

# Monday Morning, October 30, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+EM+MI+MN-MoM

### Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties

**Moderator:** Andrey Turchanin, Friedrich Schiller University Jena, Germany

8:20am **2D+EM+MI+MN-MoM1 Spontaneous Mechanical Buckling in Two-Dimensional Materials: A Power Source for Ambient Vibration Energy Harvesters**, Paul Thibado, P. Kumar, S. Singh, University of Arkansas

Internet-of-Things (IoT) is projected to become a multi-trillion-dollar market, but most applications cannot afford replacing batteries on such a large scale, driving the need for battery alternatives.

We recently discovered that freestanding graphene membranes are in perpetual motion when held at room temperature [1-3]. Surprisingly, the random up-down motion of the membrane does not follow classical Brownian motion, but instead is super-diffusive at short times and sub-diffusive at long times. Furthermore, the velocity probability distribution function is non-Gaussian and follows the heavy-tailed Cauchy-Lorentz distribution, consistent with Levy flights.

Molecular dynamics simulations reveal that mechanical buckling is spontaneously occurring, and that this is the mechanism responsible for the anomalous movement. Buckling in this system occurs when the local material suddenly flips from concave to convex.

The higher kinetic energy associated with this motion is derived from the surrounding thermal waste heat, and it may be converted into an electrical current and used as the active component of small power generators known as ambient vibration energy harvesters.

References:

[1] P. Xu, M. Neek-Amal, S.D. Barber, J.K. Schoelz, M.L. Ackerman, P.M. Thibado, A. Sadeghi, and F.M. Peeters, *Nature Comm.* **5**, 3720 (2014).

[2] M. Neek-Amal, P. Xu, J.K. Schoelz, M.L. Ackerman, S.D. Barber, P.M. Thibado, A. Sadeghi, and F.M. Peeters, *Nature Comm.* **5**, 4962 (2014).

[3] M.L. Ackerman, P. Kumar, M. Neek-Amal, P.M. Thibado, F.M. Peeters, and S.P. Singh, *Phys.*, *Rev. Lett.* **117**, 126801 (2016).

8:40am **2D+EM+MI+MN-MoM2 Topological Toughening of Graphene and other 2D Materials**, Bo Ni, H.J. Gao, Brown university

It has been claimed that graphene, with the elastic modulus of 1 TPa and theoretical strength as high as 130 GPa, is the strongest material. However, from an engineering point of view, it is the fracture toughness that determines the actual strength of materials, as crack-like flaws (i.e., cracks, holes, notches, corners, etc.) are inevitable in design, fabrication and operation of practical devices and systems. Recently, it has been demonstrated that graphene has very low fracture toughness, in fact close to that of ideally brittle solids. These findings have raised sharp questions and are calling for efforts to explore effective methods to toughen graphene. Recently, we have been exploring the potential use of topological effects to enhance the fracture toughness of graphene. For example, it has been shown that a sinusoidal graphene containing periodically distributed disclination quadrupoles can achieve a mode I fracture toughness nearly twice that of pristine graphene. Here we report working progresses on further studies of topological toughening of graphene and other 2D materials. A phase field crystal method is adopted to generate the atomic coordinates of material with specific topological patterns. We then perform molecular dynamics simulation of fracture in the designed samples, and observe a variety of toughening mechanisms, including crack tip blunting, crack trapping, ligament bridging, crack deflection and daughter crack initiation and coalescence.

9:00am **2D+EM+MI+MN-MoM3 Ferroelectric Domain Control of Photoluminescence in Monolayer WS<sub>2</sub> / PZT Hybrid Structures**, Berry Jonker, C.H. Li, K.M. McCreary, Naval Research Laboratory

Single monolayer transition metal dichalcogenides (TMDs) exhibit exceptionally strong photoluminescence dominated by a combination of distinct neutral and charged exciton contributions. The dielectric screening is very low due to their two-dimensional character relative to bulk material, and their properties are thus strongly affected by their immediate environment. Because the exciton and trion binding energies are very large (~ 600 meV and ~30 meV, respectively), these characteristic emission features persist to room temperature. The samples were fabricated by mechanically transferring

large area monolayer WS<sub>2</sub> grown by a CVD process onto 100 nm thick lead zirconium titanate (PZT) films on a conducting *n*-type strontium titanate wafer. We show here that the surface charge associated with ferroelectric domains patterned into the PZT film with a conductive atomic force microscope laterally control the spatial distribution of neutral and charged exciton populations in the adjacent WS<sub>2</sub> monolayer [1]. This is manifested in the intensity and spectral composition of the photoluminescence measured in air at room temperature from the areas of WS<sub>2</sub> over a ferroelectric domain with polarization dipole pointed either out of the surface plane or into the surface plane. The photoluminescence from areas of the WS<sub>2</sub> over up polarization domains in the PZT are dominated by neutral exciton emission, while those over down domains are dominated by trion emission, consistent with the corresponding charge produced by the domains at the WS<sub>2</sub> / PZT interface. The hysteretic character of ferroelectric materials means that the TMD properties can be selectively reconfigured in a nonvolatile manner by changing the state of the ferroic substrate. This approach enables spatial modulation of TMD properties with a spatial resolution determined by the polarization domains in the underlying ferroelectric layer, with the potential for fabrication of lateral quantum dot arrays or *p-n* junctions in any geometry of choice.

[1] C.H. Li, K.M. McCreary and B.T. Jonker, *ACS Omega* **1**, 1075 (2016).

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AORD 14IOA018-134141.

9:20am **2D+EM+MI+MN-MoM4 Mechanical Instability-driven Architecturing of Atomically-thin Materials**, SungWoo Nam, University of Illinois at Urbana-Champaign

Mechanical deformations, such as buckling, crumpling, wrinkling, collapsing, and delamination, are usually considered threats to mechanical integrity which are to be avoided or reduced in the design of materials and structures. However, if materials systems and applied stresses are carefully controlled, such mechanical instabilities can be tailored to deterministically create functional morphologies that can enable powerful new functions. In particular, in atomically-thin material systems with ultralow bending stiffness, such as graphene, mechanical deformations enable new structural properties and device-level functionalities which surpass the limits of bulk material systems. In this talk, I will present our manufacturing technique on controlled deformation and straining of atomically-thin materials, and the emergent materials properties and applications of such deformed and strained atomically-thin materials. First, I will introduce shrink-manufacturing approaches to enable controlled deformation of atomically-thin materials. Second, I will introduce a wide range of new material properties enabled by the new class of 'architected atomically-thin materials'. I will discuss the surface plasmonics enabled by crumpled topographies of graphene and will further discuss shape reconfigurability which opens the door to tunable plasmonic resonance of crumpled graphene. In addition, I will share our ongoing research efforts on strained superlattice for the modulation of electronic properties. Third and last, I will present our work on adaptive/conformal and multifunctional electronics based on mechanically deformed atomically-thin materials. Our optoelectronic sensor is based exclusively on graphene and transforms the two dimensional material into three dimensional (3D) crumpled structures. This added dimensionality enhances the photoabsorption of graphene by increasing its areal density with a buckled 3D structure, which simultaneously improves device stretchability and furthermore enables strain-tunable photoresponsivity. Our approach to manufacturing architected atomically-thin materials offers a unique avenue for enabling new materials properties and engineering of advanced device functions.

9:40am **2D+EM+MI+MN-MoM5 Excitons and Exciton Complexes in Transition Metal Dichalcogenide Monolayers**, Mark Hybertsen, Brookhaven National Laboratory **INVITED**

Ultra-thin semiconductor crystals, realized from transition metal dichalcogenides and other Van der Waals materials, exhibit fascinating optical properties. In the limit of a single monolayer of material, the Coulomb interactions between the optically excited electrons and holes are particularly strong and specifically deviate in functional form from that familiar from bulk semiconductors ( $1/\epsilon r$ ) [1]. In combination with the reduced dimensionality, the resultant interaction effects are an order of magnitude stronger than those that were previously observed in quantum well structures realized in epitaxially grown multilayers. The lowest energy excitations created by optical excitation are bound electron-hole pairs (excitons). The binding energy is on the 0.5 eV scale and the ladder of bound state energies observed deviate significantly from the spectrum predicted by the conventional hydrogenic model [2]. In the presence of excess carriers, the excitons also form a bound complex with either an excess electron or hole

(trions) [1]. As the density of optically excited excitons is increased, pairs of bound excitons form (biexcitons), with a clear spectroscopic signature [3]. All of these characteristics of excitons and exciton complexes in transition metal dichalcogenides can be understood directly from the strong and modified form of the Coulomb interaction, including both the role of the environment and the impact of the intrinsic screening response of the material. In particular, a model Hamiltonian can be fully determined from microscopic inputs and solved for the properties of the observed excitons and associated complexes. Variational solutions are semiquantitative while supplying insight. A Monte Carlo approach solves the model Hamiltonian numerically exactly and gives quantitative relationships among the exciton and exciton complex binding energies [4]. Extensions of these approaches to understand excited states in more complex combinations of such layered materials will also be discussed.

