayer. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H<sub>2</sub>O), insulating aluminum oxide was deposited uniformly on O-TiPc/HOPG. After formation of Al<sub>2</sub>O<sub>3</sub> on O-TiPc/HOPG, the band gap of surface increases from 1.7 eV to 2.7 eV, while the conductance decreased. As shown in XPS spectra, the quality of Al<sub>2</sub>O<sub>3</sub> can be improved by post annealing, consisting with transition of chemical states in O 1s peak and Al

2p. The chemical shifts of O and Al indicate that post annealing converts remained the Al-OH to Al<sub>2</sub>O<sub>3</sub>. Consequently, O-TiPc can not only act as a low-K dielectric but also induce high density ordered nucleation of ALD on central ion of O-TiPc for high-k dielectric growth.

# Tuesday Afternoon, November 11, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+AS+HI+MC+NS+PS+SP+SS-TuA

## 2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Manish Chhowalla, Rutgers University

2:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA1 Layer-Dependent Electronic and Physical Structure of 2D van der Waals Crystals, Richard Osgood, Columbia University** **INVITED**

Because of their weak Van der Waals interlayer bonding transition-metal dichalcogenide (TMDC) semiconductors can be fabricated into atomically thin two-dimensional (2D) crystals with substantial ~ 1-2 eV bandgaps. As one example, monolayer MoS<sub>2</sub> consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. The TMDC 2D system has attracted great interest because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands, i.e. 100's of meV, due to broken inversion symmetry, which makes TMDCs interesting for spin-physics physics and devices. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Recently we have made a series of direct observations of the thickness-dependent electronic-band and crystal structure of TMDCs of both exfoliated and CVD grown sample. Because of the relatively modest sample sizes we have used micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both the exfoliated and chemical-vapor-deposition-grown crystals; these measurements provide direct evidence for the shifting of the valence band maximum from gamma bar (Brillouin zone center) to kappa bar (Brillouin zone corner), as the sample thickness decreases from bulk to monolayer. Our initial results were with MoS<sub>2</sub> and are described in a preliminary way in Refs 1 and 2. Our TMDC experimental results are compared with rigorous DFT calculations of both the bands and the UV transitions matrix elements. The results show an evolution in band structure, which is consistent with an indirect-to-direct bandgap transition in going from few-layer to monolayer TMDC and can be attributed to changes in quantum confinement as the number of layer decreases. Our microARPES and, subsequently, higher resolution nanospectroscopy data provide clear measurements of the hole effective mass, the strain present in the monolayer crystal films, and the valence-band spin-orbit splitting. Our results explain the low hole mobility of monolayer MoS<sub>2</sub> compared to thicker MoS<sub>2</sub> and show clearly the strong orbit split energies. Our results, using nanoLEED and LEEM also provide insight into the structure and defects in monolayer films. Experiments using K-doping of single-crystal samples and resulting level shifts are also described.

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3:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA3 X-ray Photoemission and Electron Energy Loss Spectroscopy Investigation of the Band Gap and Band Alignment for h-BN and MoS<sub>2</sub> Materials and Interfaces, Benjamin French, J. Brockman, M. French, M. Kuhn, J.D. Bielefeld, S.W. King, Intel Corporation, E. Bersker, G. Bersuker, SEMATECH, J. DiStefano, Y.C. Lin, J.A. Robinson, Penn State University**

Hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS<sub>2</sub>) are two dimensional (2D) materials of significant interest for future nano-electronic devices. Due to a wide band gap (~ 6 eV), close lattice matching (< 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of primary interest as a potential substrate and gate dielectric in graphene channel transistor devices. In contrast, MoS<sub>2</sub> is a 2D semiconducting material with a band gap of ~ 1.8 eV that is attractive as a possible complement or alternative to

graphene for nano-electronic devices requiring a large band gap. A key property for the success of both h-BN and MoS<sub>2</sub> in such devices is the interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and chemically vapor deposited MoS<sub>2</sub>. In combination, we have utilized reflection electron energy loss spectroscopy (REELS) to investigate the band gap of both h-BN and MoS<sub>2</sub> materials to deduce the conduction band alignment. We show that in many instances the valence and conduction band offsets are significant and favorable for MoS<sub>2</sub>/h-BN transistor devices.

3:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA4 STM/STS Characterization of MoS<sub>2</sub> Monolayers and Nanostructures, A. Mills, C. Chen, Virginia Tech, Y. Yu, L. Cao, North Carolina State University, Chenggang Tao, Virginia Tech**

Atomically thin molybdenum disulfide (MoS<sub>2</sub>) and nanostructures have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. Especially, monolayer MoS<sub>2</sub>, an atomically thin semiconductor with a direct band gap, as opposed to an indirect band gap in bulk MoS<sub>2</sub>, has been demonstrated as field effect transistors, optoelectronic devices and chemical sensors. In our experimental study, Monolayer MoS<sub>2</sub> and MoS<sub>2</sub> triangular nanostructures are synthesized through a self-limiting chemical vapor deposition (CVD) approach. The precursor materials, MoCl<sub>5</sub> and sulfur, react at high temperatures to produce MoS<sub>2</sub> species and subsequently precipitate onto substrates to yield MoS<sub>2</sub> films and triangular nanostructures. Using scanning tunneling microscopy (STM), we have investigated the structural and electronic properties of monolayer MoS<sub>2</sub> grown on glassy carbon and triangular MoS<sub>2</sub> nanostructures on highly ordered pyrolytic graphite (HOPG). We will also discuss our scanning tunneling spectroscopy (STS) measurements on these structures.

4:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA8 Surface Characterization of Metal Oxide Layers Grown on CVD Graphene and Spin Precession Measurements, Akitomo Matsubayashi, University at Albany-SUNY, W. Nolting, University at Albany-SUNY, D. Sinha, University at Albany-SUNY, A. Jayanthinarasimham, J.U. Lee, University at Albany-SUNY, V.P. LaBella, University at Albany-SUNY**

Ultra thin metal oxide films grown on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel for device applications. This is particularly important for graphene based spintronic devices as tunnel barriers between the ferromagnetic metal as a spin injector and graphene have been known to increase the spin relaxation time measured utilizing non-local detection technique of spin precession by avoiding the conductivity mismatch problem. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier. We will present a systematic study of aluminum oxide layers grown on CVD graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the 0.2 nm titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium. The I-V characteristic study performed to electrically evaluate the metal oxide and the preliminary results of non-local spin precession measurements will be also addressed.

5:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA9 Morphology of CVD-grown Hexagonal Boron Nitride on Cu Foils, Karthik Sridhara, W.G. Cullen, University of Maryland, College Park, J.K. Hite, Naval Research Laboratory, M.S. Fuhrer, Monash University, Australia, D.K. Gaskill, B.N. Feigelson, Naval Research Laboratory**

Hexagonal boron nitride (h-BN) has grown into prominence as a dielectric for graphene heterostructures. h-BN and graphene have been grown using chemical vapor deposition on various transition metal substrates. Compared to graphene, the morphology of CVD-grown h-BN on Cu has not been as widely studied. Here, we present a systematic study of the morphology of hexagonal boron nitride (h-BN) grown on polycrystalline Cu foils by chemical vapor deposition. The growth of h-BN is performed at ~1000°C in atmospheric pressure CVD with Ammonia Borane (H<sub>3</sub>NBH<sub>3</sub>) as the precursor. The copper foils, used as catalytic substrates, are thermally annealed at ~1030°C for >5 hours prior to growth and cooled slowly following growth termination. We utilized Ultra-high vacuum Scanning Tunneling Microscopy (STM), ambient AFM and SEM to assess the morphology of the CVD grown h-BN films. Highly symmetric single

crystallites of h-BN are observed for sub-monolayer growth, in agreement with recent reports. We consistently observe a corrugated topographic structure within the h-BN crystallites which is distinctly different from the surrounding copper surface, and this is consistently seen in STM, AFM, and high-resolution SEM. Our aim is to understand the nature of this difference and whether it might be due to effects of differential thermal contraction between h-BN and copper. However, complications arise due to possible changes in the copper substrate topography post-growth due to surface oxidation of the copper. Preliminary results with lateral force microscopy (LFM, frictional mode) show that these corrugations are unidirectional in a single Cu grain irrespective of the orientation of the h-BN crystal and generate frictional forces 200% greater than on the surrounding copper surface, reminiscent of earlier reports of unique frictional behavior in atomically-thin membranes [1]. STM and AFM are also used to study the twin crystal boundaries of h-BN. Preliminary STM observations indicate that merging h-BN crystals consistently have a gap of about 5 nm between them. The results of this study are independent of small variations of growth conditions.

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5:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA10** **Influence of Chemisorbed Oxygen on the Growth of Graphene on Cu(100) and Cu(111) by Chemical Vapor Deposition**, *EngWen Ong*, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *T.R. Mowll*, *P. Tyagi*, University at Albany-SUNY, *H. Geisler*, SUNY College at Oneonta, *C.A. Ventrice, Jr.*, University at Albany-SUNY

The influence of chemisorbed oxygen on the growth of graphene by catalytic decomposition of ethylene in an ultra-high vacuum (UHV) chamber on both the Cu(100) and Cu(111) surfaces has been studied. A custom UHV compatible heater stage was constructed that allows heating of a crystal to temperatures as high as 1000 °C at hydrocarbon pressures of up to 100 mTorr. System recovery to the low  $10^{-10}$  Torr range is achieved within a few minutes of opening the gate valve to the turbo pump. The crystal structure of the graphene films was characterized with in-situ low energy electron diffraction (LEED), and the growth morphology was monitored by ex-situ scanning electron microscopy (SEM). For the clean Cu(100) substrate, heating from room temperature to the growth temperature while dosing with ethylene resulted in the formation of epitaxial graphene films. The crystal quality was found to depend strongly on the growth temperature. At 900 °C, well-ordered two-domain graphene films were formed. For the Cu(111) surface, heating from room temperature to the growth temperature while dosing with ethylene did not result in the formation of graphene. This is attributed to the lower catalytic activity of the (111) surface and the relatively high vapor pressure of the Cu surface. The use of an Ar overpressure to suppress Cu sublimation during the growth resulted in the formation of predominately single-domain epitaxial graphene films. Predosing either the Cu(100) or Cu(111) surface with a chemisorbed layer of oxygen before graphene growth was found to adversely affect the crystal quality of the graphene overlayers by inducing a much higher degree of rotational disorder of the graphene grains with respect to the substrate. The SEM analysis revealed that the nucleation rate of the graphene islands dropped by an order of magnitude after predosing either the Cu(100) or Cu(111) surface with a chemisorbed oxygen layer before growth. On the other hand, the average area of each graphene island was observed to increase by at least an order of magnitude. Therefore, the presence of oxygen during graphene growth affects both the relative orientation and average size of grains within the films grown on both substrates.

5:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA11** **Novel Materials Properties at Atomically Thin Limit**, *Zhi-Xun Shen*, Stanford University **INVITED**

In this talk, I will discuss recent progresses in uncovering novel materials properties at ultra-thin limit, with focus on mono-unit-cell superconductor FeSe and semiconductor MoSe<sub>2</sub> respectively.

The observation of a large superconducting-like energy gap which opens at temperatures up to 65 K in single unit cell (1UC) thick iron selenide films on SrTiO<sub>3</sub>(FeSe/STO) has generated tremendous interest. A challenge is to understand the cause of enhanced Cooper pairing strength in this system, and possibly increase superconducting T<sub>c</sub>. In this talk, we show angle-resolved photoemission spectroscopy, mutual inductance, and other measurements on 1UC and multi-UC thick FeSe films grown on Nb-doped SrTiO<sub>3</sub>. Our data provide clear evidence for strong cross-interface electron-phonon coupling in single UC, raising the possibility that large pairing gap are caused by the strong coupling between the FeSe electrons and certain

collective modes of SrTiO<sub>3</sub>. This suggests a pathway of "integrated functional components" approach to boost superconducting properties.

The intense interest of quantum systems in confined geometries is further amplified by the recent discovery of large enhancement in photoluminescence quantum efficiency and a potential route to "valleytronics" in atomically thin layered transition metal dichalcogenides (TMDs) MX<sub>2</sub> (M = Mo, W; X = S, Se, Te), which are closely related to the indirect to direct band gap transition in the single layer limit. Using angle-resolved photoemission spectroscopy (ARPES) on high quality thin film samples of MoSe<sub>2</sub> grown by molecular beam epitaxy (MBE), we have made a direct observation of a distinct transition from indirect to direct band gap as the thickness of the sample is reduced to a monolayer. The experimental band structure indicates a stronger tendency of monolayer MoSe<sub>2</sub> towards direct band gap with larger gap size than theoretical prediction. A comparison of directly measured ARPES band gap and optical data led to important new insights on semiconductor physics in 2D. Moreover, our finding of a significant spin-splitting of ~180meV at the valence band maximum (VBM) of a monolayer MoSe<sub>2</sub> film could greatly expand its possible application in spintronic devices.

If time permits, I will also discuss the superconductivity in CaC<sub>6</sub> and its implication on a possible pathway for superconducting graphene.

**Electronic Materials and Processing**  
**Room: 314 - Session EM+2D-TuA**

**High-k Dielectrics for Advance Semiconductor**

**Moderator: Andrew C. Kummel**, University of California at San Diego

2:20pm **EM+2D-TuA1** **Time-resolved XPS of ALD**, *Rainer Timm*, Lund University, Sweden **INVITED**

Atomic layer deposition (ALD) has been established as the main technique for creating MOS structures based on III-V semiconductors, but still device performance is limited by the quality of the interface towards the high-k oxide layer. X-ray photoemission spectroscopy (XPS) is a well-suited tool for analyzing the structure and chemical composition of such interfaces. However, conventional XPS studies under ultrahigh vacuum conditions can only compare the situation before and after individual half-cycles of the ALD process. Here I will show how ambient-pressure XPS can be used to study surface structure and chemistry live and *in-situ* during the ALD reaction. As an example, we have investigated the deposition of HfO<sub>2</sub> on InAs using TDMA-Hf and water as precursors, revealing several steps within the chemical reaction of InAs exposed to the Hf precursor material, which we interpret as a temperature-dependent adsorption of unreacted precursor molecules preceding the ligand exchange reaction.

3:00pm **EM+2D-TuA3** **GaSb Oxide Thermal Stability Studied by Dynamic-XPS**, *Stephen McDonnell*, *B. Brennan*, *E. Bursa*, University of Texas at Dallas, *K. Winkler*, *P. Baumann*, Omicron NanoTechnology, Germany, *R.M. Wallace*, University of Texas at Dallas

GaSb is a III-V material with applications as a potential channel material for p-type metal-oxide-semiconductor field effect transistors,<sup>1</sup> optoelectronics in the infrared region,<sup>2</sup> quantum devices,<sup>3</sup> and tunnel field effect transistors.<sup>4</sup> Prior to application specific processing it is often necessary to remove the GaSb native oxide, which can be quite thick. Such oxides can inhibit subsequent epitaxy and also be a source of traps for devices as a result of defect levels in the energy gap.<sup>5</sup> The thermal desorption of these oxides in ultra high vacuum has been examined in previous works, but is revisited in this study with dynamic-x-ray photoelectron spectroscopy (dynamic-XPS). Dynamic-XPS allows for the collection of core-level spectra in real time (i.e. data acquisition times are < 1 second). Combined with controlled heating, this allows for detailed chemical temperature-dependent chemical analysis to be carried out with temperature resolutions better than 1 Kelvin. The thermal decomposition of the native GaSb oxides is studied using dynamic-XPS. The expected transfer of oxygen from Sb-O to Ga-O before the eventual desorption of all oxides is observed. However an initial reaction resulting in the reduction of Sb<sub>2</sub>O<sub>3</sub> along with the concurrent increase in both Ga<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>4</sub> is detected in the temperature range of 450-525 K. Using the relative changes in atomic concentrations of the chemical species observed, the initial reaction pathway is proposed.

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**3:20pm EM+2D-TuA4 Combined Wet HF and Dry Atomic H Cleaning of SiGe followed by Passivation of the Clean Surface via H<sub>2</sub>O<sub>2</sub>(g) Dosing.** Sang Wook Park, T. Kaufman-Osborn, E.A. Chagarov, A.C. Kummel, University of California at San Diego

Silicon Germanium (SiGe) is a well-known material for its high mobility and useful applications in strain engineering. Its advantages can be utilized to overcome the challenges when scaling down silicon-based devices. As the interest in introducing new kinds of materials increases, the cleaning and passivation methods also become more significant in order to provide uniform and clean surfaces, which would result in improved electrical properties such as high mobility and low interface trap density (D<sub>it</sub>). In this study, combined wet and dry cleaning and passivation of SiGe(100) surface is discussed, using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS).

Wet cleaning using 2% hydrofluoric acid (HF) was implemented to strip the native oxide off the SiGe sample but left residual carbon contamination on the surface. Although the oxide layer was removed, additional oxygen adsorbed to the surface during transfer from the HF solution to vacuum chamber. This residual oxygen can be eliminated by keeping the SiGe sample covered in the HF cleaning solution until the sample is introduced to the vacuum chamber or by transferring the sample in an inert environment. Dry in-situ atomic hydrogen cleaning was then implemented to remove the carbon contamination on the surface. A post deposition anneal at 550°C was used to obtain an atomically clean, flat, and ordered SiGe surface and this was verified using STM. The oxygen and carbon contaminant levels were monitored after each cleaning procedure using a monochromatic XPS. The clean SiGe sample was dosed at room temperature with a saturation dose of H<sub>2</sub>O<sub>2</sub>(g). STM and XPS measurements indicate that H<sub>2</sub>O<sub>2</sub>(g) dosing leaves the SiGe surface, which is mostly Ge atoms due to surface segregation, terminated with an ordered monolayer of Ge-OH sites. STS measurements of the Ge-OH sites show the conduction band edge dangling bond states are eliminated due to the passivating Ge-OH bonds, but the Fermi level is pinned near the valence band edge due to the large surface dipole. When the surface is annealed to 310°C, XPS measurements indicate that the -OH species on the surface break bonds with the Ge atom and bond instead to the Si atoms, raising Si atoms towards the surface. XPS also verifies that no oxygen leaves the surface due to the 310°C anneal. Instead, the oxygen remains on the surface in the form of Si-OH or SiO<sub>x</sub> species. TMA is subsequently dosed on the surface forming and ordered monolayer of Al-O-Si bonds. STS indicates this unpins the Fermi level, leaving an electrically passive ordered layer which serves as an ideal template for further high-k ALD.

**4:20pm EM+2D-TuA7 Interfacial and Electrical Study of Crystalline Oxidation Passivation for AlGaIn/GaN HEMTs.** Xiaoye Qin, H. Dong, J.Y. Kim, R.M. Wallace, University of Texas at Dallas

AlGaIn/GaN high electron mobility transistors (HEMTs) are of significant interest for high power, high frequency and high temperature devices. However, these are known to experience significant surface related effects, such as large leakage currents and frequency dependent current collapse. Oxidation has been found to have a variety of effects on the atomic and electronic structure of nitride surfaces. Therefore, the oxidation layer and the device performance are closely related. Typically, GaN and AlN are found to form a disordered oxide layer related to high density of states when exposure to with O<sub>2</sub>. Miao *et al.*<sup>1</sup> reported that oxidation of AlN and GaN surface change the density of surface states based on density functional theory (DFT). In their work, a 2 ML crystalline oxide can cause the lowest density of surface states within the band gap. However, experimental evidence of a 2 ML crystalline oxide remains to be established.

In this study, we investigate O<sub>2</sub> plasma- exposed AlGaIn surfaces at 300 °C and 550 °C by *in situ* X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED). The results indicate that a 500°C O<sub>2</sub> remote plasma exposure is able to generate a thin 2 ML ordered oxide on AlGaIn surface and the oxide is stable during subsequent ALD processing, in contrast to arsenide surfaces.<sup>2</sup> The capacitance- voltage (C- V) results indicates that the 2 ML crystalline oxide reduces the D<sub>it</sub> and shifts the threshold voltage to positive voltages. The I-V and gate leakage current

characteristics for crystalline oxide MOSHEMTs will also be presented. This work is supported by the AFOSR Asian Office of Aerospace Research and Development (AOARD) under Grand No. FA2386- 11- 1- 4077.

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**4:40pm EM+2D-TuA8 Investigating Electrically Active Defects in High-k/InGaAs MOS System using MOS Capacitors and MOSFETs.** Paul Hurley, Tyndall National Institute, Ireland, V. Djara, IBM Research - Zurich, Switzerland, E. O'Connor, S. Monaghan, I.M. Povey, J. Lin, Tyndall National Institute, Ireland, M.A. Negara, Stanford University, B. Sheehan, K. Cherkaoui, Tyndall National Institute, Ireland **INVITED**

As silicon devices reach the limit of dimensional scaling there is a growing interest in the use of high electron mobility channels, such as In<sub>x</sub>Ga<sub>1-x</sub>As, in conjunction high dielectric constant (high-k) gate oxides for n-channel Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) and tunnel FET (TFETs) based devices. The understanding and control of electrically active defect states at the high-k/In<sub>x</sub>Ga<sub>1-x</sub>As interface and of charges within the atomic layer deposited (ALD) high-k films will be essential for the successful implementation of high mobility channel materials. The objective of this presentation will be to provide an overview of the current understanding of the density and distribution of electrically active defects at the high-k/InGaAs interface both within the InGaAs energy gap and extending into the InGaAs conduction band. The presentation will focus on InGaAs with a 53% Indium concentration. The electrically active interface state density distribution is determined from fully fabricated InGaAs MOSFET structures based on the full gate capacitance in conjunction with the Maserjian Y-function and Poisson-Schrodinger simulations. Very significant progress has been made in recent years in the passivation and intrinsic elimination of high-k/In<sub>0.53</sub>Ga<sub>0.47</sub>As interface defects to the point where genuine surface inversion for n and p type InGaAs MOS structures can be achieved and this research will be reviewed. The characteristic signatures of capacitance and conductance for an InGaAs MOS structure in inversion will also be discussed.

Electrically active defects with energies aligned with the InGaAs conduction band are significant for surface inversion mode MOSFETs and can result in a partitioning of charge between free carriers and trapped charge for devices biased above the threshold voltage. The presence of such defect also complicates the extraction of free charge and carrier mobility from device analysis. In this presentation we will also review a new approach where the technique of inversion charge pumping (initially developed for silicon MOSFETs) is applied to InGaAs MOSFETs to determine the free carrier concentration. Results will also be presented which indicate that the duty cycle of the inversion charge pumping technique can be used to discriminate between fast interface states and traps within the oxide for InGaAs MOSFETs biased beyond the threshold voltage.

**5:20pm EM+2D-TuA10 XPS Study of High-k Gate Stack and Interaction with Different Channel Materials and Metal Gate.** Malcolm Bevan, Applied Materials Inc. **INVITED**

Deposited high-k dielectrics with metal gates have replaced SiON gate with poly electrodes for several Logic nodes and rapidly followed with integration changes from planar to 3D FINFET structures. Performance is no longer through just scaling, and next generation devices have gaps that are being addressed with channel engineering using high mobility materials such as SiGe, Ge and III-V compound semiconductors. Gate stacks now involve several thin films of dissimilar material whose interfaces need to be precisely controlled as well as being conformal around the fin and between the spacers. The stack usually involves the channel material followed by a thin interface layer(iL), high-k dielectric and metal gate cap(MG cap) and each layer range from 0.5 to 2nm. In addition several layers may need plasma or thermal treatment to improve reliability and BTI of the gate stack. To understand performance of these stacks, XPS has been applied to compliment device results. In Fab XPS is a powerful tool to provide in short time information on stack thickness, composition and changes in bonding. Examples will be given to show how XPS has been used to optimize and compare high-k stack on Si, SiGe and Ge. In addition iL/high-k/TiN cap has been studied and further examples given and related to electrical device results.

Previously, it was reported that by adding the third element into the high-*k* film, the bulk and interface material and electrical properties can be improved [1]. For example, the Zr-doped HfO<sub>2</sub> film (ZrHfO) shows the higher crystallization temperature, a lower interface state density, and a larger effective *k* value than those of the un-doped HfO<sub>2</sub> film [1,2]. Furthermore, nanocrystals have been embedded into this kind of high-*k* film for the nonvolatile memory (NVM) application to replace the conventional floating-gate flash memory due to the improved device characteristics and reliability [3]. The nanocrystalline cadmium selenide (nc-CdSe) embedded ZrHfO MOS capacitor has shown excellent charge trapping and retention capabilities [4]. However, most studies on the nanocrystals embedded high-*k* memory devices are done at the room temperature. Since the temperature in the high density integrated circuit can be much higher than room temperature, it is imperative to study the reliability at a raised temperature [5]. In this paper, the temperature effects on memory functions were investigated on the nc-CdSe embedded sample in the range of 2 0°C to 120°C. Compared with the fresh *C-V* curve, the flat band voltage ( $V_{FB}$ ) of *C-V* curve shifts to the negative or positive gate voltage ( $V_g$ ) direction after being stressed at -6 V or +6 V for 10 s, respectively. With the increase of the temperature, the magnitude of the  $V_{FB}$  shift increases at -6 V stress but decreases at +6 V stress. With the increase of the temperature, the hole-trapping is enhanced due to the increase of injection and retention of holes to the trapping sites. However, at the high temperature, electrons are possibly transferred through the whole high-*k* stack with minimum trapping to the high-*k* stack. In addition, at the high temperature, the nc-CdSe embedded sample has the large relax current with the high discharge rate due to the increasing release of the trapped charges with large thermal energy. The charge retention capability of the device decreases with the increase of the temperature. For example, the device stressed at -6 V for 20 s will retain 30% of the original trapped holes at 20°C, 23% at 70°C, and 15% at 120°C, respectively, after 10 years. This is because the stored charges gain the high thermal energy and the bulk high-*k* film is more conductive at the high temperature.

# Wednesday Morning, November 12, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+NS+SS+TF-WeM

### Novel 2D Materials

Moderator: Evan Reed, Stanford University

8:00am **2D+EM+NS+SS+TF-WeM1 Silicene and Germanene: Novel Graphene-like Artificial Silicon and Germanium Allotropes, Guy Le Lay, Aix-Marseille University, France** **INVITED**

Silicene, graphene's cousin, and germanene, a new born in Terra Plana, are predicted to combine the unique electronic properties of graphene associated to quasiparticles behaving as massless Dirac fermions to a character of two-dimensional topological insulators, and, even, possibly, high temperature superconductors. In this talk, I will present fundamental results on these novel synthetic 2D materials, which do not exist in nature, but which might open the way to practical applications, because of their expected direct compatibility with the current nano/micro electronic technologies.

8:40am **2D+EM+NS+SS+TF-WeM3 Silicon Growth at the Two-Dimensional Limit on Ag(111), Andrew Mannix, B.T. Kiraly, Northwestern University, B.L. Fisher, Argonne National Laboratory, M.C. Hersam, Northwestern University, N.P. Guisinger, Argonne National Laboratory**

Bulk silicon has played a dominant role in the growth of microelectronics over the past 50 years. Considering the immense interest in two-dimensional (2D) materials (e.g., graphene, MoS<sub>2</sub>, phosphorene, etc.), the growth of Si in the 2D limit is of high relevance to the evolution of electronic materials. Utilizing atomic-scale, ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have investigated the 2D limits of Si growth on Ag(111). In agreement with previous reports of *sp*<sup>2</sup>-bonded silicene,<sup>1,2</sup> we observe the evolution of ordered 2D phases, which we attribute to apparent Ag-Si surface alloys. At sufficiently high Si coverage, we observe the precipitation of crystalline, *sp*<sup>3</sup>-bonded Si(111) domains. These domains are capped with a  $\sqrt{3}$  honeycomb phase that is indistinguishable from the  $\sqrt{3}$  honeycomb-chained-trimer (HCT) reconstruction of Ag on Si(111).<sup>3,4,5</sup> Additional evidence suggests that silicon intermixing with the Ag(111) substrate is followed by the precipitation of crystalline, *sp*<sup>3</sup>-bonded silicon nanosheets. These conclusions are supported by *ex-situ* atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Even at the 2D limit, scanning tunneling spectroscopy shows that the *sp*<sup>3</sup>-bonded silicon nanosheets exhibit semiconducting electronic characteristics.

[1] Vogt, P., *et al.* Silicene: Compelling Experimental Evidence for Graphene-like Two-Dimensional Silicon. *Phys. Rev. Lett.*, 108(15), 155501 (2012).

[2] Feng, B., *et al.* Evidence of silicene in honeycomb structures of silicon on Ag(111). *Nano Lett.*, 12(7), 3507–11 (2012)

[3] Le Lay, G. Physics and electronics of the noble-metal/elemental-semiconductor interface formation: A status report. *Surf. Sci.*, 132(1-3), 169–204 (1983).

[4] Aizawa, H., Tsukada, M., Sato, N., & Hasegawa, S. Asymmetric structure of the Si(111)- $\sqrt{3}\times\sqrt{3}$ -Ag surface. *Surf. Sci.*, 429 (0–5) (1999).

[5] Ding, Y., Chan, C., & Ho, K. Structure of the ( $\sqrt{3}\times\sqrt{3}$ ) R30° Ag/Si(111) surface from first-principles calculations. *Phys. Rev. Lett.*, 67(11), 1454–1458 (1991).

9:00am **2D+EM+NS+SS+TF-WeM4 Growth, Structure, and Properties of 2D SiO<sub>2</sub> Polymorphs, Eric Altman, J. Götz, X. Zhu, A. Sonnenfeld, U.D. Schwarz, Yale University**

Recently it has been shown that SiO<sub>2</sub> can form closed 2D bilayers; because the layers have no dangling bonds they are expected to interact solely through van der Waals interactions. Despite the expected weak interactions, hexagonal crystalline bilayers on Pd(100) are stretched 4% to match the lattice constant of the substrate. Both electron diffraction and STM reveal that the size of the crystalline domains is limited along Pd[011] and one of the other bilayer close-packed directions but was long along the third one. The formation of regular domain boundaries on the square Pd substrate is attributed to stress relief in the crystalline layer. *Ab initio* calculations indicate that much of the remaining strain energy can be relieved by allowing the film to relax along the incommensurate direction. In this way the square substrate actually aids the templating of the overlayer despite the severe geometric mismatch. The calculations also indicate that the bilayer is surprisingly compliant, explaining the lattice matching despite the weak

interaction and poor match. Amorphous bilayers could also be prepared on Pd(100). Atomic-scale features in STM images of the amorphous film could be associated with 4-9 membered rings of corner-sharing SiO<sub>4</sub> tetrahedra. In addition to the structural heterogeneity, spectroscopic STM imaging revealed electronic heterogeneity with oxygen sites joining larger rings of corner-sharing SiO<sub>4</sub> tetrahedra fading at low bias; spectra revealed two distinct electronic states responsible for this phenomenon. MBE growth of silica bilayers on graphene layers grown on epitaxial Ru on sapphire will also be discussed.

9:20am **2D+EM+NS+SS+TF-WeM5 Layer-dependent Electronic and Vibrational Properties of SnSe<sub>2</sub> and SnS<sub>2</sub> 2D Materials, Joseph Gonzales, R. Schlaf, I.I. Oleynik, University of South Florida**

Layered metal chalcogenides possess a wide range of unique electronic properties, which are currently explored for applications as novel two-dimensional electronic materials. SnS<sub>2</sub> and SnSe<sub>2</sub> layered materials consist of covalently bonded S-Sn-S (Se-Sn-Se) sheets bonded together by weak van der Waals interactions. The atomic, electronic and vibrational properties of SnS<sub>2</sub> and SnSe<sub>2</sub> thin films are investigated using first-principles density functional theory (DFT). The accurate prediction of electronic and optical properties of SnS<sub>2</sub> and SnSe<sub>2</sub> layered 2D materials is achieved by applying state of the art many-body perturbation theory in GW approximation followed by solving the Bethe-Salpeter equation (BSE) to take into account excitonic effects. The evolution of the thickness-dependent band structure, optical and Raman spectra are discussed. The strain effects due to interactions with the substrate are also considered. The first-principles results are compared with available experimental data.

9:40am **2D+EM+NS+SS+TF-WeM6 Synthesis and Properties of Large Scale, Atomically Thin Tungsten Diselenide (WSe<sub>2</sub>), Sarah Eichfeld, Y.C. Lin, L. Hossain, The Pennsylvania State University, A. Piasecki, The Pennsylvania State University, A. Azcatti, University of Texas, Dallas, S. McDonnell, R.M. Wallace, University of Texas at Dallas, J.A. Robinson, The Pennsylvania State University**

Transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe<sub>2</sub>) are of interest due to their intriguing properties including the transition from indirect gap to direct gap as the material is thinned to a single atomic layer. Stacking of these layered TMDs also allows for the possibility of bandgap tuning. These properties can suit a large range of flexible and low temperature electronic and optoelectronic devices. Current methods of WSe<sub>2</sub> research involve exfoliation or vaporization of WO<sub>3</sub> and Se powder, which limits industrial scalability. This work is focused on development of a metal-organic chemical vapor deposition process that can controllably produce highly-crystalline, atomically thin WSe<sub>2</sub> on large area substrates.

Growth of controlled monolayer tungsten diselenide (WSe<sub>2</sub>) was carried out using chemical vapor deposition in a cold wall vertical reactor. Tungsten hexacarbonyl (W(CO)<sub>6</sub>) and dimethylselenium (DMSe) served as the tungsten and selenium precursors, respectively. Use of MOCVD precursors provides a means to independently control the W and Se precursors allowing for more precise control of the individual species during growth. Process variables including temperature (500-950°C), pressure (100-700 Torr), and carrier gas, which were correlated with grain size, growth rate, and nucleation density of the WSe<sub>2</sub> to identify optimal parameters for atomically controlled synthesis. Increasing the growth pressure from 100-700 Torr results in a decrease in growth rate and nucleation density, leading to a >50x increase in grain size. Increased growth temperatures yield an increase in grain size, however, it was found that above temperatures of 800 °C the sapphire substrate begins to decompose in the growth environment, resulting in a degradation of WSe<sub>2</sub> above 800°C. Synthesis using 100% hydrogen, and also hydrogen/nitrogen mixtures was carried out. It was found that 100% hydrogen was necessary in order to achieve low carbon incorporation in the WSe<sub>2</sub> films. Characterization of these samples via Raman and photoluminescence spectroscopy verified that high quality, monolayer WSe<sub>2</sub> is readily achievable. Additional characterization (i.e. scanning electron microscopy, atomic force microscopy, etc.) verify the quality, grain size, and nucleation density of the atomic layers. Finally, we will discuss the impact of substrate choice on the quality of the WSe<sub>2</sub> atomic layers, as well as providing direct evidence that synthesis on graphene results in highly textured films, with nearly 100% commensurability to the underlying graphene.

11:00am **2D+EM+NS+SS+TF-WeM10 Growth of Transition Metal Dichalcogenides and their Alloys and on Flat and Patterned Substrates.** *E. Preciado, A. Nguyen, D. Barroso, V. Klee, S. Bobek, I. Lu, S. Naghibi, G. Von Son Palacio, T. Empante, K. Brown, K. Yang, A. Nguyen, J. Mann, Ludwig Bartels*, University of California - Riverside

The use of organic chalcogen precursors permits the CVD growth of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  alloys of any composition between pure  $\text{MoS}_2$  and  $\text{MoSe}_2$  on  $\text{SiO}_2$ . Spatially resolved vibrational and photoluminescence (PL) spectroscopy is used to characterize our samples: while we observe a continuous transition of the PL maximum with S: Se ratio, the vibrational modes behave in a more complicated, 2-mode fashion. Depending on growth conditions, compositional homogeneous and heterogeneous films can be prepared.

We present details of our growth processes and show to which extend patterns on the substrates can affect the resultant structures. The patterns range from simple hole and pillar arrays to complex waveguide structures. We find that holes to an underlying reducing substrate (silicon) are effective in seeding growth. In contrast, protrusions on the substrate have little effect, so that complex devices can be overgrown.

Ref: Mann et al., 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps:  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  Monolayers, *Advanced Materials* 26, 1399 (2014)

11:20am **2D+EM+NS+SS+TF-WeM11 Synthesis, Characterization and Radiation Response of Boro-Carbon-Oxy-Nitride: A Heterogeneous 2D Material.** *GaneshRahul Bhimanapati, M. Wetherington, M. Kelly, J.A. Robinson*, The Pennsylvania State University

Since graphene, there have been many other two-dimensional materials systems (e.g., boron nitride (hBN), borocarbon nitride (BCN), transition-metal dichalcogenides) that provide an even wider array of unique chemistries and properties to explore future applications. In fact, these other 2D materials, are sometimes far better suited for many optoelectronic and mechanical applications. Specifically, tailoring graphene/boron nitride heterostructures, which retain the character of single-atom thick sheets that can withstand large physical strains, are easily functionalized, and have entirely different optical and mechanical properties compared to graphene can provide the foundation for entirely new research avenues. In recent years, it has been shown that because of the similar crystal structure, carbon, boron, and nitrogen can coexist as atomic sheets in a layered structure. Thus, combining these materials to form a new heterogeneous material system known as boro-carbon-oxy-nitride (BCON) for potential nano-mechanical and electronic applications and to study its fundamental property relations is necessary. Here, we present the fundamental property relations of BCON and its structural response to various radiation sources such as alpha, beta and gamma particles thereby providing a means for potential radiation sensing applications.

We have developed a facile method of integrating boron nitride and graphene oxide (GO) via chemical exfoliation. Chemical exfoliation of graphene oxide and boron nitride powders is accomplished via oxidation in strong acids, as we find previous methods of sonication in polar solvents does not yield stable solutions of hBN. Upon exfoliation, GO and hBN are mixed, and the resulting BCON material can be suspended in DI water, with suspension stability depending on the pH of the GO. The study of the stability of this material at different pH conditions indicates a stable and a uniform solution is achievable at pH 4-7. Fourier transform infrared spectroscopy (FTIR) indicates the B-N-B bending in the BCON is decreased as an effect of parent GO. Further, radiation response of this material to various radiation sources such as alpha, beta and gamma radiation are studied using In-Situ X-Ray Photoelectron Spectroscopy (XPS). The structural changes of carbon 1s peak in the BCON even for very low doses of radiation energy indicate potential applications in radiation sensing.

11:40am **2D+EM+NS+SS+TF-WeM12 The Structure of 2D Glass.** *Christin Büchner*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *L. Lichtenstein*, Lawrence Berkeley National Laboratory, *M. Heyde, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

For the first time, the structure of an amorphous network is imaged in real space.[1] Through a thin film approach, silica is made accessible for investigation with scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Physical vapor deposition with subsequent annealing is employed to create an atomically flat bilayer of  $\text{SiO}_2$ , supported on a Ru(0001) single crystal. Atomic positions of oxygen and silicon can be visualized, as well as ring structures with their distributions and local neighborhoods. All atomic species on the surface can be directly assigned with chemical sensitivity imaging.[2] This allows for statistical analysis of the building units, comparing amorphous to crystalline regions, as well as experiment to theory. Pair correlation functions of the 2D film structure are

set against diffraction data of bulk silica, revealing very similar bond distributions.

Coexisting crystalline and amorphous areas allow imaging of a topological transition region.[3] The understanding of glassy structures gained from these experiments is the starting point for more in-depth structural investigations[4], but also for investigating thin films with modified composition. Al-doping or Fe-doping can be employed to create 2D-Aluminosilicates or 2D-Clays, respectively.[5] Adsorption properties of the film can be probed using single metal atoms which migrate through the film, exhibiting ring-size-selectivity.[6]

[1] L. Lichtenstein, et al., *Angew. Chem., Int. Ed.* 51, 404 (2012)

[2] L. Lichtenstein, et al., *J. Phys. Chem. C* 116, 20426 (2012)

[3] L. Lichtenstein, et al., *Phys. Rev. Lett.* 109, 106101 (2012)

[4] C. Büchner, et al., *Z. Phys. Chem.*, DOI: 10.1515/zpch-2014-0438 (2014)

[5] J. A. Boscoboinik, et al., *Angew. Chem. Int. Ed.* 51, 6005 (2012)

[6] W. E. Kaden, et al., *Phys. Rev. B* 89, 115436 (2014)

# Wednesday Afternoon, November 12, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+AS+EM+MI+MN+NS+TF-WeA

## Properties of 2D Materials

Moderator: Guy Le Lay, Aix-Marseille University

2:20pm **2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors**, Kirill Bolotin, Vanderbilt University  
**INVITED**

Monolayer molybdenum disulfide (MoS<sub>2</sub>) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS<sub>2</sub> differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS<sub>2</sub> can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS<sub>2</sub>. We investigate the transition from direct to indirect band gap in MoS<sub>2</sub> under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS<sub>2</sub> on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS<sub>2</sub> specimens. We use photocurrent spectroscopy to study excitons in pristine suspended MoS<sub>2</sub>. We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS<sub>2</sub>.

3:00pm **2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides**, Neha Nayyar, V. Turkowski, D.T. Le, T.S. Rahman, University of Central Florida

Single layer MoS<sub>2</sub> and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 – 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

3:20pm **2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS<sub>2</sub>**, Michael Watson, J.R. Simpson, Towson University & NIST, R. Yan, H. Xing, University of Notre Dame, S. Bertolazzi, J. Brivio, A. Kis, EPFL, Switzerland, A.R. Hight-Walker, NIST

We report temperature and power dependent photoluminescence (PL) of molybdenum disulfide (MoS<sub>2</sub>). Mechanical exfoliation of MoS<sub>2</sub>, from bulk provides single-layer flakes which are then transferred either to sapphire substrates or suspended over holes in Si/SiO<sub>2</sub>. We measure temperature dependence from ~100K to 400K and power dependence from ~6μW to ~7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main excitonic peak(A) at ~1.87eV which consist of both neutral excitons and charged trions (A<sup>-</sup> or A<sup>+</sup>) [1]. The A exciton peak and the A<sup>-</sup> exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE, a broad peak centred at ~1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

[1] K.F. Mak et al. Nat. Mat 12,207(2013)

[2] R.Yan and J.R.Simpson, S. Bertolazzi and J. Brivio, M. Watson, X.Wu and A. Kis, T.Luo, H.G.Xing, A.R. Hight Walker, ACS Nano 8,1 (2013)

4:20pm **2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of and TaSe<sub>2</sub> and TaS<sub>2</sub> Dichalcogenides**, Danilo Romero, University of Maryland, College Park, M. Watson, J.R. Simpson, Towson University, H. Berger, Ecole Polytechnique Federale de Lausanne, Switzerland, A.R. Hight Walker, NIST

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2H-TaSe<sub>2</sub> and 1T-TaSe<sub>2</sub>, and 1T-TaS<sub>2</sub>. In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-density phases, and superconducting ground state as function of temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2H-TaSe<sub>2</sub> and 1T-TaSe<sub>2</sub>, and 1T-TaS<sub>2</sub>, carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:40pm **2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF<sub>3</sub>Cl Phases on Graphene**, Josue Morales-Cifuentes, T.L. Einstein, Y. Wang, J. Reutt-Robey, University of Maryland, College Park

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.<sup>1</sup> Electrical detection of CF<sub>3</sub>Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.<sup>2</sup> We study the electronic properties of similar phases varying coverage and orientation of CF<sub>3</sub>Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF1, vdW-DF2).<sup>3,4</sup> Consistent with a physisorbed phase, binding energies are calculated to be on the order of 280meV, and insensitive to coverage and orientation of the CF<sub>3</sub>Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sublattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

[1] Gianluca Giovannetti et al. , PRB **76**, 073103(2007)

[2] Yilin Wang et al. , APL **103**, 201606 (2013)

[3] Jiri Klimes et al. , PRB **83**, 195131 (2011)

[4] Kyuho Lee et al. , PRB **82**, 081101(R) (2010)

5:00pm **2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials**, Jon Schuller, UC Santa Barbara  
**INVITED**

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS<sub>2</sub> and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS<sub>2</sub> mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental excitonic properties in layered nanomaterials and designing optical systems that efficiently excite and collect light from exciton species with different orientations.

5:40pm **2D+AS+EM+MI+MN+NS+TF-WeA11 Mechanical Properties of 2D-Materials**, J.M. Gonzales, University of South Florida, R. Perriot, Los Alamos National Laboratory, Ivan Oleynik, University of South Florida

Graphene and other two-dimensional (2D) materials possess extraordinary mechanical properties, which are currently being explored in various novel applications. Atomic force microscopy (AFM) nanoindentation experiments

on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic moduli, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm **2D+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers**, *Evan Reed, K.-A.N. Duerloo, Y. Li*, Stanford University

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer MoTe<sub>2</sub> is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform MoTe<sub>2</sub> under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

## **In-Situ Spectroscopy and Microscopy Focus Topic Room: 313 - Session IS+2D+MC+NS+SP+SS-WeA**

### **In-Situ Scanning Microscopy**

**Moderator:** Markus Ammann, Paul Scherrer Institut

2:20pm **IS+2D+MC+NS+SP+SS-WeA1 In Situ Studies of Model Fuel Cells**, *Zhi Liu*, Lawrence Berkeley National Laboratory **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will give an overview of science projects at ALS BL9.3.2 in heterogeneous catalysis and electro-chemistry using these new systems. Furthermore, I will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell at ALS BL9.3.1. We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

3:00pm **IS+2D+MC+NS+SP+SS-WeA3 Probing of Nanoscale Objects in Reactive Liquids through Membranes using Near-Field Microwave Microscopy**, *Alexander Tselev*, Oak Ridge National Laboratory, *A. Komakov*, National Institute of Standards and Technology (NIST)

Many functional objects (and interfaces) have to be studied in situ when the object is immersed in liquid environment. In addition, for energy, chemical, (bio-) medical and other applications, there is a need to study the encapsulated objects, which otherwise can be chemically reactive or toxic. These samples are often mesoscopically small or exist in minuscule quantities. Recently, we have developed a process for preparation of liquid-filled cells sealed with ultrathin membranes. Such cells can be implemented for in-situ studies using, for example, electron or soft x-ray microscopy due to a high transparency of these membranes to electron beams. However, in many cases electron microscopy is an invasive technique due to various

electron beam induced parasitic effects (e.g. radiolysis or beam induced deposition). To overcome these impediments, we demonstrate the scanning microwave impedance microscopy (sMIM) to image different nanoscale objects immersed in the liquid environment through 30 nm SiN membranes. In the sMIM, microwaves of a frequency of 3 GHz are sent through a coaxial cable connected to a shielded cantilever probe fully compatible with an AMF microscope. The sharp probe tip provides “focusing effect” for the electric component of the microwave. For imaging, the tip is brought into gentle mechanical contact with a membrane. Amplitude and phase of microwaves reflected from the probe are monitored. Since the wave reflection is dependent on the tip-sample system impedance, reflected waves carry information about sample local properties. The effective distance into the sample depth, where the tip-induced field enhancement takes place, is approximately equal to the tip apex radius. Since the membrane thickness is smaller compared to the tip radius of a typical probe (about 50 nm for a fresh tip), the tip-sample impedance is dependent on the dielectric properties of the material beneath membrane, and therefore, it is possible to “see” through the membrane. We demonstrate imaging of different combinations of model liquids and nanoparticles: water and water-based solutions ( $\epsilon \sim 80$ ), organic solvents ( $\epsilon \sim 10-25$ ), and oils ( $\epsilon \sim 2-3$ ) containing Ni metal, polystyrene ( $\epsilon \sim 2.5$ ) and PbO ( $\epsilon \sim 25$ ) particles. This technique can be further implemented for a broad range of objects in confined liquids, and can be used to monitor interfacial electrochemical reactions. Imaging with sMIM was performed at CNMS, which is sponsored at ORNL by the SUFD, BES, US DOE.

4:20pm **IS+2D+MC+NS+SP+SS-WeA7 Caught in the Act! Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy**, *Irene Groot*, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Netherlands **INVITED**

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra) high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts *in situ* under industrially relevant conditions.

This talk focuses on the development of scanning probe microscopy for *operando* observations of active model catalysts. In our group, we have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, *i.e.* CO oxidation, will be shown. But additionally, results for more complex reactions such as NO reduction, Fischer-Tropsch synthesis, desulphurization, and production of chlorine will be discussed.

5:00pm **IS+2D+MC+NS+SP+SS-WeA9 X-ray Photoelectron Spectroscopy Studies of H<sub>2</sub>O Dissociation on Pre-oxidized Al (111) and Cu (111) Single Crystal Surface**, *Qianqian Liu*, SUNY, Binghamton University, *X. Tong*, Brookhaven National Laboratory, *G.W. Zhou*, SUNY, Binghamton University

Dissociation of H<sub>2</sub>O molecules on ultrathin oxide overlayers formed on metal surfaces plays a critical role in many catalytic reactions. However, the effects of chemical states and thickness of oxide overlayers on the microscopic process of H<sub>2</sub>O dissociation are still poorly understood. In this work, X-ray photoelectron spectroscopy (XPS) is employed to study H<sub>2</sub>O dissociation on oxidized Al (111) and Cu (111) surfaces with controlled chemical states and thicknesses of the oxide films. For Al (111), the experiment was performed under two water vapor pressures (10<sup>-6</sup> Torr and 5 Torr) on aluminum oxide films with the thicknesses varying from 2.47 Å to 5.14 Å; for Cu (111), the experiment was performed by varying the water vapor pressure from 10<sup>-7</sup> Torr to 10<sup>-3</sup> Torr and temperature from 100°C to 450°C on the oxide film with a constant thickness. Al (2p), Cu (2p), Cu (LMM) and O (1s) spectra were monitored by XPS after each oxygen

exposure followed by subsequent H<sub>2</sub>O exposure. Upon exposing the oxide to water vapor, the O (1s) peak shifts to a higher energy and becomes broader. A detailed analysis of the spectra indicates that H<sub>2</sub>O molecules dissociate into OH groups for both oxidized Al and Cu surfaces. However, the subsequent reaction of OH groups with the oxide films on Cu (111) and Al (111) surfaces are dramatically different. On the oxidized Al(111) surface, OH is further incorporated into the aluminum oxide that results in the thickening of the oxide film, whereas on the oxidized Cu (111) surface, OH works as a reducing agent to remove oxygen from the oxide film that results in the thinning of the Cu oxide film. The microscopic processes underlying the differences in H<sub>2</sub>O dissociation on oxidized Al (111) and Cu (111) will be described in detail.

5:20pm **IS+2D+MC+NS+SP+SS-WeA10 Operando APXPS of the Liquid-Solid Interface: Au Oxidation, Ethan Crumlin, S.A. Axnanda, P.N.R. Ross, Z.L. Liu, Lawrence Berkeley National Laboratory**

Interfaces play an important role for many reaction processes and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. Previous capabilities of ambient pressure X-ray Photoelectron Spectroscopy (APXPS) have primarily only been able to observe the gas-solid and gas-liquid interfaces. However, recent enhancements now enable new APXPS systems to work at pressures larger than 20 Torr, and utilize 'Tender' X-rays (2.5 – 7 keV). These features provide new capabilities and opportunities for probing the liquid-solid and solid-solid interfaces. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source and our 'Tender' X-ray APXPS endstation that is outfitted with various *in situ/operando* features such as electrical leads to apply electrical potentials and operates at pressures >20 Torr, to observe the liquid-solid interface of a gold foil electrode that has been immersed and partially removed from a liquid electrolyte. This talk will provide details on how we used this technique to probe liquid-solid interface and in real-time observe the oxidation of the gold foil electrode under varying applied potentials and different electrolyte solutions.