Work performed in part at the CFN, which is a U.S. DOE Office of Science Facility, at BNL under Contract No. DE-SC0012704 and with resources from NERSC under Contract No. DE-AC02-05CH11231.

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11:00am **2D+EM+MI+MN-MoM9 Mechanical Properties of Polycrystalline and Defective Graphene**, *Joseph Gonzales, I.I. Oleynik, J.T. Willman*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory

Experimental investigation of mechanical properties indicates that the polycrystalline graphene grown by chemical vapor deposition is as strong as pristine. Recent experiments involving nanoindentation of graphene have also demonstrated counterintuitive increasing of Young's modulus with increasing concentrations of point defects. Using accurate description of interatomic interactions provided by novel screened environment-dependent bond order, (SED-REBO) potential, we performed large-scale molecular dynamics investigations of mechanical properties of polycrystalline and defective graphene samples under conditions mimicking nano-indentation AFM experiments. The atomically resolved characterization of the stress and strain distributions under indenter are used to understand fundamental mechanisms of graphene strength and failure. The breaking strength, the crack initiation and propagation are investigated as a function of the grain boundary structure, grain size distribution, concentration of point defects as well as the position of the indenter in respect to these extended and point defects.

11:20am **2D+EM+MI+MN-MoM10 Properties of Single Layer Transition Metal Dichalcogenides Grown by Van der Waals Epitaxy**, *Matthias Batzill*, University of South Florida **INVITED**

It is well documented that the electronic properties of transition metal dichalcogenides (TMDs) vary as their dimensions are reduced to a single layer. Also, variations depending on the substrate have been reported. In our studies we grow single- to few- layers of TMDs by molecular beam epitaxy on van der Waals substrates (mainly HOPG or bulk-MoS<sub>2</sub>). Despite the weak interactions between the monolayer and the substrate the film grows rotational aligned so that a film exhibits a single crystal orientation. This enables for example electronic structure characterization by angle resolved photoemission spectroscopy. The versatile growth procedure allows us to characterize many materials systems. First we discuss the role of the substrate for semiconducting TMDs. We study the electronics structure variation for MoSe<sub>2</sub> grown on another TMD (MoS<sub>2</sub>) and compare it with that grown on HOPG. While the band dispersion of MoSe<sub>2</sub> on HOPG resembles the expectations for free-standing MoSe<sub>2</sub> it is modified for MoSe<sub>2</sub>/MoS<sub>2</sub> due to interlayer hybridization of the chalcogen p-orbitals. A big advantage of MBE growth in vacuum is that it enables the synthesis and study of more reactive systems – like most metallic TMDs. Thus, in the second part of this talk we investigate the properties of single layer TiSe<sub>2</sub>. TiSe<sub>2</sub> is an unconventional charge density wave (CDW) material whose charge density wave transition has been associated with an excitonic insulator phase. Such an excitonic insulator is formed spontaneously if the excitonic binding energy exceeds the band gap and thus formation of excitons may become the ground state. By scanning tunneling spectroscopy we observe significant increase in the CDW-band gap opening at the  $\Gamma$ -point for the monolayer compared to few-layer materials. Furthermore, the opening of the gap varies with the substrate material, consistent with expectations for excitonic binding energies. Interestingly, we observe coherence peaks in the tunneling spectra below 50 K suggesting the formation of an excitonic condensate.

# Monday Afternoon, October 30, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+MI-MoA

### Novel 2D Materials

**Moderator:** Kathleen McCreary, Naval Research Laboratory

2:00pm **2D+MI-MoA2 Computational Characterization of 2D Perovskite Oxides Nanosheets**, *Yanfu Lu, S. Sinnott*, Pennsylvania State University

The metal oxides known as perovskites are well-known for a variety of useful properties, including piezoelectricity, ferroelectricity, and magnetism. The bulk form of these materials has been well-studied over the last few years with computational materials science methods to better understand their structure-property relationships. More recently, two-dimensional (2D) materials “beyond graphene” have attracted substantial attention because of the potential for electron confinement and engineering of the electronic structure. According to V. Gopalan & R. Engel-Herbert (*Nat. Mater.*, 2016), there are 389 theoretical predicted perovskite bulk structures,  $ABO_3$ , where over half of them have been synthesized. When the same structure is synthesized in 2D form, the stoichiometry becomes  $A_nB_{n-1}O_{3n+1}$ . To identify perovskite oxides that may be produced as free-standing nanosheets, different thickness and different crystal orientation respect to the normal surface will be considered. When density functional theory (DFT) calculations are performing to each possibility, the accurate formation energy, lattice parameter, ionic polarization, and electronic bandstructure will be obtained to reveal the new ferroelectric, magnetic, and other properties associated with the formation of 2D materials from normally three-dimensional perovskite materials. The work performed here will consist of high-throughput first principles calculations. The results will be added to a searchable on-line database of 2D materials and freely disseminated to the community.

2:20pm **2D+MI-MoA3 Electronic and Optoelectronic Physics in the van der Waals Heterojunctions**, *Philip Kim*, Harvard University **INVITED**

Recent advances of van der Waals (vdW) materials and their heterostructures provide a new opportunity to realize atomically sharp interfaces in the ultimate quantum limit. We demonstrate the enhanced electronic optoelectronic performances in the vdW heterostructures, suggesting that these a few atom thick interfaces may provide a fundamental platform to realize novel physical phenomena, such as hydrodynamic charge flows, cross-Andreev reflection across the quantum Hall edges states, and interlayer exciton formation and manipulations.

3:00pm **2D+MI-MoA5 Discovery of over 1000 New Two-dimensional Materials, 487 One-dimensional Molecular Wires and 98 Naturally Occurring Heterostructures**, *Gwoon Cheon, K.-A.N. Duerloo, A.D. Sendek, C. Porter, Y. Chen, E.J. Reed*, Stanford University

Layered materials held together by weak interactions including van der Waals forces, such as graphite, have attracted interest for both technological applications and fundamental physics. Only a few dozen two-dimensional van der Waals solids have been subject to considerable research focus, although there likely to be many more and which could have superior properties. In this work, we identify 1173 two-dimensional layered materials and 487 materials that consist of weakly bonded one-dimensional molecular chains out of 58097 inorganic materials in the Materials Project. This is an order of magnitude increase in the number of identified materials, with most materials not known as two- or one-dimensional materials. To achieve this, we developed a novel data mining algorithm that determines the dimensionality of weakly bonded components contained in bulk, 3D crystal structures based on atomic bond lengths. Data mining allows for screening of all materials in the database, including but not confined to materials belonging to known families of two- or one-dimensional materials. Moreover, we identify 98 weakly bonded heterostructures that exist as bulk materials, opening new possibilities for much-studied assembly of van der Waals heterostructures.

Data on the families of materials, band gaps and point groups for the materials identified in this work are presented. Point group and piezoelectricity in layered materials are also evaluated in single-layer forms. 325 of these materials are expected to have piezoelectric monolayers with a variety of forms of the piezoelectric tensor. This work significantly extends the scope of potential low-dimensional weakly bonded solids to be investigated.