5:40pm **IS+2D+MC+NS+SP+SS-WeA11 Water on ZnO(10-10) Investigated by Ambient Pressure X-ray Photoelectron Spectroscopy, Chris Goodwin, University of Delaware, A. Boscoboinik, Brookhaven National Lab, C. Arble, J.T. Newberg, University of Delaware**

The extent to which ZnO hydroxylates under ambient conditions can significantly influence catalytic properties. Thus, it is critical to understand the composition of different ZnO terminations as a function of relative humidity (RH) in order to elucidate the true interfacial surface terminations. In this talk we present results of ambient pressure XPS (APXPS) for water exposures to a ZnO(10-10) single crystal. It will be shown that ZnO(10-10) extensively hydroxylates at the interface, and both molecular and dissociative water increase as the RH increases. These results are consistent with simulations in the literature that highlight the efficacy for ZnO(10-10) to dissociate water.

## Plasma Science and Technology

Room: 305 - Session PS+2D-WeA

## Plasma Processing for 2D Materials, Coating, and Surface Modification

Moderator: Colin Wolden, Colorado School of Mines

2:20pm **PS+2D-WeA1 Hydrogen Plasmas Processing of Graphene, Emilie Despiau-Pujo, A.O. Davydova, G. Cunge, LTM, Univ. Grenoble Alpes/CNRS/CEA-Leti Minatec, France, L. Magaud, Institut Neel, Univ. Grenoble Alpes/CNRS, France, D.B. Graves, University of California at Berkeley**

INVITED

The successful development of graphene-based technologies relies on our capability to grow and integrate this new material into sophisticated devices. Since the presence of multilayers or defects/contaminants on the graphene surface can significantly degrade its intrinsic properties, the development of new techniques to clean graphene surfaces from polymer residues, etch graphene films layer-by-layer or pattern graphene nanoribbons (GNRs) with minimal edge disorder, are major challenges. ICP H<sub>2</sub> plasmas seem promising to specifically treat graphene films but little is known about the fundamental mechanisms of plasma-graphene interaction. We therefore develop Molecular Dynamics (MD) simulations, coupled with experiments, to assist the development of plasma processes to clean, dope and pattern graphene layers in a controlled way. We more specifically

investigate the interactions between hydrogen plasmas and various types of graphene surfaces (monolayers, multilayers, nanoribbons). Except for impacts at GNRs edges or defects location, H species are shown to experience a repulsive force which prevents any species with less than ~0.6eV to adsorb on the graphene surface. H<sup>+</sup> bombardment in the [1-10] eV range does not damage the graphene basal plane while irreversible damages are expected for E<sub>i</sub> >12 eV (penetration of atomic H through the layers or C-C bond breaking) [1]. As a first step to model graphene cleaning, we investigate the mechanisms of CH<sub>3</sub> groups (a crude approximation for resist residues) removal from graphene by atomic hydrogen. Depending on the incident energy range and the surface temperature, MD shows the possibility for chemical etching of the methyl radical without damaging the graphene basal plane [2]. Recent experiments and XPS/AFM/Raman measurements confirm that H<sub>2</sub> plasmas are promising to clean PMMA residues from graphene with almost no damage after annealing. Simulations of GNRs trimming show that lateral etching is maximum for surface temperatures ~600 K and occurs via a specific mechanism limiting the edge roughness, as also observed experimentally. Finally, energetic H<sup>+</sup> or H<sub>2</sub><sup>+</sup> bombardment of stacked multilayer graphene (s-MLG) is investigated and the possibility to store hydrogen (trapped as H<sub>2</sub> molecules) between adjacent layers or etch a full single graphene sheet is discussed. [1] Despiau-Pujo, Davydova, Cunge et al, J.Appl.Phys.113, 114302 (2013) [2] Delfour, Davydova, Despiau-Pujo et al, submitted to Phys.Rev.B (2014)

3:00pm **PS+2D-WeA3 Plasma Synthesis of WS<sub>2</sub> Films, Rachel Morrish, C.D. Sentman, T. Haak, C.A. Wolden, Colorado School of Mines**

Two-dimensional metal dichalcogenides (WS<sub>2</sub>, MoS<sub>2</sub>) have attracted great interest due to their extraordinary optical properties, catalytic performance, and electronic structure. Synthesis of WS<sub>2</sub> has been accomplished by a variety of methods, but the high temperature (> 800 °C) and/or harsh S atmosphere required by many of these procedures precludes deposition onto conductive layers and low-temperature glass substrates needed for many applications. Previously we demonstrated the advantages of plasma processing for low temperature synthesis of a related metal dichalcogenide, pyrite (FeS<sub>2</sub>). It was shown that stoichiometric FeS<sub>2</sub> films could be fabricated either by plasma-assisted sulfurization of hematite [1] or by direct deposition using pulsed plasma-enhanced chemical vapor deposition (PECVD) with mixtures of H<sub>2</sub>S and Fe(CO)<sub>5</sub>. [2] In this talk we describe how these two approaches may be readily extended to the synthesis of WS<sub>2</sub> using WO<sub>3</sub> and W(CO)<sub>6</sub>, respectively.

Thin tungsten disulfide (WS<sub>2</sub>) films were prepared on FTO coated glass substrates by H<sub>2</sub>S plasma sulfurization of sputtered WO<sub>3</sub>. The reactive environment provided by the plasma enabled the complete transformation of oxide films to stoichiometric WS<sub>2</sub> within one hour at 500 °C. An apparent activation energy of 63.6 ± 1.9 kJ/mol was calculated for the plasma conversion process, which is less than half the barrier reported for the reaction of WO<sub>3</sub> with H<sub>2</sub>S. The conversion followed Deal-Grove behavior, with the growing WS<sub>2</sub> overlayer hindering diffusion to/from the reactive interface. Calibrated light absorption and relative intensity of the second order Raman 2LA(M) peak were identified as two additional methods to progressively monitor the thickness of the WS<sub>2</sub>. The semiconducting WS<sub>2</sub> layers exhibited n-type behavior with an indirect band gap at 1.4 eV and an absorption coefficient of ~5 × 10<sup>4</sup> cm<sup>-1</sup>. Self-limiting growth of WS<sub>2</sub> thin films was accomplished by pulsed PECVD with continuous delivery of tungsten hexacarbonyl diluted in a mixture of H<sub>2</sub>S and argon. The growth rate per cycle was controlled between 0.1 – 1 Å/pulse by adjusting the precursor flowrate. It was found that the morphology and orientation of the films was a complex function of film thickness, substrate temperature, and plasma parameters. Preliminary electrochemical measurements showed that these WS<sub>2</sub> films reduced the overpotential required for the hydrogen evolution reaction by several hundred mV relative to FTO while displaying good stability.

[1] R. Morrish, R. Silverstein and C. A. Wolden, *JACS* **134** 17854 (2012).

[2] C. D. Sentman, M. O'Brien and C. A. Wolden, *JVST* **A32** 021201 (2014).

3:20pm **PS+2D-WeA4 Decoration of Graphene with Gold Alloy Nanoparticles Synthesized in Solution Plasma, Maria Antoaneta Bratescu, Aichi Science and Technology Foundation, Nagoya University, Japan, T. Ueno, N. Saito, Nagoya University, Japan**

In order to be used in electronics and optics, graphene must be in contact with other materials, which can change its electrical and optical properties. The substrate, charge impurities, doping with chemical functional groups, and metal contacts can shift the position of the Fermi level of graphene. Furthermore, graphene with plasmonic nanoparticles (NPs) can offer a new perspective for light conversion systems, by optimization of visible light absorption via the SPR of the NPs, followed by electron exchange between graphene and NPs and electron transport through graphene.

In this work we present a facile, one-step, and surfactant-free method for the synthesis and loading of stable gold and gold-alloy NP on large-area graphene without NP deterioration using an electrical discharge in a liquid solution, termed solution plasma (SP). We investigated the charge transfer process between graphene and gold-alloy NPs by Raman spectroscopy and electron energy loss spectroscopy (EELS) in high resolution transmission electron microscopy (HRTEM).

The excess charge on graphene caused by transferred electrons or holes from the NPs to graphene was calculated from the change of the Fermi level relative to the initial position and the shift of the G band. In the case of graphene with gold NPs a decrease of the surface charge concentration with  $-3.5 \times 10^{12} \text{ cm}^{-2}$ , and a movement of Fermi level with  $-0.06 \text{ eV}$ .

In the case of the AuIn and AuGa NPs the transfer of electrons from graphene to the gold-alloy NPs produces an increase of the surface charge with  $1.3 \times 10^{12} \text{ cm}^{-2}$  and  $1.9 \times 10^{12} \text{ cm}^{-2}$ , which correspond to a raising of Fermi level with  $0.02 \text{ eV}$  and  $0.03 \text{ eV}$ , respectively.

The EELS results were consistent with Raman spectroscopy results, i.e. the electrons and holes are transferred from the gold and gold-alloy NPs to graphene, respectively.

M.A. Bratescu, et al., J. Phys. Chem. C 115 (2011) 24569

S.P. Cho, et al., Nanotechnology 22 (2011) 455701.

M.A. Bratescu, et al., J. Alloys and Compounds 562 (2013) 74

M.A. Bratescu, et al., J. Phys. Chem. C 117 (2013) 26804

**4:20pm PS+2D-WeA7 Generation and Stabilization Mechanisms of Free Radicals in Plasma Polymers**, S. Ershov, F. Khelifa, P. Dubois, Rony Snyders, University of Mons, Belgium

Cladded aluminum alloys are widely used in many applications being protected by a conversion coating based offering some self-healing properties nowadays based on the use of toxic chromate compounds. For both environmental and work safety reasons it is necessary to identify an alternative to this chromate-based conversion coating (CBC).

In this context, in the framework of a collaborative project, we are working on the replacement of the CBC by a multilayer combining, among others, plasma polymer films (PPF) and conventional polymers. The key features of this multilayer is grafting of a conventional polymer on the alloy surface by using the free radicals present in the as-deposited PPF as initiating sites for a radical-based polymerization reaction. It is therefore necessary to get a complete understanding on the generation and stabilization of the PPF radicals in order to control the grafting procedure.

The aim of this work is to contribute towards the understanding of the free radicals generation mechanism in the PPF and on their stabilization by comparing the plasma polymerization of different precursors namely isopropanol, benzene and cyclohexane. *In situ* FTIR spectroscopy and a combination of XPS and chemical derivatization measurements are used to quantitatively evaluate the plasma and thin films chemistry, respectively. Grafting experiments with 2-ethylhexyl acrylate (EHA) allows to cross-check the relevance of the XPS results.

Our results reveal that, for isopropanol PPF, the surface density of free radicals is about  $\sim 1.6 \cdot 10^{14} \text{ spin/cm}^2$  and depends strongly on the injected power in the plasma. On the other hand, a significant effect of the presence of resonant structure in the plasma polymer on the radical stability is highlighted.

**4:40pm PS+2D-WeA8 Simulation of Direct Current Microplasma Discharge in Carbon Dioxide at High and Intermediate Pressures**, N. Hasan, P.R. Fernandez, Bakhtier Farouk, Drexel University

Direct current (DC) micro-plasma discharges in intermediate to high pressure (10–200 kPa) carbon dioxide are investigated for potential applications in carbon dioxide decomposition and thin film deposition. Numerical simulations are performed using a hybrid CFD model. The model contains detailed reaction mechanisms for the gas-phase discharge and the surface reactions to predict the species densities in the discharge and the deposition characteristics and its growth rate. Sixteen species and a seventy-six step reaction mechanism are considered for the gas-phase carbon dioxide discharge. A simplified surface chemistry consisting eleven reaction steps are considered in the model. The simulations are carried out for a DC pin-to-plate electrode configuration with an inter-electrode gap of 500  $\mu\text{m}$ . An external circuit is also considered along with the discharge model and surface reactions. Basic plasma properties such as electron and species density, electric field, electron temperature and gas temperature are studied. Special attention is devoted to study the influence of operating pressure and discharge current on the plasma characteristics and the deposition characteristics and its rate. The  $\text{CO}_2^+$  and  $\text{O}^-$  concentrations are found to be the dominant ions in the plasma. The simulations indicated significant gas heating in the entire regime of operation. Ion Joule heating was found to be dominant in the sheath whereas Franck–Condon heating

and heavy particle reaction induced heating was dominant in the volume. The results presented here can be utilized for the development of computational models for plasma discharge in supercritical conditions which can be used to investigate processes such as carbon nanotube synthesis, biological reaction catalysis and carbon dioxide decomposition.

**5:00pm PS+2D-WeA9 The Impact of Ambient Gas Chemistry on Lipopolysaccharide Deactivation and Polymer Modification by Plasma-Generated Radicals at Atmospheric Pressure**, Elliot Bartis, A.J. Knoll, P. Luan, C. Hart, University of Maryland, College Park, D.B. Graves, University of California, Berkeley, I.V. Adamovich, W. Lempert, The Ohio State University, J. Seog, G.S. Oehrlein, University of Maryland, College Park

In this study, lipopolysaccharide (LPS) -coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. The goal of the present work is to understand the role of plasma-environment interactions in biodeactivation and surface modifications by regulating both the proximity of the plasma to the environment and the environmental gas chemistry. The APPJ is mounted inside a vacuum chamber that can be evacuated and refilled with any gas chemistry. By changing the APPJ geometry, the plasma plume can be either exposed or protected from the ambient. By adding small  $\text{N}_2/\text{O}_2$  admixtures to Ar, we find that the  $\text{O}_2$  admixture in the APPJ is a major determining factor for both deactivation and surface modification as measured by an enzyme-linked immunosorbent assay and x-ray photoelectron spectroscopy, respectively.  $\text{N}_2$  admixture without  $\text{O}_2$  causes minimal deactivation, while  $\text{N}_2/\text{O}_2$  admixtures deactivate more with increasing  $\text{O}_2$  content. For identical  $\text{O}_2$  feed gas flows, less deactivation occurs when  $\text{N}_2$  is also added, which demonstrates that nitrogen-based species quench reactive oxygen species (ROS) responsible for biodeactivation. After plasma treatments, a new chemical species was detected on LPS surfaces that was stoichiometrically verified as  $\text{NO}_3$ . To determine if this species forms due to nitrogen and oxygen found naturally in LPS, we treated model polymer films of polystyrene, polypropylene, and poly(methyl methacrylate), as these materials contain solely carbon or only carbon and oxygen. We find that the formation of  $\text{NO}_3$  is generic to all surfaces even with no  $\text{N}_2$  in the feed gas. Thus, the reactive interaction of oxygen-based species with ambient  $\text{N}_2$  takes place, indicating that plasma-environment interactions create this moiety and providing insight into the mechanisms by which the APPJ modifies surfaces. For polystyrene films, oxygen uptake is dramatic with O/C ratios as high as 0.47 at the near surface. The oxygen uptake results in a variety of moieties including C-O, O-C-O, C-O- $\text{NO}_2$ , O-C=O, and O-(C=O)-O. APPJ treatments are also compared with a corona discharge to examine the role of long lived species such as ozone and  $\text{NO}_x$ . Results from gas-phase characterization will also be discussed. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

**5:20pm PS+2D-WeA10 Modification of LDPE Induced by an Ar/ $\text{H}_2\text{O}$  Plasma: Comparison between a Post-Discharge Treatment and a DBD Treatment**, Stephanie Collette, Université Libre de Bruxelles, Belgium, V. Cristaudo, Université catholique de Louvain, Belgium, T.R. Dufour, Université Libre de Bruxelles, Belgium, P. VVILLE, Université de Mons, Belgium, A. Delcorte, Université catholique de Louvain, Belgium, F.A.B. Reniers, Université Libre de Bruxelles, Belgium

The study of the water reactivity in plasma was achieved by injecting water vapor in the post-discharge of an RF plasma torch and in a dielectric barrier discharge (DBD), both supplied in argon as carrier gas.

The RF plasma torch operates at atmospheric pressure. Optical emission spectroscopy (OES) and mass spectrometry evidenced the production and the consumption rates of Ar, O, OH,  $\text{O}_2^+$  and  $\text{N}_2$  species. These species could be quantified as a function of the water vapor flow rate, the treatment time and the gap (distance separating the post-discharge from a solid surface) to have a better understanding of the reactivity. Some chemical reactions occurring within the post-discharge could be evidenced and their importance was determined according to their kinetic constants. The reactivity of  $\text{H}_2\text{O}$  in the post-discharge was also carried out using an indirect method: the exposure of low density polyethylene (LDPE) samples to the plasma torch, in order to correlate the amount of oxygenated radicals resulting from water vapor dissociation reactions with the amount of oxygenated functions (C-O, C=O, COO) grafted on the surface. The modified LDPE surfaces were characterized by X-ray photoelectron spectroscopy (XPS), with a special emphasis on the deconvolution of the spectral envelope of the C1s peak. For longer treatment times, we showed that the decrease in the oxygen concentration observed by XPS could result from a competition between the LDPE surface etching and its functionalization. Besides, depth profiles achieved with XPS evidenced the diffusion of O in the subsurface, thus proving the efficiency of the plasma

treatment. Those results were correlated with WCA measurements indicating a decrease of the angle from 100° to 35° and with AFM showing an increase of the RMS roughness value from 30 nm to 90 nm. ToF-SIMS analyzes were also achieved on LDPE surfaces. To compare the impact of the plasma treatment to the influence of water contained in the atmosphere, D<sub>2</sub>O was injected in the plasma torch. The use of D<sub>2</sub>O permits to selectively probe the presence of fragments from the injected water grafted on the LDPE surface.

Those results were compared to those obtained with a second plasma source, namely a DBD operating at atmospheric pressure. In this case, LDPE samples were placed directly between the two dielectric barriers. Similar species as those described in the post-discharge have been evidenced by OES and MS with however slightly different reactive mechanisms, thus explaining why the treated LDPE surfaces present a different hydrophilic state.

This work was supported by PSI-IAP 7 (plasma surface interactions (Belgian Federal Government BELSPO agency)).

5:40pm **PS+2D-WeA11 Atmospheric Plasma Polymerization of Fluorinated Precursor : Comparison of Various Liquid Precursors and Plasma Types (AC and Pulsed DC)**, *J. Hubert, Nicolas Vandencastele*, Université Libre de Bruxelles, Belgium, *C. Poleunis*, Université catholique de Louvain, Belgium, *J. Mertens*, Université Libre de Bruxelles, Belgium, *A. Delcorte, P. Bertrand*, Université catholique de Louvain, Belgium, *F.A.B. Reniers*, Université Libre de Bruxelles, Belgium

The deposition of PTFE like films by argon atmospheric plasma using various precursors, liquid at room temperature, is presented. Those compounds are: Perfluorohexane (C<sub>6</sub>F<sub>14</sub>), a fully saturated monomer, perfluoro(2-methylpent-2-ene) (C<sub>6</sub>F<sub>12</sub>) containing one unsaturated bond and Perfluorotributylamine (C<sub>12</sub>F<sub>27</sub>N), containing a central nitrogen atom to which 3 fully saturated perfluorobutyl chains are attached. The influence of the monomer structure as well as the electrical parameter of the plasma (AC or pulsed DC) on the films chemistry and deposition rate is studied.

PTFE like films are of interest because of their low surface energy which gives them interesting properties such as easiness of cleaning etc.

The surface composition of the films is studied by X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface energy of the films is studied by Water Contact Angle (WCA). The films thickness is determined by profilometry, and the composition of the plasma phase is analyzed by atmospheric Mass Spectrometry (atm-MS) and Optical Emission Spectroscopy (OES).

#### Results

Very similar atomic composition and surface energies are obtained for the tested range of experimental parameters. Difference in composition, depending on the precursor used, can however be detected in the high resolution C1s peak (XPS). The signature of the precursor can also be detected in the atm-MS results of the plasma phase. OES measurements on the other hand do not allow to easily differentiate the various precursors. The main species detected other than Ar are F and CF<sub>2</sub>. The combination of the gas phase analysis and the films composition suggest a small fragmentation of the monomer in the plasma. Indeed as the initial structure of the precursor can still be detected in the deposited films we can conclude that the chemical structure of the polymerizing species must be close to the one of the initial molecule.

Differences in deposition speed depending on the precursor type and/or the plasma type (AC or DC) are evidenced by profilometry measurements. As expected the precursor containing the unsaturated bond has a higher deposition rate. Thicker films exhibit slightly higher contact angle values (~140°) than thinner ones (~130°). This cannot be attributed to the chemical composition of the films as they are very similar but can be explained by the increased roughness of the thicker samples.

The overall composition of the films can only be slightly modified by changing the precursor structure or the plasma parameters. The deposition speed is the main parameters linked to both the precursors structure and the plasma parameters.

6:00pm **PS+2D-WeA12 Surface Modification of Nafion Membranes Exposed to an atmospheric He-O<sub>2</sub> and He-H<sub>2</sub> Post-Discharge**, *Thierry Dufour, D. Merche, H. Julie, R.F. François*, Université Libre de Bruxelles, Belgium

Nafion is commonly used as a proton-conducting polymer membrane to separate the anode and cathode compartment of proton exchange membrane fuel cells (PEMFC) and water electrolyzers. The use of plasma based technology has contributed to lower catalyst loadings, thus decreasing the production costs. In this framework, our researches have been focused on a simple and robust technique to modify Nafion surface properties, using the post-discharge of an atmospheric RF plasma torch supplied in helium as carrier gas and H<sub>2</sub> or O<sub>2</sub> as reactive gas. The modifications achieved on

Nafion samples have been compared with those of common polymers such as polyethylene, PVF and PTFE. Contrarily to these polymers, the Nafion presents more complex etching mechanisms, that may be correlated with the complexity of its molecular formula: (i) its hydrophobic region is a continuous semi-crystalline region which is Teflon®-like, being made up of main chain TFE segments, while (ii) its hydrophilic region (sulfonate group) allows water and proton/ion transport but can also swell and change in size and/or shape with water uptake (eventually forming a continuous network). We have already demonstrated that the chemical nature of the fragment species (ejected from the Nafion film) depends on the exposure time because the fluorinated backbone is not etched as efficiently as the perfluorovinyl ether groups terminated with sulfonate groups.

The morphological and chemical structural changes of the Nafion films during exposure to the post-discharge have been characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as WCA (Water Contact Angle) measurements. Moreover, a characterization of the proton conductivity and of the methanol permeability will also be introduced.

*This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency.*

# Thursday Morning, November 13, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+AS+HI+NS+SS-ThM

### Nanostructures including 2D Heterostructures, Patterning of 2D Materials

Moderator: Kirill Bolotin, Vanderbilt University

#### 8:00am 2D+AS+HI+NS+SS-ThM1 **Stitching and Stacking for Atomically Thin Circuitry**, Jiwoong Park, Cornell University **INVITED**

The development of large scale growth methods based on chemical vapor deposition (CVD) has enabled production of single-atom-thick films with diverse electrical properties, including graphene (conductor), h-BN (insulator), and MoS<sub>2</sub> (semiconductor). Precise vertical stacking and lateral stitching of these 2D materials will provide rational means for building ultrathin heterostructures with complex functionality. However, large scale production and control of these structures requires new characterization and fabrication approaches. In this talk, I will first discuss the structure and physical properties unique to CVD graphene in single and bilayers. Using the atomic-resolution imaging as well as a dark-field transmission electron microscopy (TEM) technique, our group investigated the structure of grain boundaries in CVD graphene and its impact on the mechanical, electrical, and chemical properties. This allowed us to produce CVD graphene with optimized electrical properties. We also reported a new patterned regrowth method to fabricate 2D lateral heterojunctions entirely made of graphene and h-BN, which enables the development of atomically thin integrated circuitry. If time allows, I will also discuss our recent results on the large scale growth of high quality single layer MoS<sub>2</sub> as well as graphene film with a uniform lattice orientation. Our characterization and growth approach would ultimately allow the fabrication of electrically isolated active and passive elements embedded in continuous, one-atom-thick sheets, which could be manipulated and stacked to form complex devices at the ultimate thickness limit.

#### 8:40am 2D+AS+HI+NS+SS-ThM3 **Vertical and Lateral Heterostructures of Carbon Nanomembranes (CNMs) and Graphene**, Andreas Winter, University of Bielefeld, Germany, M. Woszczyzna, R. Stosch, T. Weimann, F. Ahrelrs, Physikalisches Bundesanstalt, Germany, A. Turchanin, University of Bielefeld, Germany

Heterostructures of graphene with other 2D materials are of great interest for nanoscience and nanotechnology. However, their fabrication is still not a trivial task. Here we present the engineering and characterization of (i) vertical and (ii) lateral heterostructures of molecular thin (~1 nm) dielectric carbon nanomembranes (CNMs) made of aromatic molecules [1] and single-layer (SLG) graphene sheets. (i) The vertical CNM/SLG heterostructures with terminal amino-groups (NH<sub>2</sub>-) are assembled via the mechanical transfer onto oxidized silicon wafers. We show by complementary spectroscopy and microscopy techniques as well as by electric transport measurements that functional amino groups are brought into close vicinity of the SLG sheets and that electric transport of the SLG is not impaired by this assembly, leading to the non-destructive chemical functionalization of graphene [2]. (ii) *The lateral heterostructures* are engineered using electron-irradiation-induced crosslinking of SLG sheets with CNMs. We demonstrate reliable production of well-defined laterally patterned CNM-SLG heterostructures of various sized and architectures on solid substrates and as free-standing sheets, and characterize their properties by Raman spectroscopy and helium ion microscopy.