4:00pm **2D+MI-MoA8 Anisotropic 2D Palladium Diselenide with High Mobility for Air-stable Electronics**, *Akinola Oyedele*, University of Tennessee, *L. Liang, A.A. Puzosky, S. Yang, A. Strasser*, Oak Ridge National Laboratory, *C.M. Rouleau*, Oak Ridge National Laboratory, *B.G. Sumpter, D.B. Geohegan*, Oak Ridge National Laboratory, *K. Xiao*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Two-dimensional crystals are emerging materials for the realization of nanoelectronic devices including transistors, photodetectors, and chemical sensors. These ultra-thin electronics require candidate systems with high carrier mobility, sizeable and tunable bandgaps, and air stability, which are important for high-speed, durable applications. We present a new candidate, palladium diselenide ( $PdSe_2$ ), with a similar puckered structure to black phosphorus, into the growing family of 2D materials.  $PdSe_2$  exhibits a strong layer-dependent bandgap variation from  $\sim 0.2$  eV (bulk) to  $\sim 1.3$  eV (monolayer), and an electron mobility as high as  $\sim 330$   $cm^2V^{-1}s^{-1}$  for few-layer systems. Due to their low-symmetry,  $PdSe_2$  exhibits very interesting anisotropic behavior and the strong interlayer interaction is revealed from the large thickness-dependent Raman peak shifts, agreeing with first-principles Raman simulations. Unlike, black phosphorus,  $PdSe_2$  is air-stable, thus making it a promising candidate that will spark interest for 2D electronics.

Acknowledgement: This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

4:20pm **2D+MI-MoA9 Hexagonal Boron-Carbon-Nitrogen – A Two-dimensional Direct Band Gap Semiconductor**, *Axel Enders*, University of Bayreuth, Germany, *S. Beniwal*, University of Nebraska - Lincoln, *J. Hooper*, Jagiellonian University, Poland, *DP. Miller*, SUNY Buffalo, *P.S. Costa*, University of Nebraska - Lincoln, *S.Y. Liu*, Boston College, *E.C.H. Sykes*, Tufts University, *E. Zurek*, SUNY Buffalo

Two-dimensional h-BCN, synthesized from the precursor molecule bis-BN cyclohexane on the (111) surfaces of Ir and Rh under ultrahigh vacuum, was investigated with a comprehensively suite of in-situ local probe microscopy and spectroscopy methods. The lattice structure of h-BCN is identical to that of graphene, with the graphenic sites occupied by atoms of boron, nitrogen and carbon. The film morphology exhibits a strain driven corrugation with a periodicity of 3.2 nm, reminiscent of published results for epitaxial graphene and h-BN. Due to differences in the epitaxial fit and interfacial interactions, this corrugation is more ordered on the Rh surface. Out of several candidate structures that are feasible by connecting the B<sub>2</sub>C<sub>2</sub>N<sub>2</sub> rings of the precursor molecules, the most likely film structure was established through combined density functional theory and X-ray photoelectron spectroscopy that studies the chemical environment of the film’s atoms. Local tunneling spectroscopy shows an electronic band gap of h-BCN of 1.0 eV on Rh(111) and of 1.5 eV on Ir(111). On the basis of these measured gaps and the computationally predicted electronic band structure, especially a direct electronic band gap that is intermediate to those of the zero-band gap semiconductor graphene and the insulating h-BN, and the theoretical prediction that the band gap is dependent on the molecular tiling, it can be expected that the h-BCN layers are potentially exciting candidates for 2D electronic materials.

S. Beniwal, J. Hooper, D. P. Miller, P. S. Costa, G. Chen, S.-Y. Liu, P. A. Dowben, E. C. H. Sykes, E. Zurek, and A. Enders, “Graphene-like Boron–Carbon–Nitrogen Monolayers,” *ACS Nano*, vol. 11, no. 3, pp. 2486–2493, Mar. 2017.

## Scanning Probe Microscopy Focus Topic

Room: 10 - Session SP+2D+AS+NS+SS-MoA

### Probing Electronic and Transport Properties

**Moderators:** Phillip First, Georgia Institute of Technology, Chuanxu Ma, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Probing Atomic and Electronic Structures of 2D Electronic Materials and their Heterostructures**, *Chih-Kang Shih*, University of Texas at Dallas **INVITED**

The emerging atomic layer materials offer a remarkably wide range of building blocks of nanostructures ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). Key advantages of these van der Waals materials include a broad span of energy gaps, flexibility of stacking different types of materials to form heterostructures, tunability in material properties by doping and strain, and the relative ease of integration with other electronic and

photonic devices. This talk will be focused on the usage of scanning tunneling microscopy and spectroscopy to probe the atomic and electronic structure of transition metal dichalcogenides (TMDs) and their heterostructures, including both vertical and lateral structures.

I will first introduce a comprehensive form of scanning tunneling spectroscopy (STS) which allows us to probe not only the quasi-particle band gaps but also the critical point energy locations and their origins in the Brillouin Zone (BZ) can be revealed using this comprehensive form of STS. By using this new method, we reveal the systematic trend of the critical point energies for TMDs due to atomic orbital couplings, spin-orbital coupling and the interlayer coupling. By using the vertically stacked MoS<sub>2</sub>/WSe<sub>2</sub>, I will show how interlayer coupling can be used as a new designing parameter to create a lateral 2D electronic superlattices. I will then turn attention to MoS<sub>2</sub>/WSe<sub>2</sub> lateral heterostructure where I will show a novel method to probe 2D strain tensor and how the strain changes the band profile as well as the band alignment at the interface.

2:20pm **SP+2D+AS+NS+SS-MoA3 SP-STM Study of Antiferromagnetic CuMnAs Thin Film**, *Giang Nguyen*, Oak Ridge National Laboratory, *P. Wadley, R. Campion, K. Edmonds*, University of Nottingham, UK, *F. Maccheronzi, S. Dhesi*, 3Diamond Light Source, UK, *T. Jungwirth*, University of Nottingham, UK, *A.-P. Li*, Oak Ridge National Laboratory

Antiferromagnetic (AFM) tetragonal CuMnAs thin films have attracted great research interest recently, largely due to the capability of manipulating and detecting of their AFM states with ordinary electric current. Here we report a study on a CuMnAs thin film, grown epitaxially on GaP(001) substrates, using Spin-Polarized Scanning Tunneling Microscopy (SP-STM). An arsenic capping layer is used to protect the sample during transferring through the air which is able to be subsequently removed from the surface by thermal annealing. Atomic resolution STM topographic images of CuMnAs surface are achieved which shows an interesting surface reconstruction. Scanning tunneling spectroscopy (STS) is performed to explore the electronic structure of the thin film as well as the surface step edge. SP-STM study in combination with X-ray magnetic linear dichroism-photoelectron emission microscopic (XMLD-PEEM) measurements provides further understanding of the antiferromagnetic domain structure.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

2:40pm **SP+2D+AS+NS+SS-MoA4 Probing Spin-Dependent Chemical Potential in Topological Insulator by Spin-Polarized Four-Probe Scanning Tunneling Microscopy**, *Wonhee Ko, S.M. Hus*, Oak Ridge National Laboratory, *Y.P. Chen*, Purdue University, *A.-P. Li*, Oak Ridge National Laboratory

Conversion between the charge and the spin signal is a core technology for detection of many spin-related phenomena and for the realization of spintronic devices. Topological insulators are promising candidate for such purpose because of their surface states with non-trivial spin texture. The surface states electrons have the spin and the momentum locked to each other, so the electrical current can induce the uneven shift in the spin-dependent chemical potential for different spin directions. In this talk, we utilized spin-polarized four-probe scanning tunneling microscopy to probe the spin-dependent chemical potential of the topological insulators. Utilizing ferromagnetic tips and variable probe-spacing measurements, we detected non-vanishing spin-dependent chemical potential induced by the charge current. Various tip and surface conditions were tested to confirm its origin from the spin of charge carriers through the surface states. The result demonstrates the generation of excessive spins only by electrical means in topological insulators, which would become the critical component for the future spintronic applications.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

3:00pm **SP+2D+AS+NS+SS-MoA5 Spin-charge Transport Phenomena on the Atomic Scale Studied by Multi-probe STM**, *Christoph Tegenkamp*, Leibniz Universität Hannover, Germany **INVITED**

Low dimensional metallic structures, e.g. quantum wires and films on surfaces, reveal fascinating phenomena of condensed matter physics. Among others, 2D-superconductivity, formation of charge density waves and topologically protected edge states were realized lately with atomic precision and directly probed by electronic transport. Generally, the surface science approach benefits from the fact that the low dimensional systems can be comprehensively characterized and manipulated in view of their atomic structure and electronic bands. This is a prerequisite to understand electronic transport on the atomic scale.