[1] A. Turchanin and A. Götzhäuser, Carbon nanomembranes from self-assembled monolayers: Functional surfaces without bulk. *Prog. Surf. Sci.* 87, 108-162 (2012)

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#### 9:00am 2D+AS+HI+NS+SS-ThM4 **Gate Tunable Carbon Nanotube - Single Layer MoS<sub>2</sub> p-n Heterojunctions**, Deep Jariwala\*, V.K. Sangwan, C.-C. Wu, P.L. Prabhumirashi, M.L. Geier, T.J. Marks, L.J. Lauhon, M.C. Hersam, Northwestern University

The isolation of graphene and the subsequent reports on its electronic properties have spurred tremendous interest in a variety of two dimensional (2D) materials for electronic device applications. Layered semiconducting transition metal dichalcogenides (TMDCs) of Mo and W have emerged as

promising alternatives to graphene for optoelectronic applications due to their finite band gap in the visible portion of the electromagnetic spectrum.<sup>1</sup> The atomically thin structure of these 2D materials coupled with van der Waals bonding between adjacent layers allows their stacking into atomically sharp heterostructures with defect-free interfaces, in contrast to epitaxially grown III-V semiconductor heterostructures where the material choices are constrained by lattice matching. Additionally, the few atom thickness of the individual layers enables doping modulation of the overlying layers in a heterostructure using a global back gate. While a large number of heterostructure devices employing graphene have been reported, it's gapless band structure prevents the formation of a large potential barrier for charge separation and current rectification. Consequently, a p-n heterojunction diode derived from ultrathin materials is notably absent and significantly constrains the fabrication of complex electronic and optoelectronic circuits. Here we demonstrate a gate-tunable p-n heterojunction diode using semiconducting single-walled carbon nanotubes (s-SWCNTs) and single-layer molybdenum disulfide (SL-MoS<sub>2</sub>) as atomically thin p-type and n-type semiconductors, respectively. The vertical stacking of these two direct band gap semiconductors forms a heterojunction with electrical characteristics that can be tuned with an applied gate bias over a wide range of charge transport behavior, ranging from insulating to rectifying with forward-to-reverse bias current ratios exceeding 10<sup>4</sup>. In addition, the gate-dependent characteristics of this diode exhibit a unique 'anti-ambipolar' behavior with two off-states at either extremes of the gate voltage range and a maximum on-state current between them. This heterojunction diode also responds to optical irradiation with photoresponse time < 15 μs.<sup>2</sup> We anticipate that the novel properties and characteristics of this p-n heterojunction can be widely generalized to other atomically thin materials systems.

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2. Jariwala, D. et al. Gate-Tunable Carbon Nanotube-MoS<sub>2</sub> Heterojunction p-n Diode. *Proc. Natl. Acad. Sci. U.S.A.* 2013, 110, 18076-18080.

#### 9:20am 2D+AS+HI+NS+SS-ThM5 **Graphene Transfer onto sub 1nm Al<sub>2</sub>O<sub>3</sub>/TiOPc/Graphene Gate Stacks**, Iljo Kwak, J.H. Park, University of California at San Diego, H.C.P. Movva, University of Texas at Austin, E.K. Kinder, H.L. Lu, University of Notre Dame, A.C. Kummel, University of California at San Diego

A novel transfer method with chemically controlled interfacial adhesion is reported for the fabrication of novel logic devices. This method allows direct transfer onto gate stacks and eliminates the possibility of Au electrodes deposition could shorting the thin oxide prior to transfer. The top graphene layer was grown on a Cu layer on a SiO<sub>2</sub>/Si substrate by CVD. Au electrodes were deposited on top of the graphene by e-beam evaporation. To transfer the graphene layer, PIB (Polyisobutylene) were drop cast on top of graphene prior to bonding of the Au/graphene/Cu to a PDMS (Polydimethylsiloxane) film. The PIB serves to moderate the adhesion between the PDMS (Polydimethylsiloxane) and the Au electrodes. The PDMS provides mechanical support. Afterwards, the PDMS/PIB/Au/graphene/Cu/SiO<sub>2</sub>/Si stack was immersed in ammonium persulfate solution to dissolve the Cu, releasing the top graphene stack. The bottom gate stack was HOPG (highly ordered pyrolytic graphite) with a sub-nano Al<sub>2</sub>O<sub>3</sub> film on a monolayer TiOPc (titanyl phthalocynine) film. The monolayer TiOPc was deposited via MBE at 100C and annealed to 250C to insure a monolayer film. The TiOPc acts as a nucleation layer for the oxide ALD. The Al<sub>2</sub>O<sub>3</sub> layer was deposited by ALD using TMA (Trimethylaluminum) and H<sub>2</sub>O at 100 C. The PDMS/PIB/Au/Graphene stack was placed on the gate stack, and PDMS was removed. Using hexane solution, the rePIB layer was dissolved, leaving clean graphene surface. To measure the oxide characteristics, an AFM was converted into a capacitance meter. This measurement allows non-destructive probing of Au/graphene/Al<sub>2</sub>O<sub>3</sub>/TiOPc/graphene structure while conventional probe station could damage the oxide or electrodes.

#### 9:40am 2D+AS+HI+NS+SS-ThM6 **Effect of Monolayer Substrates on the Electronic Structure of Single-Layer MoS<sub>2</sub>**, Alfredo Ramirez-Torres, D.T. Le, T.S. Rahman, University of Central Florida

We have performed first-principles calculations based on density functional theory (DFT) utilizing the optB88-vdW functional to study structural and electronic properties of a single layer of MoS<sub>2</sub> deposited on single-layer substrates of hexagonal boron nitride (BN), graphene and silicene. All have a honeycomb structure; hence the formation of heterostructures is expected. Since the lattice mismatch between MoS<sub>2</sub> and these substrates is large, we

\* NSTD Student Award Finalist

have considered different periodicities among layers to reduce as far as possible the incommensurability between lattices. Our results show that BN barely affects the electronic structure of isolate single-layer MoS<sub>2</sub>; the DFT gap remains proximately unchanged. Graphene and silicene severely modify the electronic structure introducing additional states within the optical gap. Adsorption on graphene produces that the system turns like a zero band gap semiconductor bringing the conduction bands of MoS<sub>2</sub> down to the Fermi level of graphene. Adsorption on silicene shifts both valence and conduction bands of MoS<sub>2</sub>, towards the Fermi level of silicene, in addition to inducing a gap of about 50 meV in the silicene itself.

This work was partially supported by CONACYT (México) Postdoctoral Fellowship Program (number 204065) and DOE grant DE-FG02-07ER46354

11:00am **2D+AS+HI+NS+SS-ThM10 Ballistic Transport in Epitaxial Graphene Nanoribbons**, *Walt de Heer*, Georgia Institute of Technology  
**INVITED**

Graphene nanoribbons are essential components in future graphene nanoelectronics. However, in typical nanoribbons produced from lithographically patterned exfoliated graphene, the charge carriers travel only about 10 nanometers between scattering events, resulting in minimum sheet resistances of about 1 kW. In contrast 40 nm wide graphene nanoribbons that are epitaxially grown on silicon carbide are single channel room temperature ballistic conductors on greater than 10  $\mu\text{m}$  length scale, similarly to metallic carbon nanotubes. This is equivalent to sheet resistances below 1W surpassing theoretical predictions for perfect graphene by at least an order of magnitude. In neutral graphene ribbons, we show that transport is dominated by two modes. One is ballistic and temperature independent; the other is thermally activated. Transport is protected from back-scattering, possibly reflecting ground state properties of neutral graphene. At room temperature the resistance of both modes abruptly increases nonlinearly with increasing length, one at a length of 16  $\mu\text{m}$  and the other at 160 nm. Besides their importance for fundamental science, since epitaxial graphene nanoribbons are readily produced by the thousands, their room temperature ballistic transport properties can be used in advanced nanoelectronics as well.

11:40am **2D+AS+HI+NS+SS-ThM12 Solution-Synthesized Graphene Nanoribbons**, *Alexander Siniitskii*, University of Nebraska - Lincoln

In this talk I will discuss a recently developed bottom-up approach for gram quantities of narrow graphene nanoribbons that are less than 2 nm wide and have atomically precise armchair edges. These graphene nanoribbons have been characterized by a number of microscopic (STM, AFM, SEM, TEM) and spectroscopic (XPS, UPS/IPES, UV-vis-NIR, IR and Raman spectroscopy) techniques. The properties of graphene nanoribbons could be tuned by incorporation of nitrogen atoms in their edges. Narrow graphene nanoribbons have a large electronic bandgap, which makes them promising for applications in field-effect transistors with high on-off ratios, as well as bulk applications, including coatings, composites and photovoltaic devices.

12:00pm **2D+AS+HI+NS+SS-ThM13 Graphene Silicon Interfaces at the Two-Dimensional Limit**, *Brian Kiraly, A.J. Mannix, M.C. Hersam*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

Artificial van der Waals heterostructures have demonstrated both significant improvements of graphene's intrinsic properties and entirely new properties of their own. Early interest in these structures was based on nearly ideal carrier mobility in graphene on two-dimensional (2D) hexagonal boron nitride. Although exfoliation and reassembly of bulk vdW solids has yielded impressive initial results, this method inherently limits the geometry and constituent materials of these structures. Growth of 2D heterostructures has been demonstrated, but mainly limited to the prototypical graphene/hBN system. Adding new constituent materials, particularly those with electronic heterogeneity, to these 2D heterostructures allows them to be engineered with a variety of new properties.

We present the growth and characterization of interfaces between an atomically thin silicon layer and graphene. First, graphene is grown on Ag(111) via atomic carbon deposition at temperatures from 600°C -700°C. Following the growth of graphene, atomic silicon is evaporated on the graphene-covered Ag(111) substrate at 320°C-360°C. The resulting silicon growth results in faceted domains capped with a honeycomb lattice with periodicity 6.4 Å; Raman spectroscopy reveals peaks at 520  $\text{cm}^{-1}$  and 900-1000  $\text{cm}^{-1}$  that coincide precisely with bulk diamond cubic silicon, indicating these domains are comprised of  $sp^3$  bonded crystalline Si. These 2D sheets of silicon demonstrate both semiconducting character and a honeycomb lattice is attributed to a silver-based reconstruction of the Si(111) surface. The resulting silicon domains grow in two different configurations with respect to the dendritic graphene: (1) silicon domains appear to grow directly on the Ag(111) surface and terminate at the graphene boundaries.

These in-plane interfaces are atomically-precise and clearly resolved via scanning tunneling microscopy. Electronically, the density of states of both isolated constituent materials persist to these interfaces within the resolution of the measurement, indicating little interaction at the border. (2) The silicon growth is observed *underneath* the existing graphene flakes. The vertically stacked silicon graphene domains are identified via atomically resolved imaging *through* the graphene domains at larger biases where graphene is transparent under STM. Furthermore, the vertical materials interfaces demonstrate distinct electronic signatures from either constituent material. The resulting interfaces represent atomically pristine interfaces between graphene and a  $sp^3$  bonded semiconducting Si film, demonstrating a significant step forward in the diversification of van der Waals heterostructures.

## Helium Ion Microscopy Focus Topic

Room: 316 - Session HI+2D+AS+BI+MC-ThM

### Fundamental Aspects and Imaging with the Ion Microscope

Moderator: Gregor Hlawacek, Helmholtz-Zentrum Dresden - Rossendorf, Stuart Boden, University of Southampton

8:00am **HI+2D+AS+BI+MC-ThM1 He+ and Ne+ Ion Beam Microscopy and Microanalysis**, *David C. Joy*, University of Tennessee, Oak Ridge National Laboratory  
**INVITED**

After one hundred years of use the electron microscope is now being overtaken by ion beam systems because of their many advantages. A wide variety of different ions are available, each of which has its own particular strengths, but the two most commonly used at present are Helium (He<sup>+</sup>) and Neon (Ne<sup>+</sup>). Changing from one to the other takes only a couple of minutes to complete. For operation at beam energies between 20 and 50kV both He<sup>+</sup> and Ne<sup>+</sup> generate 'ion induced secondary electrons' (iSE) which yield images which are comparable with those from a conventional SEM but offer image resolutions of 0.4nm or less even on bulk samples, a much greater depth of field, and an enhanced signal to noise ratio. At typical imaging currents between 10-12 to 10-14Amps damage to most samples is very limited for He<sup>+</sup> although more severe for Ne<sup>+</sup> but at higher beam currents both He<sup>+</sup> and Ne<sup>+</sup> can pattern, deposit, or remove, a wide range of materials. In such applications He<sup>+</sup> provides the best resolution, but Ne<sup>+</sup> is much faster.

The production of X-rays depends on the speed of the incident particle, not on its energy. At typical operating energies the He<sup>+</sup> or Ne<sup>+</sup> ions are traveling too slowly to generate X-rays so another approach is required for chemical microanalysis. The most promising option is "Time of Flight-Secondary Ion Mass Spectrometry" (TOF-SIMS). Here the incoming ion "splashes" material from the top few layers of the specimen surface. These fragments are then characterized by determining their mass to charge ratios. The chemical data this generates is much more detailed than the bare list of elements that is produced by X-ray microanalysis.

8:40am **HI+2D+AS+BI+MC-ThM3 Gas Field Ion Sources**, *Jason Pitters, R. Urban*, National Institute for Nanotechnology, Canada, *R. Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada  
**INVITED**

Single atom tips (SATs) prepared by the spatially controlled field assisted etching method are proving to have utility as ion sources, electron sources and in scan probe applications.

As Gas Field Ion Sources (GFISs), there is potential for operation in scanning ion microscopes (SIMs) and our efforts to prepare and characterize SAT ion emission will be discussed. It will be shown that etching to a single atom tip occurs through a symmetric structure and leads to a predictable last atom. SATs can be prepared reproducibly with emission along a fixed direction for all tip rebuilds. It will also be shown that the emission properties of the SAT can be altered by shaping of the tip shank during the etching procedure. In this manner, the operating voltage can be controlled and a lensing effect of the tip base is demonstrated. During formation, the tip shape can be evaluated by using both helium and neon imaging gases. The stability of helium and neon ion beams generated by SATs will also be demonstrated and compared to other tip orientations. The remarkable robustness of these tips to atmosphere exposure will also be shown and the ability to prepare SATs from material other than tungsten will be demonstrated.

SATs also have utility in electron emission. By shaping the tip appropriately, electron emission characteristics can also be tailored and the coherence properties of an SAT will be presented as deduced from holographic measurements in a low-energy electron point source

microscope. Initial utility in scan probe experiments including atomic force microscopy and scanning tunneling microscopy will also be discussed.

9:20am **HI+2D+AS+BI+MC-ThM5 Ion Beam Profiles Generated by W(111) Single Atom Tips**, *Radovan Urban, R. Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada, *J.L. Pitters*, National Institute for Nanotechnology, Canada

Single atom tips (SATs) gained significant attention over the past decade because they serve as high brightness, field emission electron sources and gas field ion sources (GFISs). Small virtual source size makes these attractive candidates for advanced scanning imaging applications such as SEM, TEM, and scanning ion microscopy (SIM) as well as for non-staining ion beam writing applications.

The ion beam diameter  $\sigma$ , together with total ion current  $I$  generated by a single surface atom of W(111) nanotip, are crucial parameters which determine angular current density and brightness of gas field ion sources. It is, therefore, essential to understand underlying mechanisms that govern beam width. Furthermore, mapping both  $\sigma$  and  $I$  to a large parameter space of tip temperature, imaging gas pressure, and extraction voltage is necessary to optimize gas field ion source operation. In this contribution we will explore both  $\sigma$  and  $I$  as a function of temperature and extraction voltage at different imaging gas pressures using a field ion microscope (FIM) to monitor beam shape and total current. The qualitative model of our results will be also discussed. Finding “the best imaging voltage” for a SAT will be briefly discussed.

9:40am **HI+2D+AS+BI+MC-ThM6 Defect Observation by using Scanning Helium Ion Microscopy**, *Hongxuan Guo, L. Zhang, D. Fujita*, National Institute for Materials Science (NIMS), Japan

Scanning helium ion microscopy (HIM) is an innovative method to characterize surface of various materials. With a secondary electron detector (SED) and a micro plate detector (CPD), Orion Plus system can obtain surface information including morphology, composition, and crystal orientation. [1, 2] Improve the abilities of characterization of materials with HIM will benefit the develop of new materials, such as structure materials including metals, ceramics and others.

In this presentation, we will show the investigation of the crystal structure of metal with HIM. We prepared a sample stage with a reflector that can be used to obtain the transmission helium ions intensities in the samples. With this sample stage, we observed the Ni-Co base super alloy and aerogel composed with hollow nanosphere. The Rutherford backscattered image (RBI) of metal surface show different orientation of poly crystal. The nano-twins and other defects in Ni-Co base superalloy were investigated by HIM in scanning and transmission mode. The nano-twins also be observed by other techniques, such as transmission electron microscopy and electron backscatter diffraction. The scattering of helium ions with different energy was analyzed. This work provide some new methods to improve the research on defects and structure of crystal.

[1]. H. X. Guo, D. Fujita, Scanning helium ion microscopy, Characterization of Materials, 2nd Edition(Wiley, New York, 2012)

[2]. H. X. Guo, J. H. Gao, M. S. Xu, D. Fujita, Applied Physics Letters, 104, 031607, 2014

11:00am **HI+2D+AS+BI+MC-ThM10 Helium Ion Microscopy (HIM) for the Imaging of Biological Samples at Sub-nanometer Resolution**, *James Fitzpatrick*, Salk Institute for Biological Studies **INVITED**

Scanning Electron Microscopy (SEM) has long been the standard in imaging the sub-micrometer surface ultrastructure of both hard and soft materials. In the case of biological samples, it has provided great insights into their physical architecture. However, three of the fundamental challenges in the SEM imaging of soft materials are that of limited imaging resolution at high magnification, charging caused by the insulating properties of most biological samples and the loss of subtle surface features by heavy metal coating. These challenges have recently been overcome with the development of the Helium Ion Microscope (HIM), which boasts advances in charge reduction, minimized sample damage, high surface contrast without the need for metal coating, increased depth of field, and 5 angstrom imaging resolution. We demonstrate the advantages of HIM for imaging biological surfaces as well as compare and contrast the effects of sample preparation techniques and their consequences on sub-nanometer ultrastructure.

11:40am **HI+2D+AS+BI+MC-ThM12 Helium Ion Microscopy of Biological Cells**, *Natalie Frese, A. Beyer, M. Schürmann, B. Kaltschmidt, C. Kaltschmidt, A. Götzhäuser*, University of Bielefeld, Germany

In this presentation HIM images of biological cells are presented. The presented study focuses on neuronal differentiated human inferior turbinate stem cells, mouse neurons and mouse fibroblasts. The cells were prepared

by critical point drying or freeze drying and a flood gun was used to compensate charging, so no conductive coating was necessary.

Therewith, extremely small features at native cell surfaces were imaged with an estimated edge resolution of 1.5 nm. Due to the size of the structures and the preparation methods of the cells the observed features could be an indicator for lipid rafts. This hypothesis will be discussed.

12:00pm **HI+2D+AS+BI+MC-ThM13 Helium Ion Microscopy Analysis of Ag Nanoparticle Implanted Biological Samples for MILDI-MS (Matrix Implanted Laser Desorption/Ionization) Imaging**, *S. Shubeita*, Rutgers University, *L. Muller*, NIDA-IRP, *H.D. Lee, C. Xu*, Rutgers University, *D. Barbacci*, Ionwerks Inc., *K. Baldwin*, NIDA-IRP, *J.A. Schultz*, Ionwerks Inc., *L. Wielunski, Torgny Gustafsson, L.C. Feldman*, Rutgers University, *A.S. Woods*, NIDA-IRP

MILDI mass spectrometry is an emerging tool for detecting changes in brain tissue. An ~20 nm thick region of rat brain tissue implanted with  $10^{13}/\text{cm}^2$   $\text{Au}_{(400)}^{4+}$  nanoparticle (NP) ions at 40 keV, produces analytically useful signals of lipids, peptides and proteins using a pulsed nitrogen laser [1]. When a dose of  $10^{12}/\text{cm}^2$  500 eV AgNP (approximately 6 nm diameter) is implanted as a matrix, only lipids are detected [2]. To understand this it is essential to measure the spatial distribution of the nanoparticles. We have used Rutherford Backscattering and Helium Ion Microscopy imaging to determine the Ag NP distributions and areal densities in an implanted coronal rat brain section. We then correlate the ion beam analysis and imaging with individual lipid intensities from several hundred MILDI mass distributions. The results show a high degree of uniformity of the Ag atomic and particulate distribution on a sub-micron scale among different regions of the tissue. Helium Ion Microscopy provides verification of NP matrix uniformity, validating the use of MILDI for quantitative mass analysis.

This work is partially supported by NSF (DMR 1126468), NIH (R44DA030853-03) and IAMDN.

[1] A. Novikov et al, *Analytical Chemistry* 76 (2004) 7288. [2] S. N. Jackson et al, *Analyt. and Bioanal. Chem.* (e-pubed Dec 2013).

## Scanning Probe Microscopy Focus Topic

**Room: 312 - Session SP+2D+AS+EM+MC+NS+SS-ThM**

## Probing Electronic and Transport Properties

**Moderator: An-Ping Li, ORNL, Corentin Durand, ORNL**

8:00am **SP+2D+AS+EM+MC+NS+SS-ThM1 Investigation of the Electronic and Structural Properties of Metal Free Naphthalocyanine Vapor Deposited on Au(111)**, *Bryan Wiggins*, University of Chicago, *K.W. Hippias*, Washington State University

Naphthalocyanines (Ncs) are promising candidates for future components in electronic devices and applications. To maximize the efficiency of Nc devices, it is critical to understand their structural and electronic properties and how these are impacted by deposition methods. The formation of a metal free naphthalocyanine ( $\text{H}_2\text{Nc}$ ) self-assembled monolayer on a Au(111) crystal was investigated by scanning tunneling microscopy under ultra-high-vacuum conditions at room temperature. A rigorous purification and processing procedure was developed to produce high purity, low defect, and well-ordered monolayers. High-resolution STM images reveal epitaxial growth of  $\text{H}_2\text{Nc}$  on Au(111) with the observed structure having a molecular spacing of  $1.6 \pm 0.05$  nm, with molecules orientated slightly off (roughly  $2.5^\circ$ ) the low density packing direction of Au(111). A commensurate structure having 4 molecules per unit cell and unit cell parameters of  $A = 3.25 \pm 0.05$  nm,  $B = 3.17 \pm 0.05$  nm, and  $\alpha = 87.5 \pm 2^\circ$  is proposed. Orbital-mediated tunneling spectroscopy was used to examine the electronic properties of individual molecules within the thin film. The first ionization potential and electron affinity of  $\text{H}_2\text{Nc}$  adsorbed on Au(111) were measured to be  $-0.68 \pm 0.03$  and  $1.12 \pm 0.02$  eV, relative to the Fermi energy.

8:20am **SP+2D+AS+EM+MC+NS+SS-ThM2 The Fundamentals of Charge Transport at Oxide and Ferroelectric Interfaces**, *Ramsey Kraya, L.Y. Kraya*, University of Pennsylvania

Here we investigate how charge transport properties at metal-semiconductor interfaces scale down to the nanoscale regime, comparing the properties to macroscopic interfaces and providing a perspective on what it means to device manufacturing. Strontium titanate - the prototypical oxide material - has been widely studied for applications in thermoelectrics, nanoelectronics, catalysis, and other uses, and behaves as an n-type semiconductor when doped. We investigated how charge transport is effected at interfaces to strontium titanate under a wide range of conditions - by varying contact size, interface shape, dopant concentration, and surface structure and in various combinations. The results of the analysis have wide ranging

implications, especially for ferroelectric oxide materials and serves as the basis for understanding and controlling switching effects - both polarization and oxygen migration based switching.

8:40am **SP+2D+AS+EM+MC+NS+SS-ThM3 Epitaxial Graphene on Nanostructured Silicon Carbide, Phillip First**, Georgia Institute of Technology **INVITED**

Graphene grown epitaxially on silicon carbide conforms to nanofaceted step edges, even for step heights of many nanometers. The "sidewall" nanoribbons that result show astounding transport characteristics (~15 nm ballistic length at room temperature), as demonstrated by others,<sup>1</sup> but the physical basis for these results is still not certain. In our STM measurements of sidewall nanoribbons, we find an extended 1D region with electronic structure much different than 2D graphene. Spectroscopic results on graphene near nanofacet corners indicate a strain gradient and a rapid change in the doping. Such strong gradients may be key to understanding the ballistic transport in this system. P

<sup>1</sup>J. Baringhaus, M. Ruan, F. Edler, A. Tejeda, M. Sicot, Amina Taleb-Ibrahimi, A.-P. Li, Z. Jiang, E. H. Conrad, C. Berger, C. Teegenkamp and W. A. de Heer, "Exceptional ballistic transport in epitaxial graphene nanoribbons," *Nature*, **506**, 349 (2014).