In this talk I will introduce the technique of surface sensitive transport by means of 4-tip STM technique and highlight some recent examples of our group from seemingly different fields, e.g. spintronic, correlated phases and mesoscopic physics. The talk covers spin-orbit coupling related phase transitions in quasi 1D atomic wire structures (Au/Si(553), Pb/Si(557) [1,2]) as well as ballistic transmittance of electrons in epitaxially grown graphene nanostructures on SiC(0001) [3-5].

[1] C. Tegenkamp, et.al. PRL 109, 266401 (2012)

[2] C. Brand, et.al. , Nat. Comm. 6, 8118 (2015)

[3] J. Baringhaus ,et.al., Nature 506, 349 (2014)

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[5] J. Baringhaus et.al. PRL. 116, 3186602 (2016)

4:00pm **SP+2D+AS+NS+SS-MoA8 Site-specific Superconducting Atomic Contacts Studied by Scanning Tunneling Microscopy**, *Yukio Hasegawa*, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

In the trend of miniaturization of devices, electrical conductance through atomic-scale contacts is of significant importance for practical application of atom switch and single molecular devices. Because of unknown atomic geometry at the junction, however, the measured conductance often fluctuates. Here in this study we have studied the conductance properties of atomic superconducting point contact with precise control of contact geometry to investigate atomic details of conductance channel formation through it.

Using a low-temperature scanning tunneling microscopy (STM), we measured the conductance between the tip and sample surface from the tunneling to contact regimes [1]. By precisely positioning the tip on atomically specific sites of a sample surface such as on-top and hollow sites, site-specific conductance evolutions were obtained. We found using a Pb tip and Pb thin film as contact forming materials the conductance at point contact is larger at hollow site than at on-top site. Furthermore, it is found that the relation of the conductance measured is reversed just before the contact formation; at 20 pm away from the contact the conductance of the hollow site is smaller than the on-top site. These peculiar conductance behaviors can be explained by the attractive chemical force and subsequent conductance channel formation between the tip apex atom and surface atoms of the thin film.

Since the measurements were performed at low temperature (1.6 K) below the superconducting critical temperature of both materials, we obtained the evolution of the Josephson current and subharmonic in-gap structures due to multiple Andreev reflection (MAR) in the conductance spectra. From the analysis of the MAR structures, the complete set of transmission probability of conduction channels, which is often called personal identification number (PIN) of the junction as it determines all the coherent transport properties, was successfully extracted [2]. We found again site dependent evolution of transmission probabilities and the number of active conduction channels at the contact formation. We will discuss on the mechanism of channel formations based on comparison with the results of theoretical analysis.

References

[1] H. Kim and Y. Hasegawa, Phys Rev Lett 114, 206801 (2015)

[2] H. Kim, M. Kawamura, T. Kato, T. Ozaki, and Y. Hasegawa, in preparation.

4:40pm **SP+2D+AS+NS+SS-MoA10 The Difference between Electron and Hole Dopant of Magnetic Element to the Superconductivity in BaFe<sub>2</sub>As<sub>2</sub>**, *Qiang Zou, L. Li, A. Sefat, D.S. Parker, Z. Gai*, Oak Ridge National Laboratory

The effect of magnetism and spin excitation in the Fe-based superconductors (FeSC) is crucial to understand their superconductivity. Both electron-(Ni) and hole-(Cr) dopant of magnetic elements could lead to suppression of the magnetic/structural phase transition in BaFe<sub>2</sub>As<sub>2</sub>. However, the Cr doped BaFe<sub>2</sub>As<sub>2</sub> doesn't show the superconductivity. Using scanning tunneling microscopy/spectroscopy, here, we compared the electronic properties of BaFe<sub>2</sub>-xNixAs<sub>2</sub> and BaFe<sub>2</sub>-xCrAs<sub>2</sub> at various temperatures. Our results will shed the light on the microscopic understanding of relation between the superconductivity and magnetism in the FeSC. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:00pm **SP+2D+AS+NS+SS-MoA11 Rapid Measurement of I-V Curves in Scanning Probe Microscopy via Bayesian Inference**, *S. Somnath, K. Law, R. Archibald, S.V. Kalinin, S. Jesse, Rama Vasudevan*, Oak Ridge National Laboratory

Current-voltage (IV) curve acquisition is the oldest and most common spectroscopic method implemented on virtually every scanning probe

microscope (SPM) available. Though in use for three decades, the basic measurement has not altered substantially in this time-frame, with the current being detected during DC pulses applied to the SPM tip. Such measurements include both a delay time after each DC voltage change (to reduce parasitic capacitance influence), as well as an integration time, to reduce noise, limiting typical measurements to a few Hz at most. Here, we introduce a new method for IV curve acquisition, based on an AC-excitation of the SPM tip, in combination with full information acquisition from the current amplifier and Bayesian inference. IV curves are acquired on a model ferroelectric system, at rates  $\sim 500\times$  faster than the current state of the art, with higher spatial and spectral resolution. The obtained results offer a complementary channel of information to supplement existing piezoresponse force microscopy studies, allowing to probe disorder at the nanoscale. Bayesian inference further allows quantification of the capacitance contribution, which can be utilized to estimate the dielectric constant of the ferroelectric, with results agreeing with reported values. These studies highlight the utility of both complete information acquisition, and Bayesian inference, in dramatically increasing the acquisition rates of data from SPM.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE (RKV, SVK, SS). This research was conducted and partially supported (SJ) at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility. Bayesian inference portion was sponsored by the Applied Mathematics Division of ASCR, DOE; in particular under the ACUMEN project (KJHL, RA).

# Tuesday Morning, October 31, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+AS+SA+SP-TuM

## 2D Materials Characterization including Microscopy and Spectroscopy

**Moderator:** Sara Barja, Materials Physics Center, San Sebastián, Spain

8:00am **2D+AS+SA+SP-TuM1 Electronic Structure of Oxygen-Intercalated Graphene on Iridium Interface**, *Yi Lin, Y. Li*, Columbia University, *J. Sadowski*, Brookhaven National Laboratory, *J. Dadap, W. Jin, R. Osgood*, Columbia University, *M.S. Hybertsen*, Brookhaven National Laboratory

We report experimental and theoretical work to understand how oxygen intercalation changes the image potential state and surface state electronic structure in a metal/graphene interface. We use tunable angle-resolved two-photon photoemission spectroscopy to probe the evolution of the electronic band structure of an epitaxially grown monolayer graphene on Ir(111) as it undergoes through a cycle involving oxygen intercalation and deintercalation. Oxygen intercalation is carried out in situ and LEED is used to determine the crystallinity of the interface in the presence or absence of the intercalated oxygen. The image state manifold and its effective mass are examined. The photoemission intensity variation in momentum space and the observation of an oxygen induced state are discussed. Furthermore, a recently proposed effective potential model at the graphene/metal interface is developed further by us to accommodate oxygen intercalation and interpret our experimental electronic structure variation with good agreements.

We acknowledge support from the US Dept. of Energy, Office of Basic Energy Sciences, under Contract Numbers DE-FG 02-04-ER-46157, DE-FG02-90ER14104, and DESC0012704.

8:20am **2D+AS+SA+SP-TuM2 Graphene Moiré Pattern Ultra-High Resolution Atomic Force Microscopy**, *Gerald Pascual, B. Kim, K. Lee*, Park Systems Inc.

The ultra-high resolution of AFM was demonstrated in a Graphene/hexagonal Boron Nitride (hBN) sample evaluation conducted by AFM. The sample consisted of hBN substrate overlaid with a Graphene layer and was scanned under ambient air. The purpose of the evaluation was to assess the AFM ability to characterize the topography of the moiré pattern that was created when one layer was set on top of the other and offset by rotation. Using non-contact AFM mode and a standard AFM probe tip, the AFM was able to successfully image the moiré pattern super lattice constant of the sample in scans as large as 500 x 500 nm. In the higher magnification image taken at a scan size of 60 x 60 nm provides the clear evidence that not only are the super lattice constants of the moiré pattern about 15 nm [1] in width, but that the spacing between each striation on the moiré pattern is roughly 4-5 nm in length. Observations of such striations in Graphene/hBN systems have been previously reported [2]. This latter distance is in line with the expected tip radius curvature values for the AFM tip used to acquire all four sets of data.

[1] A. Zandiatashbar, B. Kim, Y. Yoo, and K. Lee, *Microscopy Today* 23(06):26-31 (2015)

[2] P. Gallagher, M. Lee, F. Amet et al., *Nature Comm.* 7 10745 (2016)

8:40am **2D+AS+SA+SP-TuM3 Surface and Interface Properties of 2D MoS<sub>2</sub> and WS<sub>2</sub> Materials**, *Chia-Seng Chang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China, *Y.H. Lee*, National Tsing-Hua University, Taiwan, Republic of China **INVITED**

Two dimensional layered transition metal dichalcogenides (2D TMD), such as MX<sub>2</sub> (M = Mo, W and X = S, Se), have offered exciting new physics and chemistry, as well as potential applications in energy harvesting, electronics, and optoelectronics. Surface and interface properties of these 2D materials are fundamental to further advance them on scientific exploration and device fabrication. In this talk, we will demonstrate the growth of various TMD monolayers using ambient-pressure chemical vapor deposition. The quality of a MS<sub>2</sub> monolayer was examined by scanning probe microscopy, electron microscopy, and optical spectroscopy. We will discuss the key issues associated with the surfaces and interfaces of these materials.

9:20am **2D+AS+SA+SP-TuM5 Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing**, *Hui Zhang*, Shanghai Institute of Microsystem And Information Technology, China, *J.-H. Guo*, Lawrence Berkeley National Laboratory, *X. Sun*, Soochow University

A large-area monolayer fluorinated graphene (FG) is synthesized by a controllable SF<sub>6</sub> plasma treatment. The functional groups of FG are elucidated by various spectroscopies, including Raman, X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Raman results suggest that the defects are introduced into the monolayer graphene during the fluorination process. The fluorine content can be varied by the plasma treatment and can reach the maximum (~24.6 at% F) under 20 s plasma treatment as examined by XPS measurement. The angle dependent NEXAFS reveals that the fluorine atoms interact with the graphene matrix to form the covalent C-F bonds, which are perpendicular to the basal plane of FG. FG is applied as gas sensing material and owns much better performance for ammonia detection compared to the pristine graphene. Based on our DFT simulation results, the fast response/recovery behavior and high sensitivity of the FG gas sensor are attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG

9:40am **2D+AS+SA+SP-TuM6 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of 2D Crystals on Silicon Oxide**, *Taisuke Ohta, M. Berg*, Sandia National Laboratories, Center for Integrated Nanotechnologies, *C. Chan*, Sandia National Laboratories, *K. Keyshar*, Rice University, *G. Gupta*, University of Louisville, *P. Ajayan*, Rice University, *A. Mohite*, Los Alamos National Laboratory

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin two-dimensional (2D) crystals to predict the performance of their heterostructures useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of 2D crystals despite their importance.

Here, we present a new approach to study the electronic properties of prototypical 2D crystals, graphene, MoS<sub>2</sub>, WS<sub>2</sub>, and MoSe<sub>2</sub> monolayer and multilayer flakes, supported on thick silicon oxide (SiO<sub>2</sub>) film using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from MoS<sub>2</sub>, WS<sub>2</sub>, to MoSe<sub>2</sub> as predicted by density functional calculations. We postulate that the defects in SiO<sub>2</sub> alleviate the charging of the 2D crystals thanks to the relatively low total photoemission current due to the low energy excitation by the DUV light. This study reveals a new metrology to uncover electronic properties intrinsic to 2D crystals supported on SiO<sub>2</sub> substrates that interact minimally with the overlying 2D crystals.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. and C. C. are supported by a U.S. DOE, Office of Energy Efficiency and Renewable Energy SunShot Initiative award for BRIDGE (DE-FOA-0000654 CPS25859). K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:00am **2D+AS+SA+SP-TuM10 STM and STS Study of MoS<sub>2</sub>/WS<sub>2</sub> Heterostructures Grown by Chemical Vapor Deposition**, *Fan Zhang*, Virginia Polytechnic Institute and State University, *Z. Lu*, Tsinghua University, PR China, *H. Zheng, K. Park*, Virginia Polytechnic Institute and State University, *L. Jiao*, Tsinghua University, PR China, *C. Tao*, Virginia Polytechnic Institute and State University

2D materials like atomically thin transition metal dichalcogenides (TMDs) have received tremendous attentions for their unique properties and high potential applications. Recent developments on synthesis of 2D heterostructures through the chemical vapor deposition (CVD) method provide an unprecedented opportunity to create and tune the intriguing electronic and optical properties of 2D materials such as engineering the band gaps. These 2D heterostructures have a wide range of applications in

electronics and optics, for example, tunneling transistors, single-photon emission devices and photovoltaic devices. To further optimize and design 2D heterostructures, it is essential to investigate the structural and electronic properties at the atomic scale, which is however still lacking.

In this presentation, we will focus on a high-quality MoS<sub>2</sub>/WS<sub>2</sub> heterostructure grown on SiO<sub>2</sub> using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both MoS<sub>2</sub> monolayer and MoS<sub>2</sub>/WS<sub>2</sub> heterobilayer. Atomically resolved STM images were obtained on the monolayer, heterobilayer and the interface between the monolayer and heterobilayer. The height histograms acquired respectively on the monolayer and the heterobilayer indicate that the heterobilayer is higher than the monolayer with a height difference of  $0.85 \pm 0.10$  nm. The roughness of the monolayer and heterobilayer was for the first time quantified by STM. The root mean square (RMS) roughness of the heterobilayer is  $0.253 \pm 0.020$  nm compared with  $0.362 \pm 0.031$  nm of the monolayer. We also performed STS measurements on the system. Our STS results and density functional theory (DFT) calculations reveal the band gaps of the heterobilayer and the MoS<sub>2</sub> monolayer, which are similar to the previously reported results on MoS<sub>2</sub>/WS<sub>2</sub> heterostructures fabricated through the mechanical exfoliation method.

11:20am **2D+AS+SA+SP-TuM11 Determine the Band Alignment of 2D Semiconductor Heterostructures by Photoelectron Spectromicroscopy.** L.Y. Chang, National Synchrotron Radiation Research Center, Taiwan, Republic of China, Y.-X. Wang, Y.-H. Ku, National Tsing Hua University, Republic of China, Y.-C. Kuo, H.-W. Shiu, **Chia-Hao Chen**, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Semiconductor heterojunction (HJ) band alignment is the most important factor for the functioning of the HJ-based devices. Therefore, the prediction and determination of the HJ band offset is always a scientifically interesting and technologically important topic. As the 2D materials emerged as the building blocks for the devices with molecular thickness, the determination of band alignment of the van der Waals HJs is becoming a critical issue.

Due to the nature of the molecular thickness and the lack of large area 2D crystal, a microscope with surface sensitivity is an ideal tool to study the fundamental properties of the 2D heterostructures.

In this regard, we have employed a synchrotron radiation based scanning photoelectron spectroscopy (SPEM) to study the chemical and electronic structures of the van der Waals HJs, include the single-layer transition metal dichalcogenides, and graphene/GaN HJs. In this presentation, I will report some of the band alignments of these 2D semiconductor heterostructures.

## Magnetic Interfaces and Nanostructures Division

### Room: 11 - Session MI+2D+AC+SA+SS-TuM

#### Novel Magnetic Order at Interfaces

**Moderators:** Axel Enders, University of Bayreuth, Germany, Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+2D+AC+SA+SS-TuM2 Transition from Spatial to Magnetic Confinement in Graphene Quantum Dots.** **Fereshte Ghahari**, D. Walkup, C. Gutierrez, NIST; Maryland NanoCenter UMD, J.R. Rodriguez-Nieva, Harvard University, K.G. Watanabe, T. Taniguchi, National Institute for Materials Science, Japan, L.S. Levitov, MIT, N.B. Zhitenev, J.A. Stroscio, NIST

Recent progress in creating and probing graphene quantum dots has offered a new platform to investigate Klein tunneling related phenomena. The quasi-bound resonances in these circular resonators can be confined even further by the application of a perpendicular magnetic field where they condense into highly degenerate Landau levels. Here, we use scanning tunneling spectroscopy to visualize the transition from spatial to magnetic confinement in quantum dots created in graphene/boron nitride heterostructures. In high magnetic fields, electrons redistribute themselves due to coulomb interactions leading to compressible regions separated by incompressible strips.