9:20am **SP+2D+AS+EM+MC+NS+SS-ThM5 Conductivity of Si(111) - 7 × 7: The Role of a Single Atomic Step, B. Martins**, University of Alberta and The National Institute for Nanotechnology, Canada, *M. Smeu, H. Guo*, McGill University, Canada, *Robert Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada

The Si(111) - 7 × 7 surface is one of the most interesting semiconductor surfaces because of its

complex reconstruction and fascinating electronic properties. While it is known that the Si - 7 × 7 is

a conducting surface, the exact surface conductivity has eluded consensus for decades as measured

values differ by 7 orders of magnitude. Here we report a combined STM and transport measurement

with ultra-high spatial resolution and minimal interaction with the sample, and quantitatively determine the intrinsic conductivity of the Si - 7 × 7 surface. This is made possible by the capability of

measuring transport properties with or without a single atomic step between the measuring probes:

we found that even a single step can reduce the surface conductivity by two orders of magnitude.

Our first principles quantum transport calculations confirm and lend insight to the experimental

observation.

9:40am **SP+2D+AS+EM+MC+NS+SS-ThM6 Asymmetric Electron Transport Revealed at Monolayer-Bilayer Graphene Junctions by Atomic-Scale Scanning Tunneling Potentiometry, K. Clark, X. Zhang, J. Park**, Oak Ridge National Laboratory, *G. Gu*, University of Tennessee, *G. He, R.M. Feenstra*, Carnegie Mellon University, *An-Ping Li*, Oak Ridge National Laboratory

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films [1]. These heterojunctions provide us fascinating playground for exploring electronic and transport properties in 2D materials. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries, changes in layer thickness, and substrate steps, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we present our recent study on an asymmetric electron transport upon bias polarity reversal at individual monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC (0001), revealed by multi-probe scanning tunneling potentiometry [2,3]. A greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, and the difference remains nearly unchanged when bias exceeds a threshold. A thermovoltage is measured across the boundary due to the thermopower difference between the two sides, which however is too small to account for the observed asymmetry. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Our theoretical analysis finds that Friedel charge oscillation opens a gap for electrons with wave vectors perpendicular to the boundary. The Friedel gaps are different on the monolayer and bilayer sides, which can shift under bias and lead to asymmetric transport upon

reversing the bias polarity. A quantitative agreement is seen between experiment and theory on both the sign and the magnitude of the asymmetry.

1 "Heteroepitaxial Growth of Two-Dimensional Hexagonal Boron Nitride Templated by Graphene Edges", L. Liu, J. Park, D. A. Siegel, K. F. McCarty, K. W. Clark, W. Deng, L. Basile, J.-C. Idrobo, A.-P. Li, G. Gu, *Science***343**, 163-167 (2014).

2 "Spatially Resolved Mapping of Electrical Conductance around Individual Domain (Grain) Boundaries in Graphene", K. W. Clark, X.-G. Zhang, I. V. Vlassioug, G. He, R. M. Feenstra, and A.-P. Li, *ACS Nano*. **7** (9), 7956-7966 (2013).

3 "Friedel Oscillation-Induced Energy Gap Manifested as Transport Asymmetric at Monolayer-Bilayer Graphene Boundaries", K. W. Clark, X.-G. Zhang, G. Gu, G. He, R. M. Feenstra, and A.-P. Li, *arXiv*: 1401.1796, *Physical Review X***4** (1), 011021 (2014).

11:00am **SP+2D+AS+EM+MC+NS+SS-ThM10 Defect-mediated Transport in CVD-grown Monolayer MoS<sub>2</sub>, Corentin Durand, J. Fowlkes**, Oak Ridge National Laboratory, *S. Najmaei, J. Lou*, Rice University, *A.P. Li*, Oak Ridge National Laboratory

Transition metal dichalcogenides like molybdenum disulfide (MoS<sub>2</sub>) have attracted great interest as candidate to fill the need of 2 dimensional semiconductor materials. By controlling the thickness, the bandgap of MoS<sub>2</sub> thin films can be tuned from 1.2 eV (bulk material, indirect bandgap) to 1.8 eV (monolayer film, direct bandgap). Recently, researchers succeeded in growing monolayered MoS<sub>2</sub> by chemical vapor deposition (CVD) on silicon dioxide (SiO<sub>2</sub>) substrate, showing the possibility of low cost scalable device fabrication. However, the mobility reported on exfoliated MoS<sub>2</sub> monolayers exceeds 200 cm<sup>2</sup>.V<sup>-1</sup>.s<sup>-1</sup>, whereas the measurements realized on CVD growth MoS<sub>2</sub> monolayers reveal a mobility value that is usually 1-2 orders of magnitude lower. Here, we study the transport properties of CVD-grown monolayer on SiO<sub>2</sub>/Si substrate. We directly measure the resistivity and the mobility of the material with a field-effect transistor architecture by using a cryogenic four-probe scanning tunneling microscope (STM), the Si substrate being used as back-gate. In order to ensure reliable electrical contacts, we fabricate platinum pads (4x4 μm<sup>2</sup>) on individual MoS<sub>2</sub> crystal domains by using an electron-beam induced deposition technique. The combination of the STM scanners and a scanning electron microscope (SEM) enables us to connect the STM tips on those pads and thereby establish the contacts on this material without any subsequent lithography process, avoiding contaminations introduced by other technological steps. An electron hopping process in localized charge trapping states appears to dominate the transport behavior. We performed temperature-dependent measurements in the range of 82 K to 315 K which demonstrate a variable range hopping (VRH) transport with a very low mobility. Furthermore, the effects of electronic irradiation are examined by exposing the film to electron beam in the SEM in an ultra-high vacuum environment. We found that the irradiation process affect the mobility and also the carrier concentration of the material, with conductance showing a peculiar time-dependent relaxation behavior. It is suggested that the presence of defects such as vacancies and antisites create charge trapping states, leading to the low mobility. This is consistent with recent density functional theory calculations where these defects are shown to create localized gap states that can act as scattering centers and thereby reduce the mobility.

11:20am **SP+2D+AS+EM+MC+NS+SS-ThM11 Coherent One Dimensional Boundaries in Graphene and Hexagonal Boron Nitride Heterostructures, Jewook Park**, Oak Ridge National Laboratory, *L. Liu*, The University of Tennessee Knoxville, *D.A. Siegel, K.F. McCarty*, Sandia National Laboratories, *L. Basile, J.-C. Idrobo, K. Clark*, ORNL, *W. Deng*, The Univ. of Tennessee Knoxville, *C.P. Durand*, ORNL, *G. Gu*, The Univ. of Tennessee Knoxville, *A.P. Li*, ORNL

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures where graphene and other atomic layer films such as monolayer hexagonal boron nitride (hBN) form phase-separated domains or both materials grow epitaxially onto a common crystalline substrate. By implementing the concept of epitaxy to 2D space, we developed and applied a new growth technique to hybrid isostructural but electrically dissimilar materials, such as the 2D epitaxial growth of hBN templated by graphene edge [1]. Scanning tunneling microscopy and spectroscopy measurements revealed a single-atomic-layer, in-plane heterostructure between graphene and hBN, as well as an abrupt 1D zigzag oriented boundary. In addition, the dI/dV conductance map unveiled the 1D interfacial states that are extended along, but localized at the boundary. We investigated spatial and energetic distributions of 1D boundary states. Also, low-energy electron microscopy and micro low-energy electron diffraction confirmed the heterostructure at mesoscopic scale and established that the graphene edge solely determines the crystallography of the hBN regardless of underlying the Cu(100) lattice. The Z-contrast scanning transmission electron microscopy further indicates

an atomically sharp interface with a transition width of  $\sim 0.5$  nm. We suggest that the graphene-hBN epitaxial heterostructure provides an excellent platform to explore heteroepitaxy in 2D space, and the unique functionalities at the 1D interface. [1] Lei Liu *et al. Science* **343** 163 (2014)

11:40am **SP+2D+AS+EM+MC+NS+SS-ThM12 Charge and Spin Density Waves in Quasi One-Dimensional Atomic Wires, Herbert Pfnür, Leibniz Universität, Germany INVITED**

Although free one-dimensional (1D) objects should exist only at  $T=0$ , atomic single wires or arrays embedded into a two- or three-dimensional environment exist even at room temperature and above, since they are stabilized by lateral interactions. These interactions not only stabilize, but also strongly modify the properties of the wires. Their 2D or 3D coupling, however, does not generally prevent observation of 1D properties with their complex variety of instabilities. Furthermore, these coupling can result in special 1D behavior not predicted by standard theories either in 1D or 2D. I will show several examples how atomic wires and wire arrays grown by self-assembly on semiconducting surfaces of Si and Ge acting as insulating substrates can be used to study in detail fundamental aspects of low-dimensional physics, such as charge density waves [1] and Luttinger liquid behavior [2], partially under explicit control of the atomic structure. Due to the low symmetry in these structures, large Rashba-type spin-orbit coupling is expected to lift the spin degeneracy of the metal-induced surface states. In this context new types of spin order were proposed, e.g. for Au/Si(553) [3] and found to be consistent with experiment. As a further example, the Pb/Si(557) system close to monolayer coverage turned out to be an intriguing model system that demonstrates the wealth of phenomena to be expected in quasi-1D physics. Adsorbate induced electronic stabilization leads to (223) refaceting of the (557) surface, to opening of a band gap, to Fermi nesting normal to the steps [4], and to the formation of a charge density wave. Rashba splitting is so large that it causes in-plane anti-ferromagnetic spin polarization along the steps with twice the step periodicity resulting in a combined spin-charge density wave. New superstructures are formed by an excess Pb coverage up to 0.1ML due to ordered step decoration indicating strong electron-electron correlation across steps. This leads to new long range ordered states and formation of a sequence of 1D charge density waves up to a concentration of 1.5 ML, but also, as very recent angular and spin resolved photoemission studies show, to new ordered spin states.

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# Thursday Afternoon, November 13, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+MI+MN+NS+SS+TF-ThA

## Novel Quantum Phenomena in 2D Materials

**Moderator:** Alexander Sinitskii, University of Nebraska-Lincoln

2:20pm **2D+EM+MI+MN+NS+SS+TF-ThA1 Optoelectronics of Two-Dimensional Semiconductors, Xiaodong Xu, University of Washington INVITED**

Two dimensional transition metal dichalcogenides are a recent addition to the 2D electronic materials family. They have shown outstanding electrical and optical properties for new optoelectronic device concepts. In this talk, we will first discuss the unique interplay between spin, valley, and layer pseudospins in bilayer  $\text{WSe}_2$ . Such coupling effects lead to electrical control of spin states and optical generation of valley coherence through interlayer triions, where electrons and holes are localized in different layers. We will then talk about optoelectronic devices based on monolayer  $\text{WSe}_2$ , including p-n junctions as light emitting diodes and hybrid monolayer semiconductor/photonic crystal cavity devices. We will conclude the talk with a discussion of the optoelectronic properties of  $\text{MoSe}_2$ - $\text{WSe}_2$  heterostructures.

3:00pm **2D+EM+MI+MN+NS+SS+TF-ThA3 Theory of Graphene Transport Barriers in the Specular Limit, Daniel Gunlycke, C.T. White, Naval Research Laboratory**

Offering room-temperature ballistic electron transport well over one micron, while being atomically thin and planar, graphene is undeniably a promising material for future nanoelectronic devices. Presently, however, switchable devices have normally low on-off ratios, a reflection of the challenge of selectively blocking electron and hole carriers from propagating across the graphene surface. This has stimulated a lot of research on different methods for making graphene nanoribbons that exhibit suitable band gaps. An alternative way to obtain a controllable gap takes advantage of resonant tunneling across a pair of transport barriers. For the latter approach, the key is to find a barrier that is fairly reflective but not so much as to effectively cut off all transport across it.

In this presentation, we present a model for straight transport barriers in graphene in the specular limit. Using the Lippmann-Schwinger equation, we obtain the wave function, from which we derive the reflection and transmission probabilities, as well as the local density of itinerant states. This local density of states exhibits fluctuations arising from quantum interference between incoming and outgoing matter waves that allow the transport properties of a barrier to be estimated without explicitly probing the current across the barrier. Our model is tested against exact multi-channel, tight-binding quantum transport calculations for graphene with weak local potentials, local strain, local adsorption, and a locally defective structure. As the model parameters are related to observable quantities, they could be obtained from theory and/or experiment, allowing the model to be adopted even when the precise details of the barrier are unknown.

3:20pm **2D+EM+MI+MN+NS+SS+TF-ThA4 Tip-induced Potential Confinement on Graphene in Scanning Tunneling Microscopy Measurement, Yue Zhao, J. Chae, J.E. Wyrick, NIST/CNST, F.D. Natterer, Ecole Polytechnique Fédérale de Lausanne (EPFL), France, S. Jung, Korea Research Institute of Standards and Science (KRISS), A.F. Young, C.R. Dean, L. Wang, Y. Gao, Columbia University, J.N. Rodrigues, Graphene Research Centre, NUS, Singapore, K. Watanabe, T. Taniguchi, National Institute for Materials Science (NIMS), Japan, S. Adam, Graphene Research Centre, NUS, Singapore, J.C. Hone, K. Shepard, P. Kim, Columbia University, N.B. Zhitenev, J.A. Stroscio, NIST/CNST**

Graphene is a two-dimensional-electron-gas(2DEG) system with exposed surface, which allows scanning tunneling microscopy (STM) to investigate the electron-electron interaction associated with the Dirac nature on a local scale, with a variety of tuning knobs, such as carrier density, spatially varying disorder potential, and applied magnetic field. However, the electron-electron interaction in graphene is sensitive to the disorder details. Moreover, tip induced potential confinement can significantly complicate the interpretation of STM experiment. Utilizing a high mobility graphene device with low residual disorder, we can minimize the effect of local potential fluctuation, to better understand the role tip-induced potential plays in the measurement. We observed the emergency of large spectra gaps, modification to graphene Landau levels (LLs), and quantum dots with changing size due to the spatially inhomogeneous tip gating.

4:00pm **2D+EM+MI+MN+NS+SS+TF-ThA6 Topological Phase Transitions and Spin-orbit Density Waves, Hugo Dil, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland INVITED**

In recent years systems where the spin-orbit interaction (SOI) is not just a perturbation but the main energy scale have received increasing attention. In combination with a broken inversion symmetry in the crystal structure or at interfaces, SOI will lift the spin degeneracy and induce a complex Fermi surfaces and spin textures with spin momentum locking [1,2]. Furthermore, the SOI can drive the system through a phase transition to a so-called topological insulator. Being an insulator in the bulk these systems are characterized by spin-polarized, topologically protected interface states.

After a short introduction to the role of topology in the band structure of solids I will give an overview of our main spin- and angle-resolved photoemission (SARPES) results on a variety of non-interacting topological insulators [3]. One of the questions is how the spin texture evolves around a topological transition. We explored the occurrence of spin polarized states around a SOI driven topological transition [4] and around a structure driven topological transition [5]. In both cases we observe spin-polarized precursor states, which indicate that although the topological transition is sharp, the response of the system is more gradual.

From a fundamental point of view the truly interesting aspect of non-trivial spin textures lies in their combination with other interactions. This can result in a variety of phenomena, cumulating in the creation of the elusive Majorana Fermion. An example of a combination of interactions is our recent verification with SARPES of  $\text{Sb}_2\text{Te}_3$  as a topological Kondo insulator [6]. In topologically trivial systems, interactions can lead to the formation of a so-called spin-orbit density wave. I will show how the combination of a large spin-splitting and Fermi nesting leads to the formation of such a state and can explain the anisotropic behavior of Pb nanowires [7]. Furthermore, I will present our recent SARPES results for transition metal oxide surfaces where a subtle interplay between ferroelectricity and magnetic order results in the formation of a single spin-polarized energy contour. The occurrence of superconductivity in such systems could render it a 2D Majorana platform.

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4:40pm **2D+EM+MI+MN+NS+SS+TF-ThA8 The Symmetry Dependent Band Structure of  $\text{MoS}_2$ , Duy Le, University of Central Florida, T. Komesu, University of Nebraska-Lincoln, Q. Ma, University of California, Riverside, E.F. Schwier, H. Iwasawa, Hiroshima University, Japan, M. Shimada, Higashi-Hiroshima, Japan, T.S. Rahman, University of Central Florida, L. Bartles, University of California, Riverside, P.A. Dowben, University of Nebraska-Lincoln**

We will present results of density functional theory (DFT) based calculations of symmetry dependent band structures of single crystal  $\text{MoS}_2(0001)$  surface together with symmetry-polarized angle resolved photoemission spectroscopy (ARPES) derived experimental band structure. The good agreement of the DFT band structure with the experimentally derived bands with even and odd symmetries, attests to the reliability of the results. We performed ARPES at the Hiroshima Synchrotron, determining the  $\text{MoS}_2$  band structure separately for both p- and s-, polarized to distinguish even and odd symmetry, and the experimentally determined dispersion, in accordance with expectations and experimental confirmation of  $C_{3v}$  symmetry, argues in favor of an experimental band structure obtained from single domains. The comparison of theory and experiment provides strong indications that the bands at the top of the valence band are dominated by Mo 4d states. These states and indeed placement of the valence band can be perturbed by adsorbates. Indeed, we find that, under the effect of Na adsorption, the changing placement of the valence band structure of  $\text{MoS}_2$  clearly indicate the Na atoms donate electrons to  $\text{MoS}_2$  and that the Fermi energy level shifts as much as 0.5 eV with respect to the top of  $\text{MoS}_2$ 's valence band. Surprisingly, Na adsorption does not perturb the  $\text{MoS}_2$  band dispersion significantly. We will discuss these results in the light of those obtained for single layer  $\text{MoS}_2$  for insights and clarity.

5:00pm **2D+EM+MI+MN+NS+SS+TF-ThA9 CuIn<sub>m</sub>P<sub>2</sub>S<sub>6</sub> - Room Temperature Layered Ferroelectric**, Alex Belianinov, P. Maksymovych, Oak Ridge National Laboratory, A. Dziugys, Vilnius University, Lithuania, Q. He, Oak Ridge National Laboratory, E. Eliseev, National Academy of Sciences of Ukraine, A. Borisevich, Oak Ridge National Laboratory, A. Morozovska, NAS of Ukraine, J. Banys, Vilnius University, Lithuania, Y. Vysochanskii, Uzhgorod University, Ukraine, S.V. Kalinin, Oak Ridge National Laboratory

We have utilized ambient and Ultra High Vacuum Scanning Probe Microscopy tools to explore ferroelectric properties in cleaved 2D flakes of copper indium thiophosphate, CuIn<sub>m</sub>P<sub>2</sub>S<sub>6</sub> (CITP), and report on size effect and presently achievable limits of ferroelectric phase stability. CITP is an unusual example of a layered, anti-collinear, uncompensated, two-sublattice ferroelectric system. These are the only materials known to display “2-D” ferroelectric semiconductor behavior in a van-der-Waals crystal. The material exhibits a first-order phase transition of order–disorder type from the paraelectric to the ferroelectric phase at  $T_c = 315$  K. Our observations suggest the presence of stable ferroelectric polarization as evidenced by domain structures, rewritable polarization, and hysteresis loops. These observations suggest that flakes above 100 nm have bulk-like polarization and domain structures, whereas below 50 nm polarization disappears. Furthermore, the materials have measurable ionic mobility, as evidenced both by macroscopic measurements and by formation of surface damage above tip bias of 4 V, likely due to copper reduction. We ascribe this behavior to well-known instability of polarization due to depolarization field, along with internal screening by mobile Cu ions, as suggested by their high ionic mobility.

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5:20pm **2D+EM+MI+MN+NS+SS+TF-ThA10 Doping Efficiency and Mechanisms of Single and Randomly Stacked Bilayer Graphene by Iodine Adsorption**, Hokwon Kim, A. Tyurnina, Univ. Grenoble Alpes/CEA, LETI, France, J.-F. Guillet, J.-P. Simonato, J. Dijon, Univ. Grenoble Alpes/CEA, LITEN, France, D. Rouchon, D. Mariolle, N. Chevalier, O.J. Renault, Univ. Grenoble Alpes/CEA, LETI, France

The precise control of graphene's conductivity and work function is crucial in developing practical applications of graphene based electronics. In order to enhance the conductivity of graphene, we employed a simple doping method where graphene films produced by chemical vapor deposition and transferred onto SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and WO<sub>3</sub> substrates are p-doped with iodine vapor through physisorption at temperature of ~ 100 °C [1-3]. The work function values and iodine to carbon ratios of the one-layer (1L) and two-layer (2L) folded regions were analyzed by high spatial- and energy resolution X-ray photoelectron emission microscopy (XPEEM) on a NanoESCA instrument. After the iodine doping, the work function values were significantly increased up to ~0.4 eV and ~0.5 eV, respectively, for 1L and 2L graphene on SiO<sub>2</sub>/Si. This higher degree of doping by iodine was corroborated by I 3d<sub>5/2</sub> core level imaging of the same area where the 2L graphene exhibited significantly larger concentration of iodine (2 at. % versus 1 at. %) likely due to the intercalation of iodine at the inter-layer space.

The main iodine species identified by high resolution core level X-ray photoemission spectroscopy and Raman spectroscopy were I<sub>3</sub><sup>-</sup> and I<sub>5</sub><sup>-</sup> polyiodide anionic complexes with slightly higher concentration of I<sub>3</sub><sup>-</sup> in 2L than 1L graphene possibly due to different doping mechanisms. Temperature dependent ultra-high-vacuum, in-situ annealing of the doped films has demonstrated that most of iodine is removed above 300 °C for the both 1L and 2L regions, although a significant removal of iodine is observed for 2L graphene at temperature as low as 100 °C. Surprisingly, after the complete removal of iodine by annealing, the work function value did not return to the original one before the doping treatment and remained at a much higher value. This can be ascribed to the residual hydrocarbon contaminations interacting with the atomic defects within the graphene layer that lead to unintentional n-type doping in our samples[4].

Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

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5:40pm **2D+EM+MI+MN+NS+SS+TF-ThA11 Use of XPS for Device Characterization**, P. Aydogan, E.O. Polat, C. Kocabas, Sefik Suzer, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is utilized to investigate a number of devices made of graphene. The main objective of the technique is to trace chemical and location specific surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of graphene; (i) acting as a simple resistive element between two gold electrodes, (ii) a semiconducting sheet controlled by a back-gate, and (iii) between the source and the drain metal electrodes in a full transistor geometry, have been analyzed by recording the Au4f of the metal electrodes, the C1s of the graphene layer, and the O1s (or N1s) peaks of the silicon oxide (or nitride) of the substrate. The advantage of this technique is its ability to assess element specific surface electrical potentials of devices under operation based on the deviations of the core level peak positions in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to various stimuli gives unprecedented information about the chemical nature as well as the location of structural and/or other types of defects as a result of doping, oxidation, reduction, etc.

## Helium Ion Microscopy Focus Topic

Room: 316 - Session HI+2D+AS+MC-ThA

### Nanoengineering with Helium Ion Beams

Moderator: Armin Götzhäuser, University of Bielefeld, Germany, David C. Joy, University of Tennessee, Oak Ridge National Laboratory

2:20pm **HI+2D+AS+MC-ThA1 Helium Ion Microscopy (HIM) Technology for Imaging, Characterization, and nano-Fabrication for nano-Device Materials and Structures**, Shinichi Ogawa, NeRI, AIST, Japan **INVITED**

Several unique applications of a helium ion microscopy (HIM) technology have been studied. In comparison with electron, helium ion has larger cross section, and it realized HIM observation with less current because of higher efficiency of secondary electron generation with maximum distribution energy of 1 eV [1], a few eV in a SEM case, for imaging, which results in less power implant (less thermal damage input) into samples. Utilizing these features, a low dielectric constant material pattern of 70 nm line with less deformation (thermal damage) and a Cu metal line underneath a 130 nm dielectric of band gap of a few eV were imaged [2]. Luminescence from a SiO<sub>2</sub> sample was detected at imaging conditions [3], in which no damage was observed by a transmission electron microscopy (TEM) - electron energy loss spectroscopy method [4]. As one of nano-fabrication applications, we found that a helium ion irradiation using the HIM functionalizes a gate control of carrier conduction in a single-layer graphene at an appropriate amount of helium ion dose to graphene which enable gate bias control of current with an on-off ratio of two orders of magnitude at room temperature [5], [6]. A few nm diameter tungsten particles were deposited onto a TEM sample under the helium ion beam irradiation in W(CO)<sub>6</sub> gas atmosphere with high special resolution accuracy, which realized precise electron tomography and re-construction [7], and tungsten pillars of a few nm height with 40 nm diameter were formed with a straight hole of a few nm diameter through a center of the pillars [8]. The research on graphene material is granted by JSPS through FIRST Program initiated by CSTP.

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3:00pm **HI+2D+AS+MC-ThA3 MEMS Temperature Controlled Sample Stage for the Helium Ion Microscope**, *Jose Portoles, P.J. Cumpson*, Newcastle University, UK

The Helium microscope allows the imaging of samples with magnifications beyond those of electron microscopes with the added advantages of directly imaging insulators without being so critically dependent on a need to conductive coating the samples. This facilitates the imaging of for instance organic structures without the need of surface modification. The large depth of focus allows simultaneously focusing details of the sample at different depths. When using a temperature controlled stage this allows the samples to stay focused as thermal expansion produces vertical displacements of the sample surface, however due to the large magnifications in-plane thermal expansions are still an issue. We have investigated a solution based on a thermally actuated X-Y MEMS stage by exploiting the ability of MEMS actuators to provide smooth electronic control of lateral displacements in the micron range in order to compensate for lateral thermal expansion at the point of observation. The difficulties involved in producing relatively large out of plane displacements with a MEMS device can be neglected due to the large instrumental depth of focus. The device we present has been fabricated using a "silicon on insulator" (SOI) MEMS process, and can be driven at low voltages and currents using a standard vacuum feedthrough to the instrument's analysis chamber and compensate lateral thermal expansion in order to keep any spot on a small specimen in the field of view at high magnifications. The small size of the heating stage makes it rapid in its thermal response.