8:40am **MI+2D+AC+SA+SS-TuM3 Chiral and Proximity Induced Magnetism in Magnetic Multilayers and 2D Heterostructures.** **Hyunsoo Yang**, National University of Singapore, Singapore **INVITED**

Topologically non-trivial chiral spin textures are present in systems with a strong Dzyaloshinskii-Moriya interaction (DMI) with a spatial extent of only tens to a few hundred nanometers. Thin film heavy metal/ferromagnetic bi- and multilayers have emerged as an ideal candidate for the development of such devices due to their tunability through a variation of the constituent components and relative layer thicknesses. However, to date, no chiral spin

textures have been observed in thick ferromagnetic multilayers in which the disparate magnetic layers are exchange coupled. Furthermore, previous observations required either the presence of an out-of-plane bias field or careful tuning of a geometric confining potential to stabilize the skyrmion structure. In this work, we have imaged the formation of room temperature Néel skyrmions in a symmetric Co/Pd multilayer with Lorentz transmission electron microscopy for the first time [1]. Importantly, the size of the observed skyrmions is significantly smaller than previously reported systems in which non-multilayer films are used. The formation and resolution of the internal spin structure of room temperature skyrmions without a stabilizing out-of-plane field in thick magnetic multilayers opens up a new set of tools and materials to study the physics and device applications associated with magnetic chiral ordering.

Due to the unique topology associated with their band structure, two-dimensional (2D) transition metal dichalcogenides (TMDs) such as WSe<sub>2</sub>, MoS<sub>2</sub> and WTe<sub>2</sub> provide a unique platform to develop novel electronics using the spin-valley degree of freedom. The incorporation of the heavy metal in the TMD suggests strong intrinsic spin orbit interactions, and could further result in a chiral DMI. However, confirmation of the DMI in such films and its effects on the spin ordering in the overlying magnetic layer is lacking. Further, it has recently been predicted that orbital hybridization at the TMD/FM interface may occur and result in generation of a non-negligible magnetic moment in the TMD layer. In the present study we explore the interface induced magnetism in TMD/FM films. Finally, we also explore the effects of DMI and generation of chiral spin textures that result from it by measuring the imbalance between left and right-handed domains within the ferromagnetic layer. As the polarized neutron scattering is strongly dependent on spin chirality, this method has been utilized to study chiral magnetism in multilayer structures with strong DMI.

[1] S. Pollard et al. "Observation of stable Néel skyrmions in cobalt/palladium multilayers with Lorentz transmission electron microscopy" Nat. Comm. 8, 14761 (2017).

9:20am **MI+2D+AC+SA+SS-TuM5 Surface Magnetism Induced by Interstitial Defects in PbO.** **Elvis Arguelles**, Osaka University, Japan, S. Amino, A.L.M.T. Corp, Japan, H. Nakanishi, S. Aspera, H. Kasai, National Institute of Technology, Akashi College, Japan, W.A. Dino, Osaka University, Japan

We investigated the possibility of employing the polycrystalline  $\alpha$ PbO as a spintronics device by *first principles* calculations based on the density functional theory (DFT). In particular, we explored the effects of 3d transition metal atom, Fe on the structural and electronic properties of the layered  $\alpha$ PbO (001) surface. Since it has been proven that ferromagnetic signals in experiments are often detected in thin films[1] we used a 2x2, 3-layered surface slab model of  $\alpha$ PbO with 20 Å of vacuum space to simulate this environment in this study. The impurity atoms are placed in between the surface and subsurface of the crystal. The results show that the interstitial Fe interstitial forms shorter bonds with the oxygen atoms located at the surface and second layers. Also, this impurity is found to induce magnetism in the host crystal with magnetic moment value of 2.25  $\mu_B$ , which is highly localised on the transition metal.

In the bonding process, the Fe's lower energy lying *d* states form overlaps with nearest neighbour oxygen atoms with non-bonding *d* states situated near or at the Fermi level and are spin split. These spin split orbitals induce spin polarisation of *p* impurity states of oxygen atoms in the subsurface. Moreover, the magnetic order is determined using the energy difference between the antiferromagnetic and ferromagnetic states. The energy difference is 0.068 eV, suggesting that Fe interstitial impurities induce ferromagnetism in  $\alpha$ PbO [2]. In this workshop, the effects of charge carriers to the magnetic properties will be briefly discussed. Finally, the position of the Fermi level in the density of states (DOS) suggests that in the case of  $\alpha$ -PbO with Fe interstitials where the minority non-bonding *d* states are partially filled, the Zener's ferromagnetic double exchange mechanism may be dominant and stabilizing the ferromagnetic state.

References:

- [1] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. 93, 177296 (2007)
- [2] E. F. Arguelles, S. Amino, S. Aspera, H. Nakanishi, and H. Kasai, J. Phys. Soc. Jpn. 84, 045002 (2015)

9:40am **MI+2D+AC+SA+SS-TuM6 XMCD Quest for Magnetic Proximity Effect in Ferromagnetic Insulator/Non-Magnetic Metal Interfaces.** **Andrei Rogalev**, F. Wilhelm, European Synchrotron Radiation Facility, France

The rise of spin current physics together with enormous technological advances to engineer layered structures with tailored spin-orbit interactions have placed 4d and 5d transition metals at the heart of the emerging fields of spinorbitronics, magnonics and caloritronics. In this context, magnetic

properties at the interfaces between a ferromagnetic materials and non magnetic metals with large spin-orbit coupling play a central role. Some of those heavy metals like Pt or Pd are known to exhibit so-called magnetic proximity effect, i.e. they acquire interfacial induced magnetic moments whenever they are in contact with 3d metallic ferromagnets. However, when they are grown on magnetic insulators, e.g. yttrium iron garnet (YIG), whether induced magnetic moments are indeed ubiquitous is still an open question as contradictory reports have been published. This is indeed the key question for correct interpretation of the spin Hall magnetoresistance or the newly discovered unidirectional magnetoresistance phenomena and, in more general, to understand mechanisms of pure spin currents generation. To answer this question and to unravel a possible role of magnetic proximity effects at ferromagnetic/non-magnetic interfaces, X-ray magnetic circular dichroism (XMCD) spectroscopy appears to be the method of choice due to its element selectivity and high sensitivity. In this talk, we present a thorough review of XMCD experiments aimed at detection of magnetic proximity effect in a variety of ferromagnetic insulator/non-magnetic metal interfaces.

11:40am **MI+2D+AC+SA+SS-TuM12 Depth-Dependent Measurement of Atomic Valence and Magnetization in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  Magnetic Thin Films**, *Mikel Holcomb, R. Trappen, S. Kumari, N. Mottaghi, S. Yousefi Sarraf, C.-Y. Huang, G. Cabrera*, West Virginia University

Magnetic thin films often lose their magnetic order and even bulk materials can have significant deviations of the magnetic order and other properties near surfaces and interfaces. In strongly correlated oxides, there are many competing parameters affecting the material properties, complicating the understanding of these systems. We utilize a combined approach of bulk and surface sensitive techniques measuring many film thicknesses to back out layer-by-layer properties in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) thin films. Strong changes from the bulk are observed for surfaces and interfaces. We will compare these models with theoretical predictions. LSMO has been widely proposed for diverse applications such as tunnel junctions and solid oxide fuel cells. Experimental support is provided by NSF (DMR-1608656). Theoretical support is provided by DoE (DE-SC0016176).

12:00pm **MI+2D+AC+SA+SS-TuM13 Coherent Magnetization Rotation of FeGa/NiFe Multilayers via Strain-Inducing Electric Field**, *Colin Rementer*, University of California at Los Angeles, *M.E. Jamer*, NIST, *A. Barra*, University of California at Los Angeles, *J. Borchers, A.J. Grutter, B.J. Kirby*, NIST, *G.P. Carman, J.P. Chang*, University of California at Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable electronics, extendable to implantable electronic devices. Antenna miniaturization could be enabled by multiferroic materials, which enable the efficient control of magnetic via electricity. Multiferroic antennae, composed of coupled ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude. This requires a magnetic material that is low loss, has an easily rotatable magnetization and is able to convert magnetic field to strain via magnetostriction.

Galfenol ( $\text{Fe}_{84}\text{Ga}_{16}$ , or FeGa) is a promising magnetic material due to its large magnetostriction (>200 ppm), high piezomagnetic coefficient (3 ppm/Oe), and high stiffness (70 GPa), but has high loss in the GHz regime. Permalloy ( $\text{Ni}_{81}\text{Fe}_{19}$  or NiFe) is a soft magnetic material that has very low loss in the GHz regime (<20 Oe) but almost no magnetostriction. In this work, multilayer laminates containing alternating FeGa/NiFe layers were fabricated to reduce loss at high frequencies and properties were tuned via layer number and thickness. In this work, optimized multilayer laminates containing alternating FeGa/NiFe layers were shown to exhibit desirable magnetic softness (<20 Oe), narrow FMR line width (<40 Oe), high permeability (>400), and strong magnetostriction (> 70 microstrain). The focus of this work is to determine if the rotation of the magnetization of the individual layers is coherent with applied strain.

Polarized neutron reflectometry was used to determine the depth profiles of the structure and in-plane vector magnetization as functions of applied magnetic field and voltage. Initial studies showed that a FeGa/NiFe superlattice with the structure (20 nm FeGa/7 nm NiFe)/20 nm FeGa demonstrated coherent and linear rotation of magnetization with applied strain. To probe the thickness dependence of this rotation, three single NiFe/FeGa bilayers were fabricated on PMN-PT [011] with 40 nm, 20 nm and 7 nm of NiFe on a base layer of 20 nm FeGa. Application of 400 V results in an enormous increase in spin-flip scattering, unambiguously demonstrating a substantial rotation of the magnetization perpendicular to the applied magnetic field direction for all samples measured. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. These measurements provide direct evidence of a voltage-induced rotation of the both the NiFe and FeGa magnetization as well as a means to separate the response of the magnetostrictive and non-magnetostrictive layer components.



# Tuesday Afternoon, October 31, 2017

## 2D Materials Focus Topic

Room: 16 - Session 2D+BI+MN+SS-TuA

## Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Matthias Batzill, University of South Florida

2:20pm **2D+BI+MN+SS-TuA1 Preserving Chemically Modified Graphene from Thermal and Chemical Loss of Functionality**, *Keith Whitener, W.-K. Lee*, Naval Research Laboratory, *R. Stine*, NOVA Research, *J.T. Robinson, D. Kidwell, C. Tamana, P.E. Sheehan*, Naval Research Laboratory

Chemical functionalization can dramatically alter graphene's properties, enabling one to tune its chemical and physical properties for a wide range of applications. To be useful, these modifications must be stable; however, some of these chemical modifications can be unstable, allowing the material to partially revert to unfunctionalized graphene over time. In this talk, we present our detailed studies of the kinetics of graphene hydrogenation and dehydrogenation. Single layer hydrogenated graphene can be dehydrogenated via thermal, mechanical, and chemical routes. Interestingly, bilayer graphene is much more robust to both chemical and thermal dehydrogenation than is single layer graphene. Possible mechanisms for this difference in reactivity will be discussed. Finally, we leverage the insights from these studies to first fabricate functional chemistries and electronic devices on graphene and then to transfer the devices *in toto* onto arbitrary substrates including biological ones. This enables graphene to act like a chemical "sticky note", transferring chemical and physical properties from one surface to another.

2:40pm **2D+BI+MN+SS-TuA2 Chemical Vapor Sensing with 1T/2H Phase Engineered MoX<sub>2</sub> Films**, *Adam Friedman, A.T. Hanbicki, F.K. Perkins, G.G. Jernigan, J.C. Culbertson, P.M. Campbell*, Naval Research Laboratory

Transition metal dichalcogenides (TMDs) show remarkable potential for use in chemical vapor sensor devices. They are inexpensive, inherently flexible, low-power, can be grown in large areas, and have shown high sensitivity and selectivity to electron donor analyte molecules. However, for most devices the conductance response is dominated by Schottky contacts, to the detriment of the sensitivity and obscuring the intrinsic sensing capability of the devices. We use contact engineering to transition the contacts in a MoS<sub>2</sub> FET-based chemical vapor sensor to the 1T conducting phase, leaving the channel in the 2H semiconducting state, thus providing functional Ohmic contacts to the device. We show that the resultant sensors have greatly improved electrical characteristics, are more selective, and recover fully after chemical vapor exposure—all major improvements to previous MoS<sub>2</sub> sensor devices. We study the dynamics of the sensing reactions identifying two possible models for the chemical sensing reaction with physisorption likely dominant. Additionally, we present both conductance and optical evidence that the phase transition can be induced in MoX<sub>2</sub> films by a saturating dose of strong electron donor vapor. We find that the conductance response to strong electron donors in both monolayer MoS<sub>2</sub> and MoSe<sub>2</sub> FET devices ceases after moderate exposure, with final value of the conductance being on order of that expected for the 1T phase. We also examine chemically exposed TMD films intermittently interrogated with Raman and photoluminescence spectroscopy. We observe the appearance of weak characteristic 1T phase Raman features for MoS<sub>2</sub> and we observed a quenching of the photoluminescence of both TMD films that is recoverable with annealing. The data cannot be explained solely by doping mechanisms. Our results suggest a mechanism for a new type of passive chemical vapor sensor.

[1] F.K. Perkins, A.L. Friedman, et al., *Nano Lett.* **13**, 668-673 (2013).

[2] A.L. Friedman, F.K. Perkins, et al., *Sol. St. Elec.* **101**, 2-7 (2014).

[3] A.L. Friedman, F.K. Perkins, et al., *Nanoscale* **8**, 11445 (2016).

3:00pm **2D+BI+MN+SS-TuA3 Nanopores in 2D Materials**, *Aleksandra Radenovic*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Atomically thin nanopore membranes are considered to be a promising approach to achieve single base resolution with the ultimate aim of rapid and cheap DNA sequencing. Recently, we made advances in using nanopore platform for its integration with 2D materials such as graphene or MoS<sub>2</sub>. Translocation of various types of DNA exhibits a signal amplitude that is five times higher than in the case of solid-state Si<sub>3</sub>N<sub>4</sub> membranes and a SNR of more than 10. These features are highly desirable for event detection and we take advantage of them by showing the electric-field induced unfolding of a

48 kbp long DNA molecule within the nanopore which manifests itself in the quantization of the current drop. Although single nucleotide identification and DNA sequencing using biological pores have already been demonstrated their fragility, difficulties related to measuring pA-range ionic currents together with their dependence on biochemical reagents, make solid state nanopores an attractive alternative. In this talk I will address novel applications that address identification of single nucleotides but as well go beyond DNA sequencing. We use novel solid state nanopore platform based on atomically thin nanopore membranes in 2D materials such as graphene or molybdenum disulfide for DNA detection, sequencing, water desalination and osmotic power generation.

4:20pm **2D+BI+MN+SS-TuA7 Spectroscopic Observation of Oxygen Dissociation on Nitrogen-Doped Graphene**, *Mattia Scardamaglia*, University of Mons, Belgium, *T. Susi*, University of Vienna, Austria, *C. Struzzi*, University of Mons, Belgium, *R. Snyders*, University of Mons, Belgium, *G. Di Santo, L. Petaccia*, Elettra-Sincrotrone Trieste, Italy, *C. Bittencourt*, University of Mons, Belgium

The reactivity of carbon nanomaterials towards oxygen is very poor, limiting their potential applications as low-cost, high-yield catalysts. However, nitrogen doping is an established way to introduce active sites that facilitate interaction with gases [1,2]. This boosts the materials' reactivity for gas/bio sensing and enhances their catalytic activity for the oxygen reduction reaction, promising to substitute expensive metals in fuel cell cathodes. Despite this interest, the role of differently bonded nitrogen dopants in the interaction with molecular oxygen is obscured by experimental challenges and has so far resisted clear conclusions. We study the interaction of molecular oxygen with graphene doped via nitro-gen plasma by *in situ* high-resolution synchrotron techniques, supported by density functional theory core level simulations [3,4]. The interaction with oxygen gas leads to the dissociation of the molecule and the formation of carbon-oxygen single bonds on the graphene surface, along with a band gap opening and a rounding of the Dirac cone. The change of the N 1s core level signal indicates that graphitic nitrogen is responsible for the observed mechanism: it catalyses the dissociation of an adsorbed oxygen molecule, after which the two O atoms chemisorb with epoxy bonds to the nearest and next-nearest carbon neighbours of the graphitic nitrogen. Our findings help resolve existing controversies and offer compelling new evidence of the ORR pathway.