3:20pm **HI+2D+AS+MC-ThA4 Monte Carlo Simulations of Focused Neon Ion Beam Induced Sputtering of Copper**, *Rajendra Timilsina, P.D. Rack*, The University of Tennessee Knoxville, *S. Tan, R.H. Livengood*, Intel Corporation

A Monte Carlo simulation has been developed to model the physical sputtering and nanoscale morphology evolution to emulate nanomachining with the Gas Field Ion Microscope. In this presentation, we will present experimental and simulation results of copper vias milled by a focused neon ion beam. Neon beams with a beam energy of 20 keV and a Gaussian beam profile with full-width-at-half-maximum of 1 nm were simulated to elucidate the nanostructure evolution during the physical sputtering of high aspect ratio features. In this presentation we will overview our simulation attributes which includes an evolving real-time sputtered via profile considering both the sputtered and re-deposited material. The sputter yield and sputter profile vary with the ion species and beam parameters and are related to the distribution of the nuclear energy loss in the material. We will also illustrate how the effective sputter yield is aspect-ratio dependent due to the change in the effective escape angle of the sputtered species. Quantitative information such as the sputtering yields, dose dependent aspect ratios and resolution-limiting effects will be discussed. Furthermore, we will show that the calculated nuclear energy loss and implant concentration ahead of the sputtering front correlates to observed damage revealed by transmission electron microscopy.

4:00pm **HI+2D+AS+MC-ThA6 Circuit Edit Nanomachining Study using Ne+ & He+ Focused Ion Beam**, *Richard Livengood, S. Tan*, Intel Corporation

**INVITED**

FIB nanomachining has been used extensively for over 20 years for the purpose of rewiring integrated circuits to validate design changes, isolate process faults, and generate engineering samples. During this time frame, the minimum feature size of an IC (Moore's Law) has scaled from 500nm to 14nm (36X) compared with ~6X scaling of Ga+ FIB. As a result FIB nanomachining capabilities have been steadily eroding over the last several generations, limiting the types of circuit modifications that can be successfully completed. There are however, several promising new ion beam scaling R&D initiatives that provide hope of enabling further nanomachining scaling into the sub 10nm process node.

One such technology is GFIS (gas field ion source) technology. He+ GFIS based FIBs have been successfully used to image with sub 0.5nm resolution and nanomachine sub 10 nm structure in Au, Graphene, and other thin film structures.[1, 2, 3] More recently He+ and Ne+ GFIS sputtering properties have been studied for nanomachining in bulk semiconductor films.[4] In this paper, we will show our latest results on GFIS FIB GAE (gas assisted etch) nanomachining and IBID properties and electrical invasiveness impact.

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4:40pm **HI+2D+AS+MC-ThA8 Evaluation of EUV Resist Performance below 20-nm CD using Helium Ion Lithography**, *D.J. Maas*, TNO Technical Sciences, Netherlands, *Nima Kalhor*, TU Delft, Netherlands, *W. Mulckhuysse, E. van Veldhoven*, TNO Technical Sciences, Netherlands, *A. van Langen-Suurling, P.F.A. Alkemade*, TU Delft, Netherlands, *S. Wuister, R. Hoefnagels, C. Verspaet, J. Meessen, T. Fliervoet*, ASML, Netherlands

For the introduction of EUV lithography, development of high performance EUV resists is of key importance. This development involves studies into sensitivity, resolving power and pattern uniformity. We have used a sub-nanometer-sized 30 keV helium ion beam to expose chemically amplified (CAR) EUV resists.

There are remarkable similarities in the response of resists to He<sup>+</sup> ions and EUV photons. Both primary particle beams traverse the resist and meanwhile interact with the target atoms. The low backscattering of the He<sup>+</sup> ions results in ultra-low proximity effects, which is similar to EUV exposure  $s$ . Absorption of an EUV photon creates a high-energy electron that relaxes by the excitation of Secondary Electrons (SEs). A collision of a 20-30 keV helium ion with a target atom directly releases low-energy SEs. Each ion scatters several times in the resist layer, thus enabling resist exposures at very low doses per CH. The energy spectra of SEs generated by EUV and He<sup>+</sup> are remarkably alike. These SEs, in turn, activate the resist.

In this paper we show 30 keV He<sup>+</sup> ions exposures of contact holes and lines with a CD of 8 – 30 nm at 20 nm half-pitch in a chemically amplified EUV resist. We will demonstrate the potential of using He<sup>+</sup> ion lithography [1,2] in the study of EUV resists.

[1] V. Sidorkin et al., *Sub-10-nm nanolithography with a scanning helium beam*, *J. Vac. Sci. Technol. B* 27, L18 (2009)

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5:00pm **HI+2D+AS+MC-ThA9 Helium Ion Beam Lithography for Nanoscale Patterning**, *X. Shi*, University of Southampton, UK, *D.M. Bagnall*, University of New South Wales, UK, *Stuart Boden*, University of Southampton, UK

Electron beam lithography (EBL), the modification of thin films of resist by a focused beam of electrons to create a pattern that is subsequently transferred into the substrate, is a key technology in the development of nanoscale electronic devices. However, with the demand for ever smaller features and pattern dimensions, new lithographic techniques are required to extend beyond existing limits of EBL. One such emerging technology is helium ion beam lithography (HIBL), driven by the development of the helium ion microscope, a tool capable of producing a high intensity beam of helium ions focused to a sub-nanometer spot [1]. Preliminary studies on HIBL using typical EBL resist materials such as PMMA and HSQ have shown that HIBL has several advantages over EBL, including a smaller spot size (potentially leading to higher resolution patterning) and a decrease in the exposure dose required and so the potential for faster pattern definition and therefore higher throughput. Furthermore, proximity effects, which are caused by beam scattering leading to inadvertent exposure of surrounding material, and are problematic when producing high density patterns in EBL, are massively reduced in HIBL [2], [3].

Here, the latest results from an experimental investigation into the HIBL technique will be presented. Areas of PMMA films of various thicknesses are exposed to different helium ion doses. After subsequent development in MIBK/IPA, atomic force microscopy is used to measure residual layer thickness in order to generate exposure response curves for different initial thicknesses of resist. High sensitivity is confirmed with full exposure of 50 nm thick layers achieved with a helium ion dose of only ~2  $\mu\text{C}/\text{cm}^2$ . Experiments to characterise minimum feature size and proximity effects are currently underway. The use of other high resolution resists will also be investigated with the aim of providing a thorough assessment of the capabilities and limitations of this emerging nano-patterning technique.

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5:20pm **HI+2D+AS+MC-ThA10 Sub-100nm Nanofabrication using Helium and Neon Ion Beams**, *James Sagar, C. Nash, N. Braz, T. Wootton, M.J.L. Sourribes, T.-T. Nguyen, R.B. Jackman, P.A. Warburton*, London Centre for Nanotechnology, UK

Sub-100nm Nanofabrication using Helium and Neon Ion Beams

J. Sagar<sup>1</sup>, C. R. Nash<sup>1</sup>, N. Braz<sup>1,2</sup>, T. Wootton<sup>1,2</sup>, M. J. L. Sourribes<sup>1,2</sup>, T.-T. Nguyen<sup>1,2</sup>, R. B. Jackman<sup>1,2</sup>, and P. A. Warburton<sup>1,2</sup>

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Using a Zeiss Orion NanoFab we have created sub-100nm devices for experiments in quantum electronics and nanophotonics. The Orion NanoFab has the ability form an ion beam with either helium or neon gas. This makes the Nanofab a much more versatile instrument for nanofabrication since large area mills can be performed using Ne without the need for a Ga FIB column. The use of a Ne gas field ion source (GFIS) in the Orion NanoFab allows fabrication of sub-100nm devices on timescales comparable to that of conventional liquid Ga FIB but with considerably enhanced fidelity due to an increased sputter yield (ten times greater than that of He) whilst retaining a small probe size ( $\leq 5$ nm). Using a Ne ion beam we have fabricated two kinds of nanoscale superconducting devices: a superconducting nanowire based on a compound low- $T_C$  superconductor; and an array of nanoscale Josephson junctions based on a compound oxide high- $T_C$  superconductor. The use of an inert-gas ion species in these devices is extremely important as Ga implantation into superconducting materials has previously been shown to suppress superconductivity. The extremely small probe size of the He GFIS has allowed us to create sub-20nm apertures in a variety of materials. Sub-20nm apertures in InAs nanowires and in graphene have been fabricated for experiments in quantum coherent electronics and quantum nanophotonics respectively.

# Thursday Evening Poster Sessions

## 2D Materials Focus Topic

Room: Hall D - Session 2D-ThP

## 2D Materials Poster Session

**2D-ThP1 Extremely Low Impact Energy SIMS Characterization of Graphene**, Alexander Merkulov, F. Horreard, CAMECA, France, W. Strupinski, ITME, Poland, A. Davis, CAMECA Instruments Inc

Characterization of graphene forms an important part of graphene research and involves measurements based on various microscopic and spectroscopic techniques. Characterization involves determination of the number of layers and the purity of sample in terms of absence or presence of defects or doping species.

A quantitative estimation of the layer thicknesses can be obtained using attenuated secondary electrons emitted from the substrate. Transmission electron microscopy (TEM) can be directly used to observe the number of layers on viewing the edges of the sample, each layers corresponding to a dark line. The information on the defectness of the graphene layer or presence of dopant species can be provided by surface sensitive technique such as XPS and SIMS (Secondary Ion Mass Spectrometry).

The extreme sensitivity of SIMS to any doping constituents in the surficial layer could provide the important information, difficult to obtain by other technique. Application of SIMS to graphene is not yet established. This work is having the goal to advance in finding an approach for graphene layers characterization.

SIMS is a destructive technique based on physical sputtering and consecutive ionization of sputtered atomic or molecular particles. All problems inherent to sputtering itself, such as recoil mixing and ion enhanced diffusion reduce the depth resolution necessary for monoatomic layers characterization. In order to avoid such effect, an Extremely Low Impact Energy (EXLIE) ion beam approach is employed in our experiments. Sputtering with different ionic species and under different angles is performed, targeting the best possible depth resolution in graphene layers.

These EXLIE SIMS measurements are among the first SIMS results obtained on such structures. SIMS as many of the characterization processes needs subsequent tests to determine the validity of the results, using different SG, FG and SLG structures. The SIMS quantification aspects will be also discussed.

**2D-ThP3 Synthesis and Characterization of Large-Area and Highly Crystalline Molybdenum Disulfide Atomic Layers by Chemical Vapor Deposition**, Yoosook Kim, S.-H. Park, J.S. Kim, Y.H. Ko, Sungkyunkwan University, Republic of Korea, C. Jeon, Korea Basic Science Institute, Republic of Korea, C.-Y. Park, Sungkyunkwan University, Republic of Korea

The Isolation of few-layered transition metal dichalcogenides has mainly been performed by mechanical and chemical exfoliation with very low yields. In particular, the two-dimensional layer of molybdenum disulfide ( $\text{MoS}_2$ ) has recently attracted much interest due to its direct-gap property and potential application in optoelectronics and energy harvesting. However, the synthetic approach to obtain high-quality and large-area  $\text{MoS}_2$  atomic thin layers is still rare. In this account, a controlled thermal reduction sulfurization method is used to synthesize large- $\text{MoO}_x$  thin films are first deposited on  $\text{Si/SiO}_2$  substrates, which are then sulfurized (under vacuum) at high temperatures. Samples with different thicknesses have been analyzed by Raman spectroscopy and TEM, and their photoluminescence properties have been evaluated. We demonstrated the presence of single-, bi-, and few-layered  $\text{MoS}_2$  on as-grown samples. It is well known that the electronic structure of these materials is very sensitive to the number of layer, ranging from indirect band gap semiconductor in the bulk phase to direct band gap semiconductor in mono-layers. This synthetic approach is simple, scalable, and applicable to other transition metal dichalcogenides. The transferability of  $\text{MoS}_2$  films onto other arbitrary substrates like  $\text{SiO}_2/\text{Si}$  makes our  $\text{MoS}_2$  a perfect candidate for engineering a variety of applications in nanoelectronics and optoelectronics. Furthermore, this thermal reduction-sulfurization method of synthesizing large  $\text{WS}_2$  could now be implemented for the synthesis of other TMDs such as  $\text{WSe}_2$ ,  $\text{MOSe}_2$ ,  $\text{NbS}_2$ ,  $\text{NbSe}_2$ , etc.

**2D-ThP6 XPS Depth Profiling: A Viable Alternative to Secondary Ion Mass Spectrometry**, Michael Williams, Clark Atlanta University, B.R. Strohmeier, Thermo Fisher Scientific

Secondary ion mass spectrometry (SIMS) is a workhorse for the depth profile characterization of epitaxial materials in the optoelectronics industry. Most notable is its parts-per-billion sensitivity and nm depth resolution for the III-V semiconductors. XPS depth profiling was used to study the effect of substrate temperature on the composition and growth rate of InGaAs/InP multiple layers grown by chemical beam epitaxy. The results are in excellent agreement with published results from SIMS analysis. We show that XPS with its characteristic sensitivity to the environment of the constituent elements in conjunction with argon ion sputtering yields depth profile information on layered systems that exceeds the utility of SIMS.

**2D-ThP7 Investigation of Luminescent Properties of  $\text{Ca}_5(\text{PO}_4)_3\text{OH}:\text{Gd}^{3+},\text{Pr}^{3+}$  Phosphor for Application in Displays, Phototherapy Lamps and Thermoluminescence Dosimetry**, Puseletso Mokoena, University of the Free State, South Africa, L. Chithambo, Rhodes University, South Africa, H.C. Swart, O.M. Ntwaeaborwa, University of the Free State, South Africa

Luminescent properties of calcium phosphate phosphors are being investigated today for many applications in different types of light emitting devices. We have investigated the photoluminescent (PL), cathodoluminescent (CL) and thermoluminescent (TL) properties of hydroxyapatite or  $\text{Ca}_5(\text{PO}_4)_3\text{OH}:\text{Gd}^{3+},\text{Pr}^{3+}$  phosphor for application in phototherapy lamps, information displays and TL dosimetry, respectively. This phosphor was prepared by co-precipitation method and the concentrations of  $\text{Gd}^{3+}$  and  $\text{Pr}^{3+}$  in the  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  host were varied. The PL data were recorded in air under excitation by a monochromatized xenon lamp, the CL was measured in vacuum with a Gatan MonoCL4 attached to Jeol JSM-7800F field emission scanning microscope and the TL glow curves were recorded using a Riso TL/OSL reader (model TL/OSL-DA-20) system. In addition, the structure, particle morphology, and chemical states and composition of the phosphor were analyzed by x-ray diffraction, scanning electron microscopy and x-ray photoelectron spectroscopy respectively. The phosphor exhibited a narrowband ultraviolet B (UVB) emission located at 313 nm when excited with the xenon lamp or high energy electrons. This emission was attributed to the  $^1\text{P}_{1/2} \rightarrow ^8\text{S}_{7/2}$  transition of  $\text{Gd}^{3+}$  and was shown to improve considerably by incorporation of  $\text{Pr}^{3+}$  suggesting that there was energy transfer from  $\text{Pr}^{3+}$  to  $\text{Gd}^{3+}$ . The TL glow curves were measured in order to investigate the nature of the electron trapping centers and to determine the related activation energy. A single prominent peak was observed at 347 K at a constant heating rate of 5  $\text{K}\cdot\text{s}^{-1}$ . The TL kinetic parameter (activation energy) was deduced by the initial rise method, peak shape method and variable heating rates method.

**2D-ThP8 Influence of the Deposition Time in Optical and Electric Characteristics of Ge Nanoparticles Grown in  $\text{SiO}_2$  by LPCVD Technique**, Melissa Mederos Vidal, S.N. Mestanza Muñoz, Federal University of ABC, Brazil, I. Doi, J.A. Diniz, University of Campina, Brazil

Germanium nanoparticles (Ge-nps) have potential applications for electronic flash memories and light emitters in visible and near infrared wavelengths, with the main advantage of being compatible with actual device technology. It is known that, in floating gate devices, semiconductor nanoparticles are the charge-storage nodes placed in the gate oxide between the gate and de channel. Thus, as a result of the smaller bandgap, superior carrier mobilities, and higher excitonic Bohr radius compared to Silicon (Si), quantum confinement effects are much more obvious in Ge-nps, making this compound more ideal for memory devices. On the other hand, efficient light emission from Ge-nps in  $\text{SiO}_2$  matrix has been already demonstrated being that this can be tuned by changing the size of the nanoparticle and their existence is attributed to the presence of oxide defects, nanoparticles interface, quantum effects, Ge oxygen deficient centers, etc. So, in this context, the present work proposes the study of the influence that the improvement of the Ge-nps quality grown in  $\text{SiO}_2$  by LPCVD under different time of deposition, have on their photoluminescence and memory characteristics. For that, measurements as Raman Spectroscopy (RS), Atomic Force Microscopy (AFM) and photoluminescence spectroscopy (PL) were carried out. All samples were made on p-type Si (100) wafer covered by a 8 nm- $\text{SiO}_2$ -thermal-layer, using a vertical CVD reactor PMC 200 Phoenix Materials Corporation. The synthesis method was realized following a two-steps process: a first step, where took place the functionalization of  $\text{SiO}_2$  surface by the deposition of Si nuclei from the  $\text{SiH}_4$  pyrolysis, and a second step, where the selective growth of Ge nps over Si nuclei happens from  $\text{GeH}_4$  pyrolysis. Fig 1 shows the Normalized PL spectra for different Ge-nps size where a shift in the PL

peak position towards longer wavelengths is observed with the increase of nanoparticle-size and, a raise in the intensity of the peak can be note with the enhance of the density of nanoparticle. For the memory characterization, circular MOS capacitors with 200  $\mu\text{m}$  of diameter were fabricated containing these Ge-nps. Fig 2 shows the schematic of the MOS device (a) and the C-V curve comparison between a standard MOS capacitor and one containing the Ge NPs (b). According to this Fig., can be assumed that the major contribution to the memory property of the device comes from the nanoparticles in the gate dielectric since, for the capacitor without nanoparticles hardly hysteresis is observed.

**2D-ThP9 Enhanced Electrical Conductivity of Transparent Carbon Nanotube Sheet by Acid Treatment**, *J. Kim, JinHong Kim*, University of Texas at Dallas

**Enhanced electrical conductivity of transparent carbon nanotube sheet by acid treatment**

Jinhong Kim, Daewoong Jung, Maeum Han and Gil S. Lee\*

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Considerable efforts were dedicated to fabricate flexible transparent conductive films (TCFs) with high transmittance and low resistance for utilizing in various applications. To date, the most commonly used material for TCFs is indium tin oxide (ITO) due to its high transparency and low electrical resistance. However, there are several disadvantages with using ITO films in future applications, such as the brittleness and problems with polymer substrates. Recently, researches focused on developments in flexible TCFs, either through optimized structural configuration or exploring new materials to replace ITO films.

Carbon nanotubes (CNTs) have received increasing attentions as ITO replacement due to their excellent mechanical, electrical, thermal properties. Our previous work produced transparent, conductive CNT sheets by using a simple spinning method [1-2]. These CNT sheets had sheet resistances of 0.75-1 k $\Omega$ /sq and transmittances of ~85-90 %. However, there was a trade-off effect between sheet resistance and transmittance of TCFs during transferring process of CNTs. An increasing number of CNT layers in the TCFs can decrease the sheet resistance as well as the transmittance, simultaneously. Therefore, key challenge is how to realize the highly conductive CNT sheet without a degrading of transmittance.

Simple acid treatment was conducted to improve the electrical conductivity of the CNT sheets. The transferring CNT sheets on glass substrates were immersed in 60 % nitric acid for 1 hour. After the acid treatment, highly conductive CNT sheets were obtained with slightly increased transmittance. The acid treatment leads further inter-connection between the individual CNTs to form continuous electrical pathway, result in high conductivity of the CNT sheet. These results lead us to believe that the CNT sheets with low sheet resistance (450  $\Omega$ /sq) and high optical transmittance (90%) can be potential candidate for flexible TCF applications.

Reference

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2. Jung et al. *Jpn. J. Appl. Phys.*, **52** (2013), 03BC03

**2D-ThP11 CVD Processes for the Growth of Single Layer Transition Metal Dichalcogenides and Alloys**, *Ariana Nguyen, D. Barroso, E. Preciado, V. Klee, S. Bobek, C. Lee, S. Naghibi, I. Lu, G. Von Son Palacio, T. Empante, K. Brown, K. Yang, A. Nguyen, P. Rigas, W. Coley, L. Bartels*, University of California - Riverside

Transition metal dichalcogenides (TMD) present an exciting material system that provides tunable and direct  $\pi$ -bandgap semiconducting properties at the single-layer limit. While monolayer TMD materials can be fabricated through exfoliation, we demonstrate single layer films and islands of MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, etc. as well as their alloys that are grown in a CVD-like processes on SiO<sub>2</sub> and similar materials at process temperatures of  $\leq 700^\circ\text{C}$ . The resultant films can extend in a continuous fashion across cm-scale substrates and are composed of micron-scale rotational domains. By means of alloying, their band gaps can be tuned in a continuous fashion between 1.9 and 1.6 eV. We present how the use of organic chalcogen precursors allows more versatile alloying and homogeneous growth over extended areas. We also explore variations in the growth mode as a function of process pressure.

**2D-ThP15 Studying Graphene & Other 2D Materials With A Multiprobe Cryogenic System That Provides For Simultaneous Raman & Other Optical Modalities With A Wide Variety of Functional SPM Probes**, *J. Ernstoff*, Nanonics Imaging Ltd., Israel, *Aaron Lewis*, Hebrew University of Jerusalem, Israel, *O. Zinoviev, A. Komissar, E. Maayan*, Nanonics Imaging Ltd., Israel

This presentation will address the revolution that is occurring in 2D materials such as Graphene, MoS<sub>2</sub>, WeSe<sub>2</sub>, etc., and the variety of measurement modalities that are needed to fully understand these materials at cryogenic temperatures.

It is a challenge to study such materials at temperatures down to 10<sup>o</sup>K when one considers the wide variety of physical phenomena that have to be applied to get a full picture of the functionality of the material under study. This involves questions of structure, nanometric photoconductivity, electrical properties, thermal properties, near-field optical in the apertured and scattering modes, Kelvin probe, and of course Raman. All of these phenomena are common not only to 2D materials but also to carbon nanotubes.

Today's scientific challenges demand a system where one can image these phenomena and correlate such images with the nanometric structure of the material under study. This requires a multiprobe scanned probe microscopy system working at such extreme temperatures, which allows for multiple SPM on-line while maintaining complete optical accessibility. More specifically, the probes which can investigate near-field photoconductivity and Kelvin probe have to be capable of being on-line at the same time and also come into contact with one another to obtain overlapping images of nanometric spaces while still allowing for reflection Raman. This is necessary as many of these systems are incorporated into opaque devices. Such a system will be presented in this presentation with results on graphene.

**2D-ThP17 Development of Low-k Dielectric for Graphene device**, *YoungGon Lee, L. Cheng*, University of Texas at Dallas, *Y. Kim*, Gwangju Institute of Science and Technology, *G. Mordi*, Samsung, *HH. Hwang, A. Lucero*, University of Texas at Dallas, *BH. Lee*, Gwangju Institute of Science and Technology, *J. Kim*, University of Texas at Dallas

Graphene bilayer pseudo-spin field effect transistor (BiSFET) has been suggested as one of the most promising nanoelectronics since it has a lot of advantages such as low power operation and good scalability.[1] For graphene based 2D devices like BiSFET, it is preferable to have an extremely thin insulator layer with a low-k dielectric constant conformally deposited on the graphene surface. In this work, the transport behavior of non 2D crystalline low-k dielectrics, 3,4,9,10-parylene tetracarboxylic dianhydride (PTCDA), has been investigated to apply the graphene based device as an interlayer tunnel barrier for BiSFET. PTCDA thin films were evaporated on highly ordered pyrolytic graphite (HOPG) and Si surfaces using the molecular beam deposition. Then, Ru/Al was deposited using E-beam evaporator for electrical measurement.

PTCDA devices grown on Si substrate exhibit a rectifying behavior because Schottky can be formed at interface between PTCDA layer and Si substrate. The dielectric constants around  $\sim 1.6 - 2.2$  were extracted from capacitance at built-in potential. These results are consistent with previous papers about organic-inorganic Schottky diode.[2] However, as the PTCDA film thickness is scaled down from 20 to 5 nm, the reverse currents increase up to six orders of magnitude possibly because of the tunneling current. In order to explore the tunneling behavior of PTCDA layer on the graphene, the current behaviors of PTCDA layer on HOPG has been investigated. Similar to the current behavior of thin PTCDA layer on Si substrate, PTCDA device on HOPG exhibit tunneling behavior; the current increase linearly with the applied bias in low bias region, whereas it changes exponentially as a function of applied bias in high bias region. The tunneling current of PTCDA layer shows thickness dependence. These behaviors can be modeled by direct tunneling equation. [3] Capacitances around  $\sim 9$  and  $\sim 16$  pF in 3 and 1 nm PTCDA layer on HOPG, respectively, were identified using a time domain reflectometry (TDR) measurement, which are coincide with the value of PTCDA on Si substrate. In addition, there is a weak temperature dependence in current of thin PTCDA device.

In summary, non-2D crystalline low-k dielectric has been developed for the tunnel barrier of graphene based device. The thickness of PTCDA film was successfully scaled down to a few layers. It has also demonstrated that the devices fabricated with thin PTCDA films on HOPG exhibit feasibility of direct tunneling behaviors.

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**2D-ThP18 Charge Exchange and Energy Loss of Slow Highly Charged Ions Passing Through Carbon Nano Membranes, René Heller, R.A. Wilhelm, Helmholtz-Zentrum Dresden - Rossendorf, Germany, E. Gruber, R. Ritter, TU Wien - Vienna University of Technology, Austria, S. Facsko, Helmholtz-Zentrum Dresden - Rossendorf, Germany, F. Aumayr, TU Wien - Vienna University of Technology, Austria**

The interaction of slow highly charged ions (HCI) with solid surfaces has been excessively investigated within the recent past. Numerous systematic experiments on the nano structure creation by HCI impact have been carried out and revealed in a variety of different models describing phenomena as the creation of nano hillocks, mono atomic deep pits and etch pits on different kind of (bulk) materials [1-5].

Recently, we have investigated the interaction of slow HCI with one nanometer thin carbon nano sheets. We could show that HCIs can efficiently induce the creation of nm-sized pores in these membranes [6]. However, the extremely small thickness of this kind of target offered us a second opportunity - the observation of the projectile right after the interaction process in terms of its energy loss and charge exchange.

The results of those measurements show an unexpected two-fold ion charge state distribution after passing the membrane comprising (a) ions with very high charge states (close to the initial one) that almost lost no kinetic energy as well as (b) very low charged ions that lost a significant amount of kinetic energy. The balance of both contributions was found to depend strongly on the initial ion charge state. From these findings we draw a microscopic picture of the interaction process that is presented in the present contribution.

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**2D-ThP20 An Efficient Dry-Transfer Technique with Thermal Annealing for Enabling High-Performance Multilayer MoS<sub>2</sub> Transistors, Xuqian Zheng, R. Yang, Z. Wang, P.X.-L. Feng, Case Western Reserve University**

We report the first dry-transferred pristine molybdenum disulfide (MoS<sub>2</sub>) field-effect transistors (FETs) fabricated without any post-transfer lithographical and chemical processes, by using a facile, completely-dry-transfer technique with high throughput and high alignment precision. We show that the device performance can be greatly boosted by thermal annealing.

MoS<sub>2</sub> FETs have shown significant potential for enabling 2D electronic devices [1], by demonstrating increasingly competitive performance including high mobility, contact quality, and excellent On/Off ratios. All the MoS<sub>2</sub> FETs reported to date, however, are fabricated using electron-beam- or photo-lithography on top of MoS<sub>2</sub> flakes, and/or polymer-assisted transfer of MoS<sub>2</sub> sheets followed by dissolving the polymer [2], both of which involve multiple wet processing steps. Such processes may contaminate or even degrade the MoS<sub>2</sub> surface, and adversely affect device performance[3].

Here, we demonstrate multilayer MoS<sub>2</sub> FETs fabricated by using a completely-dry transfer method, which not only obviates the undesirable wet chemistry steps, but also has high device yield and more scalable device geometry. Using the technique, we fabricate the electrodes at wafer scale, aligning each flake to the electrodes during the transfer, which significantly improves the efficiency and yield, achieving nearly 100% success rate in obtaining pristine MoS<sub>2</sub> FETs. This dry-transfer process is readily applicable to substrates with much thinner high-k dielectric layers to attain low-threshold-voltage, low-power operations. Also, the performance of as-transferred devices can be further improved through vacuum annealing treatments. While experiments suggest that annealing may lead to dissolving of graphene into metal and thus improve contact [4], annealing effect on MoS<sub>2</sub> devices remains to be systematically explored. We find that the devices' performance typically exhibit noticeable improvement after initial annealing, and further enhancement can often be achieved via additional annealing. With annealing treatments at increasing temperatures, reliable reduction in device resistance is observed, together with consistent increase in mobility up to  $\mu=76\text{cm}^2/(\text{V}\cdot\text{s})$ , improvement in On/Off ratio exceeding  $10^7$ , and enhancement in transconductance. Furthermore, while

sometimes annealing can even convert non-Ohmic contacts into Ohmic, occasionally such conversion may not be completed, but still clear improvement can be observed.

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# Friday Morning, November 14, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+MS+NS-FrM

## 2D Materials: Device Physics and Applications

Moderator: Daniel Gunlycke, Naval Research Laboratory

8:20am **2D+EM+MS+NS-FrM1 1, 2, 3... Ripples, Gaps and Transport in Few-layer Graphene Membranes, ChunNing(Jeanie) Lau**, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a new model system for condensed matter physics, as well as a promising candidate for electronic materials. Though single layer graphene is gapless, bilayer and trilayer graphene have tunable band gaps that may be induced by out-of-plane electric fields or arise from collective excitation of electrons. Here I will present our results on mechanical manipulation and transport measurements in bilayer and trilayer graphene devices with mobility as high as 400,000 cm<sup>2</sup>/Vs. We demonstrate ripple formation due to thermally or mechanically induced strain, the presence of an intrinsic gapped state in bilayer and trilayer graphene at the charge neutrality point and evidence for quantum phase transition. Our results underscore the fascinating physics in these 2D membranes, and have implications for band gap engineering for graphene electronics and optoelectronic applications.

9:00am **2D+EM+MS+NS-FrM3 Photoinduced Doping in Heterostructures of Graphene and Boron Nitride, Jairo Velasco Jr., L. Ju**, UC Berkeley, *E. Huang*, Stanford University, *S. Kahn, C. Nosiola, H.-Z. Tsai*, UC Berkeley, *W. Yang*, Beijing National Laboratory for Condensed Matter Physics, Republic of China, *T. Taniguchi, K. Wantanabe*, National Institute for Materials Science (NIMS), Japan, *Y. Zhang*, Fudan University, Republic of China, *G. Zhang*, Beijing National Laboratory for Condensed Matter Physics, Republic of China, *M.F. Crommie, A. Zettl, F. Wang*, UC Berkeley

Van der Waals heterostructures (VDH) provide an exciting new platform for materials engineering, where a variety of layered materials with different electrical, optical and mechanical responses can be stacked together to enable new physics and novel functionalities. Here we report an emerging optoelectronic phenomenon (i.e. photo-induced modulation doping) in the graphene-boron nitride VDH (G/BN heterostructure). We find it enables flexible and repeatable writing and erasing of charge doping in graphene with visible light. We demonstrate that the photo-induced modulation doping maintains the remarkable carrier mobility of the G/BN heterostructure, and it can be used to generate spatially varying doping profiles like *pn* junctions. Our work contributes towards understanding light-matter interactions in VDHs, and innovates a simple technique for creating inhomogeneous doping in high mobility graphene devices. This opens the door for new scientific studies and applications.

9:20am **2D+EM+MS+NS-FrM4 Two-dimensional Resistance Map of Graphene p-n Junction in the Quantum Hall Regime, Nikolai N. Klimov, S. Le, C.A. Richter**, National Institute of Standards and Technology (NIST), *J. Yan*, University of Massachusetts, Amherst, *E. Comfort, J.U. Lee*, SUNY-University of Albany, *D.B. Newell*, National Institute of Standards and Technology (NIST)

Graphene, a two dimensional (2D) electronic system with a unique band structure, is a promising material for future electronic devices, especially for electrical metrology [1]. Currently, devices based upon GaAs heterostructures 2D electron gases (GaAs-2DEG) are used to realize a single quantum resistance standard value of  $(\frac{1}{2})h/e^2 = 12,906.4035 \Omega$  with metrological accuracy. It is important to realize resistance values over a wider resistance scale to expand the technical relevance of quantum resistance standards.

In the past, attempts have been made by using parallel or series GaAs-2DEG Hall bars to achieve multiple or fractional resistance values of  $h/e^2$ . However, the difficulties of fabricating ideal contacts and metal interconnects between the Hall bars severely limit the yield of properly operating devices. Graphene, with its ability to create both electron and hole 2D gases on a single Hall bar device without metal interconnects, is an ideal platform to overcome this difficulty [2].

We have fabricated a graphene FET p-n junction device in a Hall bar geometry and experimentally characterized it at large magnetic fields to determine the range of quantized resistance values that can be obtained. The device features two doped polysilicon split gates that are buried in a SiO<sub>2</sub> substrate within 100 nm-150 nm from the surface of graphene. The fabrication process achieves an atomically smooth dielectric surface, which is needed to preserve the intrinsic band structure of graphene. Independent

voltage control on these gates allows separate tuning of both type and concentration of charge carriers in the two parts of graphene conducting channel. In addition, a very narrow 150 nm gap between split gates gives a very sharp junction. Measurement of the sample's resistance at different gate values and measurement configurations in the quantum Hall regime allows us to fully characterize the device and to obtain multiples or fractions of the resistance value  $h/e^2$ . We will show that our experimental results can be explained by the Landauer-Büttiker edge-state transport model with the assumption of a partial mixing at the p-n interface. Potential application of graphene p-n junction devices for resistance standards with a wide range of resistance values other than  $h/2e^2$  will be discussed.

References:

[1] A. Tzalenchuk, *et al.*, Nature Nanotech., 5, 186 (2010)

[2] M. Woszczyzna, *et al.*, APL, 99, 022112 (2011)

9:40am **2D+EM+MS+NS-FrM5 Electrical Breakdown and Current Carrying Ability of Multilayer MoS<sub>2</sub> Transistors, Philip Feng, R. Yang, Z. Wang**, Case Western Reserve University

We report the first study of electrical breakdown of multilayer molybdenum disulphide (MoS<sub>2</sub>) transistors through precision electrical measurements and simulation that shows the effect of varying the device size and conductivities on the breakdown limit. We demonstrate that the multilayer devices have better current carrying capabilities compared to thin layer devices. We also study the effect of varying MoS<sub>2</sub> thickness upon electron mobility in the channel.

MoS<sub>2</sub> has recently emerged as a new two-dimensional (2D) semiconducting crystal with attractive properties, such as the absence of dangling bonds, high thermal stability, and having a thickness-dependent bandgap [#\_edn1]. While prototype single- and few-layer MoS<sub>2</sub> FETs and circuits have been demonstrated, in practice multilayer (up to 10s of nanometers) devices may be more desirable for certain applications: they can have higher carrier mobility and density of states under the same dielectric environment, greater mechanical strength, higher current limit and better manufacturability [#\_edn2] [#\_edn3]. While the breakdown of single layer MoS<sub>2</sub> transistors has been demonstrated [#\_edn4], breakdown of multilayer devices has not been studied.

In this work, we study the electrical breakdown of devices with different thicknesses through experimental demonstration and simulation with finite element method (FEM). We observe that the breakdown process happens gradually with multiple voltage sweeping cycles, and thicker devices generally show higher breakdown current, which is also demonstrated in the simulation. The highest breakdown current in the measurement is 1.2mA, which is one of the highest current reported results so far for MoS<sub>2</sub> transistors. Simulation also shows that with higher conductivity channel, the breakdown current and breakdown current density both increase. The high field transport characteristics of multilayer MoS<sub>2</sub> transistors demonstrate that the devices could drive high loads in circuits and could be used for circuits that require high power or current. The thickness dependence of mobility shows that the device performance can be further improved by carefully tuning the device parameters.

[i] [#\_ednref1] Q. H. Wang, *et al.*, Nat. Nanotechnol. 7, 699 (2012).

[ii] [#\_ednref2] D. Jariwala, *et al.*, ACS Nano 8, 1102 (2014).

[iii] [#\_ednref3] R. Ganatra, Q. Zhang, ACS Nano (2014), DOI: 10.1021/nn405938z.

[iv] [#\_ednref4] D. Lembke, A. Kis, ACS Nano 6, 10070 (2012).

10:00am **2D+EM+MS+NS-FrM6 Lithography-free Fabrication of Graphene Devices, Nick Thissen, R.H.J. Vervuurt**, Eindhoven University of Technology, Netherlands, *J.J.L. Mulders*, FEI Electron Optics, Netherlands, *J.W. Weber, A.J.M. Mackus, W.M.M. Kessels, A.A. Bol*, Eindhoven University of Technology, Netherlands

Graphene device fabrication on large-area graphene typically involves several patterning steps using electron beam or optical lithography, followed by graphene etching and metallization for application of metallic contacts. However, the resist films and lift-off chemicals used in lithography introduce compatibility issues, such as the difficulty of removing the resist from the graphene. This resist residue has a negative influence on the thermal and electrical properties of the graphene and interferes with functionalization of the graphene. This motivates the development of a 'bottom-up', direct-write, lithography-free fabrication method.

In this work, a lithography-free fabrication method for graphene-based devices was developed. As a first step, the method involves direct

patterning of large-area graphene by focused ion beam (FIB) in order to isolate graphene from the bulk. The patterning of the graphene is performed in a DualBeam (SEM / FIB) system, in which a 30 kV FIB is used to locally remove graphene from the substrate. An *in situ* Raman microscope allows for direct observation of the graphene quality before and after FIB processing, from which it was determined that a low Ga-ion dose of 10 C/m<sup>2</sup> is sufficient for complete graphene removal. By optimizing the pattern design, the ion beam current and the background pressure in the DualBeam system, unintentional damage of the graphene by scattered ions is almost completely prevented.

After FIB patterning, as a second step a direct-write atomic layer deposition (ALD) technique is applied in the same system to locally deposit contacts to the isolated graphene. In the direct-write ALD technique, the patterning capability of electron beam induced deposition (EBID) is combined with the material quality of ALD. A thin seed layer consisting of small Pt grains in amorphous carbon is deposited on the graphene by EBID in the desired contact pattern. Subsequently, a selective ALD process purifies the seed layers and builds them into high-quality Pt contacts. This combined approach yields virtually 100% pure Pt (resistivity of 12 μΩcm) with a lateral resolution of 10 nm<sup>11</sup>. This chemical approach to contact deposition is expected to yield lower contact resistances compared to conventional physical deposition techniques.

By combining patterning and direct contact deposition in the same system, graphene devices were fabricated from large-area graphene without the use of lithography. First results from sub-optimal devices demonstrate field-effect mobilities approaching 500 cm<sup>2</sup>/Vs and contact resistances as low as (40 ± 30) Ω.

[1] A.J.M. Mackus et al., *Nanoscale* **4**, 4477 (2012)

#### 10:40am 2D+EM+MS+NS-FrM8 Electronic Transport in Transition Metal Dichalcogenides, Joerg Appenzeller, Purdue University INVITED

Since the discovery of graphene for electronic applications, there has been a substantial worldwide effort to explore other layered materials. Transition metal dichalcogenides (TMDs) like MoS<sub>2</sub>, MoSe<sub>2</sub>, or WSe<sub>2</sub>, to just name a few, not only offer the desired ultra-thin body structure that translates into superior electrostatics as desirable for nanoelectronics applications, but also exhibit a sizable band gap. While to date the ideal application space for these materials has not been identified, it is obvious that only through a detailed understanding of the underlying transport in these layered materials intrinsic properties that lend themselves to particular applications can be uncovered.

In my presentation I will first discuss the benefits of an ultra-thin body structure for scaled tunneling FET applications including tunneling devices. Contacts play a particularly crucial role in this context and can easily mask the intrinsic performance of TMDs as will be discussed based on experimental Schottky barrier tunneling data obtained from MoS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub> field-effect transistors. A careful analysis of all these material systems reveals details about Schottky barrier heights for electron and hole injection as well as the band gap. These findings are then put into the context of channel length scaling and layer thickness dependence of three-terminal TMD devices based on MoS<sub>2</sub> transistors. Last, experimental data on the band-to-band tunneling in partially gated WSe<sub>2</sub> device structures will be discussed and projections about the potential usefulness of TMDs for tunneling device applications will be made.

#### 11:20am 2D+EM+MS+NS-FrM10 Controlled Synthesis and Fuel Cell Application of Carbon Nanowalls, Hiroki Kondo, S. Imai, K. Ishikawa, M. Sekine, M. Hori, Nagoya University, Japan, M. Hiramatsu, Meiji University, Japan

Carbon nanowalls (CNWs) are one of carbon nanomaterials and contain stacks of graphene sheets vertically standing on a substrate. Each wall with the top edge is continuous crystallographically through bending or branching and composed of nanographite domains. Recently, we have developed the formation method of the ultra-high-density over 10<sup>13</sup> cm<sup>-2</sup> Pt nanoparticles on the whole surface area of the CNWs with a diameter of 2-3 nm employing metal-organic chemical fluid deposition (MOCFD) method in supercritical fluid (SCF). They are promising as a catalytic electrodes for a polymer electrolyte fuel cell because of its high-specific-surface-area and high aspect ratio. On the other hand, while it is known that Pt nanoparticles are poisoned by CO below 100°C, it is reported that Pt-Au nanoparticles are excellent candidate for a low-temperature anode electrocatalyst. In this study, supporting processes of Pt-Au nanoparticles on the CNWs using the SCF-MOCFD method and their catalytic properties were investigated.

We used the SCF-MOCFD system to support Pt and Au nanoparticles on the CNWs. Firstly, Pt nanoparticles were supported using 1wt% (CH<sub>3</sub>C<sub>3</sub>H<sub>4</sub>)(CH<sub>3</sub>)<sub>3</sub>Pt solution (2 ml). Then, Au nanoparticles were subsequently supported using (CH<sub>3</sub>)<sub>2</sub>Au(CH<sub>3</sub>COCHCOCH<sub>3</sub>) solution (1 ml). Both precursors were diluted by n-hexane [CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>].

According to the SEM images of the CNWs after the supporting processes of only Pt nanoparticles and, both Pt and Au ones, the nanoparticles are supported on the entire surface area of each CNWs in the both cases. It is also found that the diameter and its distribution of the nanoparticles decrease after the second Au supporting process, while its density increases. This means that the relatively large Pt nanoparticles are effectively removed and small Au nanoparticles are simultaneously supported at the second supporting process. On the other hand, we evaluated cyclic voltammetry (CV) characteristics using CNWs with different-density Pt nanoparticles, in which density of 3.0x10<sup>12</sup> cm<sup>-2</sup> and diameter of 1.1 nm obtained for 10 min supporting and, density of 8.3x10<sup>12</sup> and diameter of 1.5 nm obtained for 30 min supporting. Peaks related to adsorption and desorption of hydrogen were found in both cases. With increasing the supporting time, the specific surface area of Pt evaluated from the CV about twofold increased. However, according to the TEM images, the ratio of surface area of Pt nanoparticles are about fivefold. It is deduced that some parts of Pt nanoparticles are inactive. Therefore, these results indicate that not the crystallinity control of CNWs are essential to improve the catalytic performance.

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Guo, H.: SP+2D+AS+EM+MC+NS+SS-ThM5, 32  
Guo, H.X.: HI+2D+AS+BI+MC-ThM6, 22  
Gustafsson, T.: HI+2D+AS+BI+MC-ThM13, 22

## — H —

Haak, T.: PS+2D-WeA3, 17  
Hanbicki, A.T.: 2D+EM+NS+PS+SS+TF-MoM4,  
1  
Haque, M.A.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
Hart, C.: PS+2D-WeA9, 18  
Hasan, N.: PS+2D-WeA8, 18  
He, G.: 2D+EM+NS+PS+SS+TF-MoM6, 1;  
SP+2D+AS+EM+MC+NS+SS-ThM6, 23  
He, Q.: 2D+EM+MI+MN+NS+SS+TF-ThA9, 26  
Heller, R.: 2D-ThP18, 31  
Hemmi, A.: 2D+AS+EM+NS+SS-MoA1, 3;  
2D+EM+NS+PS+SS+TF-MoM8, 2  
Hernández, S.: 2D+AS+BI+PS+SS-TuM5, 7  
Hernandez, S.C.: 2D+AS+BI+PS+SS-TuM6, 7  
Hersam, M.C.: 2D+AS+EM+NS+SS-MoA7, 3;  
2D+AS+HI+NS+SS-ThM13, 21;  
2D+AS+HI+NS+SS-ThM4, 20;  
2D+EM+NS+SS+TF-WeM3, 13  
Heyde, M.: 2D+EM+NS+SS+TF-WeM12, 14  
Hight Walker, A.R.: 2D+AS+BI+PS+SS-TuM10,  
7; 2D+AS+EM+MI+MN+NS+TF-WeA7, 15  
Hight-Walker, A.R.:  
2D+AS+EM+MI+MN+NS+TF-WeA4, 15  
Hippis, K.W.: SP+2D+AS+EM+MC+NS+SS-  
ThM1, 22  
Hiramatsu, M.: 2D+EM+MS+NS-FrM10, 33  
Hite, J.K.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA9, 9; MC+2D+AP+AS-MoA4, 5  
Hoefnagels, R.: HI+2D+AS+MC-ThA8, 27  
Hofer, W.: 2D+AS+EM+NS+SS-MoA10, 4  
Hone, J.C.: 2D+EM+MI+MN+NS+SS+TF-ThA4,  
25  
Hopstaken, M.J.P.: MC+2D+AP+AS-MoA1, 4  
Hori, M.: 2D+EM+MS+NS-FrM10, 33  
Horreard, F.: 2D-ThP1, 29  
Hossain, L.: 2D+EM+NS+SS+TF-WeM6, 13  
Hu, J.J.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
Huang, E.: 2D+EM+MS+NS-FrM3, 32  
Hubert, J.: PS+2D-WeA11, 19  
Hurley, P.K.: EM+2D-TuA8, 11  
Hwang, H.H.: 2D-ThP17, 30

## — I —

Iannuzzi, M.: 2D+AS+EM+NS+SS-MoA1, 3  
Idrobo, J.-C.: SP+2D+AS+EM+MC+NS+SS-  
ThM11, 23  
Im, H.: MC+2D+AP+AS-MoA9, 6  
Imai, S.: 2D+EM+MS+NS-FrM10, 33  
Ishikawa, K.: 2D+EM+MS+NS-FrM10, 33  
Iwasawa, H.: 2D+EM+MI+MN+NS+SS+TF-  
ThA8, 25

## — J —

Jackman, R.B.: HI+2D+AS+MC-ThA10, 28  
Jariwala, D.: 2D+AS+HI+NS+SS-ThM4, 20  
Jayanthinarasimham, A.:  
2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 9  
Jeon, C.: 2D-ThP3, 29  
Jeon, M.H.: 2D+AS+EM+NS+SS-MoA8, 4  
Jespersion, M.L.: 2D+EM+NS+PS+SS+TF-MoM5,  
1  
Johnson, N.: MC+2D+AP+AS-MoA7, 5  
Jonker, B.T.: 2D+EM+NS+PS+SS+TF-MoM4, 1  
Joy, D.C.: HI+2D+AS+BI+MC-ThM1, 21  
Ju, L.: 2D+EM+MS+NS-FrM3, 32  
Julie, H.: PS+2D-WeA12, 19  
Jung, S.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25  
Junkermeier, C.: 2D+AS+BI+PS+SS-TuM5, 7  
Junkermeier, C.: 2D+AS+EM+NS+SS-MoA3, 3

## — K —

Kahn, S.: 2D+EM+MS+NS-FrM3, 32  
Kalhor, N.: HI+2D+AS+MC-ThA8, 27  
Kalinin, S.V.: 2D+EM+MI+MN+NS+SS+TF-  
ThA9, 26  
Kaltschmidt, B.: HI+2D+AS+BI+MC-ThM12, 22  
Kaltschmidt, C.: HI+2D+AS+BI+MC-ThM12, 22  
Kaszuba, P.: MC+2D+AP+AS-MoA11, 6  
Kaufman-Osborn, T.: EM+2D-TuA4, 11  
Kelly, M.: 2D+EM+NS+SS+TF-WeM11, 14  
Kessels, W.M.M.: 2D+EM+MS+NS-FrM6, 32  
Khelifa, F.: PS+2D-WeA7, 18  
Kim, MC+2D+AP+AS-MoA10, 6  
Kim, H.: 2D+EM+MI+MN+NS+SS+TF-ThA10,  
26  
Kim, J.: 2D-ThP17, 30; 2D-ThP9, 30  
Kim, J.S.: 2D-ThP3, 29  
Kim, J.Y.: EM+2D-TuA7, 11  
Kim, K.N.: 2D+AS+EM+NS+SS-MoA8, 4  
Kim, K.S.: 2D+AS+EM+NS+SS-MoA4, 3;  
2D+AS+EM+NS+SS-MoA8, 4  
Kim, P.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25  
Kim, S.P.: 2D+AS+BI+PS+SS-TuM4, 7  
Kim, Y.: 2D-ThP17, 30; 2D-ThP3, 29  
Kinder, E.K.: 2D+AS+HI+NS+SS-ThM5, 20  
King, S.W.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA3, 9  
Király, B.T.: 2D+AS+EM+NS+SS-MoA7, 3;  
2D+AS+HI+NS+SS-ThM13, 21;  
2D+EM+NS+SS+TF-WeM3, 13  
Kis, A.: 2D+AS+EM+MI+MN+NS+TF-WeA4, 15  
Klee, V.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-  
ThP11, 30  
Klimov, N.N.: 2D+EM+MS+NS-FrM4, 32  
Knoll, A.J.: PS+2D-WeA9, 18  
Ko, Y.H.: 2D-ThP3, 29  
Kocabas, C.: 2D+EM+MI+MN+NS+SS+TF-  
ThA11, 26  
Kodambaka, S.: 2D+EM+NS+PS+SS+TF-  
MoM10, 2  
Koley, G.: 2D+AS+BI+PS+SS-TuM11, 8  
Komakov, A.: IS+2D+MC+NS+SP+SS-WeA3, 16  
Komesu, T.: 2D+EM+MI+MN+NS+SS+TF-ThA8,  
25  
Komissar, A.: 2D-ThP15, 30  
Kondo, H.: 2D+EM+MS+NS-FrM10, 33  
Kraya, L.Y.: SP+2D+AS+EM+MC+NS+SS-  
ThM2, 22  
Kraya, R.: SP+2D+AS+EM+MC+NS+SS-ThM2,  
22  
Kuhn, M.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA3, 9  
Kummel, A.C.: 2D+AS+BI+PS+SS-TuM13, 8;  
2D+AS+HI+NS+SS-ThM5, 20; EM+2D-  
TuA4, 11  
Kuo, Y.: EM+2D-TuA12, 12  
Kwak, I.J.: 2D+AS+BI+PS+SS-TuM13, 8;  
2D+AS+HI+NS+SS-ThM5, 20

## — L —

LaBella, V.P.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA8, 9  
Lau, C.N.: 2D+EM+MS+NS-FrM1, 32  
Lauhon, L.J.: 2D+AS+HI+NS+SS-ThM4, 20  
Laursen, T.: MC+2D+AP+AS-MoA6, 5  
Le Lay, G.: 2D+EM+NS+SS+TF-WeM1, 13  
Le, D.T.: 2D+AS+BI+PS+SS-TuM3, 7;  
2D+AS+EM+MI+MN+NS+TF-WeA3, 15;  
2D+AS+HI+NS+SS-ThM6, 20;  
2D+EM+MI+MN+NS+SS+TF-ThA8, 25  
Le, S.: 2D+EM+MS+NS-FrM4, 32  
Lee, B.H.: 2D-ThP17, 30  
Lee, C.: 2D-ThP11, 30  
Lee, H.D.: HI+2D+AS+BI+MC-ThM13, 22  
Lee, J.U.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA8, 9; 2D+EM+MS+NS-FrM4, 32  
Lee, W.T.: MC+2D+AP+AS-MoA10, 6  
Lee, Y.G.: 2D-ThP17, 30  
Lempert, W.: PS+2D-WeA9, 18

Leobandung, E.: MC+2D+AP+AS-MoA1, 4  
Lewis, A.: 2D-ThP15, 30  
Lherreron, B.: MC+2D+AP+AS-MoA10, 6  
Li, A.P.: SP+2D+AS+EM+MC+NS+SS-ThM10,  
23; SP+2D+AS+EM+MC+NS+SS-ThM11, 23;  
SP+2D+AS+EM+MC+NS+SS-ThM6, 23  
Li, J.: 2D+EM+NS+PS+SS+TF-MoM6, 1  
Li, Q.: 2D+AS+BI+PS+SS-TuM4, 7  
Li, Y.: 2D+AS+EM+MI+MN+NS+TF-WeA12, 16  
Lichtenstein, L.: 2D+EM+NS+SS+TF-WeM12, 14  
Lin, J.: EM+2D-TuA8, 11  
Lin, Y.C.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA3, 9; 2D+EM+NS+SS+TF-WeM6, 13  
Liu, L.: SP+2D+AS+EM+MC+NS+SS-ThM11, 23  
Liu, Q.Q.: IS+2D+MC+NS+SP+SS-WeA9, 16  
Liu, X.-Z.: 2D+AS+BI+PS+SS-TuM4, 7  
Liu, Z.: IS+2D+MC+NS+SP+SS-WeA1, 16  
Liu, Z.L.: IS+2D+MC+NS+SP+SS-WeA10, 17  
Livengood, R.H.: HI+2D+AS+MC-ThA4, 27;  
HI+2D+AS+MC-ThA6, 27  
Lock, E.H.: 2D+AS+BI+PS+SS-TuM5, 7  
Lou, J.: 2D+EM+NS+PS+SS+TF-MoM1, 1;  
SP+2D+AS+EM+MC+NS+SS-ThM10, 23  
Lu, H.L.: 2D+AS+HI+NS+SS-ThM5, 20  
Lu, I.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-  
ThP11, 30  
Luan, P.: PS+2D-WeA9, 18  
Lucero, A.: 2D-ThP17, 30

## — M —

Ma, Q.: 2D+EM+MI+MN+NS+SS+TF-ThA8, 25  
Maas, D.J.: HI+2D+AS+MC-ThA8, 27  
Maayan, E.: 2D-ThP15, 30  
Mackus, A.J.M.: 2D+EM+MS+NS-FrM6, 32  
Magaud, L.: PS+2D-WeA1, 17  
Majumdar, A.: MC+2D+AP+AS-MoA1, 4  
Maksymovych, P.: 2D+EM+MI+MN+NS+SS+TF-  
ThA9, 26  
Mann, J.: 2D+EM+NS+SS+TF-WeM10, 14  
Mannix, A.J.: 2D+AS+EM+NS+SS-MoA7, 3;  
2D+AS+HI+NS+SS-ThM13, 21;  
2D+EM+NS+SS+TF-WeM3, 13  
Mariolle, D.: 2D+EM+MI+MN+NS+SS+TF-  
ThA10, 26  
Marks, T.J.: 2D+AS+HI+NS+SS-ThM4, 20  
Martins, B.: SP+2D+AS+EM+MC+NS+SS-ThM5,  
23  
Mastro, M.A.: MC+2D+AP+AS-MoA4, 5  
Matsubayashi, A.:  
2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 9  
Matsui, F.: 2D+EM+NS+PS+SS+TF-MoM8, 2  
McCarty, K.F.: 2D+EM+NS+PS+SS+TF-MoM10,  
2; SP+2D+AS+EM+MC+NS+SS-ThM11, 23  
McConney, M.E.: 2D+EM+NS+PS+SS+TF-  
MoM5, 1  
McCreary, K.M.: 2D+EM+NS+PS+SS+TF-  
MoM4, 1  
McDonnell, S.: 2D+EM+NS+SS+TF-WeM6, 13;  
EM+2D-TuA3, 10  
Mederos Vidal, M.: 2D-ThP8, 29  
Meessen, J.: HI+2D+AS+MC-ThA8, 27  
Merche, D.: PS+2D-WeA12, 19  
Merkulov, A.V.: 2D-ThP1, 29  
Mertens, J.: PS+2D-WeA11, 19  
Mestanza Muñoz, S.N.: 2D-ThP8, 29  
Meyer, D.J.: MC+2D+AP+AS-MoA4, 5  
Mills, A.: 2D+AS+HI+MC+NS+PS+SP+SS-  
TuA4, 9  
Mok, H.S.: 2D+EM+NS+PS+SS+TF-MoM10, 2  
Mokoena, P.: 2D-ThP7, 29  
Monaghan, S.: EM+2D-TuA8, 11  
Morales-Cifuentes, J.R.:  
2D+AS+EM+MI+MN+NS+TF-WeA8, 15  
Mordi, G.: 2D-ThP17, 30  
Morozovska, A.: 2D+EM+MI+MN+NS+SS+TF-  
ThA9, 26  
Morrish, R.M.: PS+2D-WeA3, 17  
Moszkowicz, L.: MC+2D+AP+AS-MoA11, 6  
Motoyama, MC+2D+AP+AS-MoA10, 6  
Movva, H.C.P.: 2D+AS+HI+NS+SS-ThM5, 20

Mowll, T.R.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 10; 2D+EM+NS+PS+SS+TF-MoM3, 1  
 Mulckhuysen, W.: HI+2D+AS+MC-ThA8, 27  
 Mulders, J.J.L.: 2D+EM+MS+NS-FrM6, 32  
 Racker, L.: HI+2D+AS+BI+MC-ThM13, 22  
 Murata, Y.: 2D+EM+NS+PS+SS+TF-MoM10, 2  
 Muratore, C.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
 Myers-Ward, R.L.: 2D+AS+BI+PS+SS-TuM5, 7  
 Myung, Y.: MC+2D+AP+AS-MoA9, 6

— **N** —  
 Naghibi, S.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-ThP11, 30  
 Najmaei, S.: SP+2D+AS+EM+MC+NS+SS-ThM10, 23  
 Nakayama, T.: MC+2D+AP+AS-MoA6, 5  
 Nash, C.: HI+2D+AS+MC-ThA10, 28  
 Nath, A.: 2D+AS+BI+PS+SS-TuM5, 7  
 Natterer, F.D.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25  
 Nayyar, N.: 2D+AS+EM+MI+MN+NS+TF-WeA3, 15  
 Negara, M.A.: EM+2D-TuA8, 11  
 Newberg, J.T.: IS+2D+MC+NS+SP+SS-WeA11, 17  
 Newell, D.B.: 2D+EM+MS+NS-FrM4, 32  
 Nguyen, A.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-ThP11, 30  
 Nguyen, T.-T.: HI+2D+AS+MC-ThA10, 28  
 Nie, S.: 2D+EM+NS+PS+SS+TF-MoM10, 2  
 Noltling, W.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 9  
 Nosiglia, C.: 2D+EM+MS+NS-FrM3, 32  
 Novak, S.W.: MC+2D+AP+AS-MoA6, 5  
 Ntwaeaborwa, O.M.: 2D-ThP7, 29

— **O** —  
 O'Connor, E.: EM+2D-TuA8, 11  
 Oehrlein, G.S.: PS+2D-WeA9, 18  
 Ogawa, S.: HI+2D+AS+MC-ThA1, 26  
 Okada, T.: 2D+AS+EM+NS+SS-MoA9, 4  
 Oleynik, I.I.: 2D+AS+EM+MI+MN+NS+TF-WeA11, 15; 2D+EM+NS+SS+TF-WeM5, 13  
 Ong, E.W.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 10; 2D+EM+NS+PS+SS+TF-MoM3, 1  
 Osgood, R.M.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA1, 9  
 osofsky, M.: 2D+AS+BI+PS+SS-TuM5, 7  
 Osterwalder, J.: 2D+AS+EM+NS+SS-MoA1, 3; 2D+EM+NS+PS+SS+TF-MoM8, 2  
 Oyer, A.J.: 2D+AS+BI+PS+SS-TuM6, 7

— **P** —  
 Park, C.-Y.: 2D-ThP3, 29  
 Park, D.-G.: MC+2D+AP+AS-MoA1, 4  
 Park, J.: 2D+AS+HI+NS+SS-ThM1, 20; MC+2D+AP+AS-MoA9, 6; SP+2D+AS+EM+MC+NS+SS-ThM11, 23; SP+2D+AS+EM+MC+NS+SS-ThM6, 23  
 Park, J.H.: 2D+AS+BI+PS+SS-TuM13, 8; 2D+AS+HI+NS+SS-ThM5, 20  
 Park, S.-H.: 2D-ThP3, 29  
 Park, S.W.: EM+2D-TuA4, 11  
 Perriot, R.: 2D+AS+EM+MI+MN+NS+TF-WeA11, 15  
 Pfnür, H.: SP+2D+AS+EM+MC+NS+SS-ThM12, 24  
 Phelps, R.: MC+2D+AP+AS-MoA11, 6  
 Phuong, P.V.: 2D+AS+EM+NS+SS-MoA8, 4  
 Piasecki, A.: 2D+EM+NS+SS+TF-WeM6, 13  
 Pitters, J.L.: HI+2D+AS+BI+MC-ThM3, 21; HI+2D+AS+BI+MC-ThM5, 22  
 Polat, E.O.: 2D+EM+MI+MN+NS+SS+TF-ThA11, 26  
 Poleunis, C.: PS+2D-WeA11, 19  
 Portoles, J.F.: HI+2D+AS+MC-ThA3, 27  
 Povey, I.M.: EM+2D-TuA8, 11  
 Prabhunirashi, P.L.: 2D+AS+HI+NS+SS-ThM4, 20  
 Preciado, E.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-ThP11, 30

— **Q** —  
 Qin, X.: EM+2D-TuA7, 11

— **R** —  
 Rack, P.D.: HI+2D+AS+MC-ThA4, 27  
 Rahman, T.S.: 2D+AS+BI+PS+SS-TuM3, 7; 2D+AS+EM+MI+MN+NS+TF-WeA3, 15; 2D+AS+HI+NS+SS-ThM6, 20; 2D+EM+MI+MN+NS+SS+TF-ThA8, 25  
 Raman, S.: MC+2D+AP+AS-MoA9, 6  
 Ramirez-Torres, A.: 2D+AS+HI+NS+SS-ThM6, 20  
 Rastegar, A.: MC+2D+AP+AS-MoA6, 5  
 Rawal, T.B.: 2D+AS+BI+PS+SS-TuM3, 7  
 Reed, E.J.: 2D+AS+EM+MI+MN+NS+TF-WeA12, 16  
 Reinecke, T.: 2D+AS+BI+PS+SS-TuM5, 7; 2D+AS+EM+NS+SS-MoA3, 3  
 Renault, O.J.: 2D+EM+MI+MN+NS+SS+TF-ThA10, 26  
 Reniers, F.A.B.: PS+2D-WeA10, 18; PS+2D-WeA11, 19  
 Reutt-Robey, J.: 2D+AS+EM+MI+MN+NS+TF-WeA8, 15  
 Richter, C.A.: 2D+EM+MS+NS-FrM4, 32  
 Rigas, P.: 2D-ThP11, 30  
 Ritter, R.: 2D-ThP18, 31  
 Robinson, J.: 2D+AS+BI+PS+SS-TuM4, 7; 2D+AS+BI+PS+SS-TuM5, 7; 2D+AS+BI+PS+SS-TuM6, 7; 2D+AS+EM+NS+SS-MoA3, 3; 2D+EM+NS+PS+SS+TF-MoM4, 1  
 Robinson, J.A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 9; 2D+EM+NS+SS+TF-WeM11, 14; 2D+EM+NS+SS+TF-WeM6, 13  
 Robinson, Z.R.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 10; 2D+EM+NS+PS+SS+TF-MoM3, 1  
 Rockett, A.: MC+2D+AP+AS-MoA7, 5  
 Rodrigues, J.N.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25  
 Romero, D.: 2D+AS+EM+MI+MN+NS+TF-WeA7, 15  
 Ross, P.N.R.: IS+2D+MC+NS+SP+SS-WeA10, 17  
 Roth, S.: 2D+EM+NS+PS+SS+TF-MoM8, 2  
 Rouchon, D.: 2D+EM+MI+MN+NS+SS+TF-ThA10, 26

— **S** —  
 Sadana, D.K.: MC+2D+AP+AS-MoA1, 4  
 Sagar, J.: HI+2D+AS+MC-ThA10, 28  
 Saito, N.: PS+2D-WeA4, 17  
 Samukawa, S.: 2D+AS+EM+NS+SS-MoA9, 4  
 Sangwan, V.K.: 2D+AS+HI+NS+SS-ThM4, 20  
 Sardashti, K.: 2D+AS+BI+PS+SS-TuM13, 8  
 Sarney, W.L.: MC+2D+AP+AS-MoA2, 5; MC+2D+AP+AS-MoA3, 5  
 Schamis, M.S.: MC+2D+AP+AS-MoA1, 4  
 Schlaf, R.: 2D+EM+NS+SS+TF-WeM5, 13  
 Schuller, J.: 2D+AS+EM+MI+MN+NS+TF-WeA9, 15  
 Schultz, J.A.: HI+2D+AS+BI+MC-ThM13, 22  
 Schürmann, M.: HI+2D+AS+BI+MC-ThM12, 22  
 Schwarz, U.D.: 2D+EM+NS+SS+TF-WeM4, 13  
 Schwier, E.F.: 2D+EM+MI+MN+NS+SS+TF-ThA8, 25  
 Sekine, M.: 2D+EM+MS+NS-FrM10, 33  
 Sentman, C.D.: PS+2D-WeA3, 17  
 Seog, J.: PS+2D-WeA9, 18  
 Shamberger, P.J.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
 Sheehan, B.: EM+2D-TuA8, 11  
 Sheehan, P.E.: 2D+AS+BI+PS+SS-TuM4, 7; 2D+AS+BI+PS+SS-TuM5, 7; 2D+AS+BI+PS+SS-TuM6, 7; 2D+AS+EM+NS+SS-MoA3, 3  
 Shen, Z.-X.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA11, 10  
 Shenoy, V.B.: 2D+AS+BI+PS+SS-TuM4, 7  
 Shepard, K.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25

Shi, X.: HI+2D+AS+MC-ThA9, 27  
 Shimada, M.: 2D+EM+MI+MN+NS+SS+TF-ThA8, 25  
 Shubeita, S.: HI+2D+AS+BI+MC-ThM13, 22  
 Siegel, D.A.: SP+2D+AS+EM+MC+NS+SS-ThM11, 23  
 Simonato, J.-P.: 2D+EM+MI+MN+NS+SS+TF-ThA10, 26  
 Simpson, J.R.: 2D+AS+EM+MI+MN+NS+TF-WeA4, 15; 2D+AS+EM+MI+MN+NS+TF-WeA7, 15  
 Singh, A.: 2D+AS+BI+PS+SS-TuM11, 8  
 Sinha, D.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 9  
 Simitskii, A.: 2D+AS+HI+NS+SS-ThM12, 21  
 Slinkman, J.: MC+2D+AP+AS-MoA11, 6  
 Smeu, M.: SP+2D+AS+EM+MC+NS+SS-ThM5, 23  
 Smith, R.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
 Snyders, R.: PS+2D-WeA7, 18  
 Sonnenfeld, A.: 2D+EM+NS+SS+TF-WeM4, 13  
 Sourribes, M.J.L.: HI+2D+AS+MC-ThA10, 28  
 Sridhara, K.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 9  
 Stevenson, R.: 2D+EM+NS+PS+SS+TF-MoM5, 1  
 Stine, R.: 2D+AS+BI+PS+SS-TuM5, 7  
 Stosch, R.: 2D+AS+HI+NS+SS-ThM3, 20  
 Strohmeier, B.R.: 2D-ThP6, 29  
 Stroschio, J.A.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25  
 Strupinski, W.: 2D-ThP1, 29  
 Sudarshan, T.: 2D+AS+BI+PS+SS-TuM11, 8  
 Sun, Y.: MC+2D+AP+AS-MoA1, 4  
 Suzer, S.: 2D+EM+MI+MN+NS+SS+TF-ThA11, 26; MC+2D+AP+AS-MoA7, 5  
 Svensson, S.P.: MC+2D+AP+AS-MoA2, 5; MC+2D+AP+AS-MoA3, 5  
 Swart, H.C.: 2D-ThP7, 29

— **T** —  
 Tamanaha, C.R.: 2D+AS+BI+PS+SS-TuM5, 7  
 Tan, S.: HI+2D+AS+MC-ThA4, 27; HI+2D+AS+MC-ThA6, 27  
 Taniguchi, T.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25; 2D+EM+MS+NS-FrM3, 32  
 Tao, C.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 9  
 Thissen, N.F.W.: 2D+EM+MS+NS-FrM6, 32  
 Timilsina, R.: HI+2D+AS+MC-ThA4, 27  
 Timm, R.: EM+2D-TuA1, 10  
 Ting, M.: MC+2D+AP+AS-MoA3, 5  
 Tong, X.: IS+2D+MC+NS+SP+SS-WeA9, 16  
 Tsai, H.-Z.: 2D+EM+MS+NS-FrM3, 32  
 Tselev, A.: IS+2D+MC+NS+SP+SS-WeA3, 16  
 Tsoi, S.: 2D+AS+BI+PS+SS-TuM5, 7  
 Turchanin, A.: 2D+AS+HI+NS+SS-ThM3, 20  
 Turkowski, V.: 2D+AS+EM+MI+MN+NS+TF-WeA3, 15  
 Tyagi, P.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 10; 2D+EM+NS+PS+SS+TF-MoM3, 1  
 Tyurnina, A.: 2D+EM+MI+MN+NS+SS+TF-ThA10, 26

— **U** —  
 Uddin, M.A.: 2D+AS+BI+PS+SS-TuM11, 8  
 Ueno, T.: PS+2D-WeA4, 17  
 Urban, R.: HI+2D+AS+BI+MC-ThM3, 21; HI+2D+AS+BI+MC-ThM5, 22

— **V** —  
 van Langen-Suurling, A.: HI+2D+AS+MC-ThA8, 27  
 van Veldhoven, E.: HI+2D+AS+MC-ThA8, 27  
 Vandecasteele, N.: PS+2D-WeA11, 19  
 Velasco Jr., J.: 2D+EM+MS+NS-FrM3, 32  
 Ventrice, Jr., C.A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 10; 2D+EM+NS+PS+SS+TF-MoM3, 1  
 Verspaget, C.: HI+2D+AS+MC-ThA8, 27  
 Vervuurt, R.H.J.: 2D+EM+MS+NS-FrM6, 32  
 Viville, P.: PS+2D-WeA10, 18

- Voevodin, A.A.: 2D+EM+NS+PS+SS+TF-MoM5, **1**
- Von Son Palacio, G.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-ThP11, 30
- Vysochanskii, Y.: 2D+EM+MI+MN+NS+SS+TF-ThA9, 26
- **W** —
- Wacaser, B.A.: MC+2D+AP+AS-MoA1, 4
- Waite, A.: 2D+EM+NS+PS+SS+TF-MoM5, 1
- Wallace, R.M.: 2D+EM+NS+SS+TF-WeM6, 13; EM+2D-TuA3, 10; EM+2D-TuA7, 11
- Walton, S.G.: 2D+AS+BI+PS+SS-TuM5, 7; 2D+AS+BI+PS+SS-TuM6, 7
- Wang, B.: 2D+EM+NS+PS+SS+TF-MoM5, 1
- Wang, F.: 2D+EM+MS+NS-FrM3, 32
- Wang, L.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25
- Wang, Y.: 2D+AS+EM+MI+MN+NS+TF-WeA8, 15
- Wang, Z.: 2D+EM+MS+NS-FrM5, 32; 2D-ThP20, 31
- Watanabe, K.: 2D+EM+MS+NS-FrM3, 32
- Warburton, P.A.: HI+2D+AS+MC-ThA10, 28
- Watanabe, K.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25
- Watson, M.: 2D+AS+EM+MI+MN+NS+TF-WeA4, **15**; 2D+AS+EM+MI+MN+NS+TF-WeA7, 15
- Weber, J.W.: 2D+EM+MS+NS-FrM6, 32
- Weimann, T.: 2D+AS+HI+NS+SS-ThM3, 20
- Wells, R.: MC+2D+AP+AS-MoA11, 6
- Wetherington, M.: 2D+EM+NS+SS+TF-WeM11, 14
- Wheeler, V.D.: 2D+AS+BI+PS+SS-TuM5, 7
- White, C.T.: 2D+EM+MI+MN+NS+SS+TF-ThA3, 25
- Widom, M.: 2D+EM+NS+PS+SS+TF-MoM6, 1
- Wielunski, L.: HI+2D+AS+BI+MC-ThM13, 22
- Wiggins, B.C.: SP+2D+AS+EM+MC+NS+SS-ThM1, **22**
- Wilhelm, R.A.: 2D-ThP18, 31
- Williams, M.D.: 2D-ThP6, **29**
- Winkler, K.: EM+2D-TuA3, 10
- Winter, A.: 2D+AS+HI+NS+SS-ThM3, **20**
- Wolden, C.A.: PS+2D-WeA3, 17
- Wolkow, R.: HI+2D+AS+BI+MC-ThM3, 21; HI+2D+AS+BI+MC-ThM5, 22; SP+2D+AS+EM+MC+NS+SS-ThM5, **23**
- Wong, A.: MC+2D+AP+AS-MoA11, 6
- Woods, A.S.: HI+2D+AS+BI+MC-ThM13, 22
- Wootton, T.: HI+2D+AS+MC-ThA10, 28
- Woszczyna, M.: 2D+AS+HI+NS+SS-ThM3, 20
- Wu, C.-C.: 2D+AS+HI+NS+SS-ThM4, 20
- Wuister, S.: HI+2D+AS+MC-ThA8, 27
- Wyrick, J.E.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25
- **X** —
- Xing, H.: 2D+AS+EM+MI+MN+NS+TF-WeA4, 15
- Xu, C.: HI+2D+AS+BI+MC-ThM13, 22
- Xu, X.D.: 2D+EM+MI+MN+NS+SS+TF-ThA1, **25**
- **Y** —
- Yan, J.: 2D+EM+MS+NS-FrM4, 32
- Yan, R.: 2D+AS+EM+MI+MN+NS+TF-WeA4, 15
- Yang, K.: 2D+EM+NS+SS+TF-WeM10, 14; 2D-ThP11, 30
- Yang, R.: 2D+EM+MS+NS-FrM5, 32; 2D-ThP20, 31
- Yang, W.: 2D+EM+MS+NS-FrM3, 32
- Yeom, G.: 2D+AS+EM+NS+SS-MoA4, 3; 2D+AS+EM+NS+SS-MoA8, 4
- Young, A.F.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25
- Yu, K.M.: MC+2D+AP+AS-MoA3, 5
- Yu, Y.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 9
- **Z** —
- Zalalutdinov, M.: 2D+AS+EM+NS+SS-MoA3, 3
- Zettl, A.: 2D+EM+MS+NS-FrM3, 32
- Zhang, G.: 2D+EM+MS+NS-FrM3, 32
- Zhang, L.: HI+2D+AS+BI+MC-ThM6, 22
- Zhang, L.Z.: 2D+AS+EM+NS+SS-MoA10, 4
- Zhang, S.: EM+2D-TuA12, **12**
- Zhang, X.: SP+2D+AS+EM+MC+NS+SS-ThM6, 23
- Zhang, Y.: 2D+EM+MS+NS-FrM3, 32
- Zhao, Y.: 2D+EM+MI+MN+NS+SS+TF-ThA4, **25**
- Zheng, X.-Q.: 2D-ThP20, **31**
- Zhitenev, N.B.: 2D+EM+MI+MN+NS+SS+TF-ThA4, 25
- Zhou, G.W.: IS+2D+MC+NS+SP+SS-WeA9, 16
- Zhu, X.: 2D+EM+NS+SS+TF-WeM4, 13
- Zinoviev, O.: 2D-ThP15, 30