1. Liu, X., Dai, L. (2016) Carbon-Based Metal-Free Catalysts. *Nat. Rev. Mater.*, **1**, 16064.

2. Ni, S., Li, Z., Yang, J. (2012) Oxygen Molecule Dissociation on Carbon Nanostructures with Different Types of Nitrogen Doping. *Nanoscale*, **4**, 1184-1189.

3. Scardamaglia, M. et al., (2016) Tuning Nitrogen Species to Control the Charge Carrier Concentration in Highly Doped Graphene. *2D Mater.*, **3**, 11001.

4. Scardamaglia, M. et al., (2017) Spectroscopic observation of oxygen dissociation on nitrogen-doped graphene. Submitted

4:40pm **2D+BI+MN+SS-TuA8 Back to Black: Can Molecular Networks Preserve the Surface of Black Phosphorus?**, *Vladimir Korolkov*, The University of Nottingham, UK, *I.G. Timokhin, R. Haubrichs*, CristalTech Sàrl, Switzerland, *S. Yang, M. Schröder*, University of Manchester, UK, *P.H. Beton*, The University of Nottingham, UK

Black phosphorus (BP), one of several allotropic forms of phosphorus, has a layered structure and is a narrow gap semiconductor with a bulk band gap of ~0.3 eV. Similar to other layered materials it can be exfoliated with scotch tape to form a single layer of black phosphorus known as phosphorene. Unlike gapless graphene, phosphorene has a band-gap which was predicted, and later confirmed to be ~2 eV. The band gap is thickness dependent and thus can be easily tuned. Since the first reports of exfoliation of BP, and some 100 years after the first high-pressure synthesis of black phosphorus crystals by Bridgman in 1914, phosphorene or few layered BP has been widely used to construct transistors, including flexible devices.

One of the biggest challenges in BP and phosphorene research remains its stability under atmospheric conditions.

In this work we explore a new route to the solution of this problem through an investigation of the compatibility of BP with the formation of supramolecular networks which have monolayer thickness and are stabilised by non-covalent *in-plane* interactions, specifically hydrogen bonding. We find that supramolecular networks can be formed on BP and demonstrate this for a mono-component nanoporous array of trimesic acid (TMA) and the bimolecular network formed by cyanuric acid (CA) and melamine (M). While the more open TMA array does not passivate the BP surface, the hexagonal melamine cyanurate (CA.M) array is highly effective and provides

protection under ambient conditions over a period of more than three months. In addition, we identify the orientation of the CA.M relative to the rows of phosphorus atoms at the surface and, normal to the rows, observe moiré effects which are characteristic of a well-ordered interfacial structure. We have further demonstrated that CA.M monolayers on BP provide a stable platform for the sequential growth of additional molecular layers, for example, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB), leading to the formation of a supramolecular heterostructure and demonstrating the facility for further functionalisation of the BP substrate.

Our work demonstrates that a single layer of CA.M can successfully passivate the surface of BP and preserve it intact for at least 3 months. We believe that this facile approach of depositing a passivating organic monolayer stabilised by in-plane non-covalent bonding could be extended to the protection of other two-dimensional materials with air sensitive atomically flat surfaces, and is likely compatible with other solvents and molecules.

The work also presents outstanding examples of high resolution AFM imaging achieved under ambient conditions.

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5:00pm **2D+BI+MN+SS-TuA9 Defect-mediated Properties of Single-layer MoSe<sub>2</sub>**, *Sara Barja*, Materials Physics Center, San Sebastián, Spain, *S. Wickenburg*, *Z.-F. Liu*, *Y. Zhang*, Molecular Foundry, Lawrence Berkeley Lab, *A. Pulkkin*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *S. Refaely-Abramson*, *B. Schuler*, Molecular Foundry, Lawrence Berkeley Lab, *H. Ryu*, Lawrence Berkeley National Laboratory, *D. Qiu*, University of California at Berkeley, *M. M. Ugeda*, CIC nanoGUNE, Spain, *Z.-X. Shen*, Stanford Institute of Materials and Energy Sciences, *S.-K. Mo*, *M.B. Salmeron*, Lawrence Berkeley National Laboratory, *M.F. Crommie*, University of California at Berkeley, *D.F. Ogletree*, Molecular Foundry, Lawrence Berkeley Lab, *O.V. Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *J.B. Neaton*, *A. Weber-Bargioni*, Molecular Foundry, Lawrence Berkeley Lab

**INVITED**

Properties of two-dimensional transition metal dichalcogenides are highly sensitive to the presence of defects in the crystal structure. A detailed understanding of the defect electronic structure may lead not only to the control of the material's properties through defect engineering towards a particular device application, but also may lead the emergence of novel physico-chemical functionalities. We show how linear mirror twin boundaries and individual atomic defects in single-layer MoSe<sub>2</sub> alter the electronic structure of the pristine semiconductor. Such linear and point defects tend to be highly localized in the plane, which imposes the need of experimental and theoretical characterization of the defects at the atomic level. Using non-contact atomic force microscopy and scanning tunneling spectroscopy, we directly correlate the morphology and electronic properties of structural defects in MoSe<sub>2</sub> at the defect-length scale. We provide direct evidence for the existence of isolated, one-dimensional charge density waves at mirror twin boundaries in single-layer MoSe<sub>2</sub>. We also determine the local density of states of Se vacancies in monolayer MoSe<sub>2</sub> and discuss the correlation to density functional theory calculations, studying the role of the GW approximation to reproduce the energetics of the valence and conduction band as measured in the experimental dI/dV spectra.

5:40pm **2D+BI+MN+SS-TuA11 Scalable Flexible Graphene Gate TMD Biosensors**, *RamSurya Gona*, *C.H. Naylor*, *A.T. Johnson*, University of Pennsylvania

Two dimensional transition metal dichalcogenides, such as MoS<sub>2</sub> and WS<sub>2</sub>, have been shown to be promising materials for use in bio-sensing. I will present our work on the fabrication of scalable flexible MoS<sub>2</sub> field effect transistors with patterned graphene back-gate. Flexible devices were fabricated on a Kapton substrate and incorporating graphene as the back-gate material due to its biocompatibility and its favorable physical properties. Monolayer MoS<sub>2</sub> single-crystal flakes were grown over large area by chemical vapor deposition, and then transferred onto a pre-patterned electrode array, resulting in a device yield > 70% and an average mobility of 1.0 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. To create nano-biosensors, the surface of the MoS<sub>2</sub> was functionalized via a reengineered mu-opioid receptor and the devices were tested against opioid solutions of various concentrations. This work provides a pathway for the integration of MoS<sub>2</sub> and other TMDs onto flexible/wearable/implantable devices that for trace detection of opioids or other chemicals. This work was supported by the National Science Foundation through EFRI 2DARE ENG-1542879

6:00pm **2D+BI+MN+SS-TuA12 Development and Validation of Polarized Models for Peptide-Graphene Interactions**, *Amanda Garley*, University of Colorado Boulder, *N. Saikia*, Michigan Technological University, *R. Berry*, Air Force Research Laboratory, *H. Heinz*, University of Colorado Boulder

Biosensor technologies require the understanding of interactions between organic and inorganic materials to tune electric response functions, such as

peptide assembly on graphitic substrates. Laboratory characterization of specific interactions and molecular assembly can be complemented by atomistic molecular simulations, as well as by quantum-mechanical analysis of band gaps and expected conductivity.

As a first step, we improved common dispersive interatomic potentials for graphite to include pi electron density at virtual sites. The new model reproduces experimental cation-pi energy, X-ray structure, density, cleavage energy, hydration energy, contact angle and elastic constants. As a result we have improved existing models which gave the wrong sign of hydration energies and deviations up to 1000% in these properties from experiment. The parameters are embedded in CHARMM, CVFF, TEAM-AMBER, and other common force fields as part of the INTERFACE force field. An analysis of binding residues, binding energies, conformations, and dynamic information of molecular mobility on the surfaces will be presented.

## 2D Materials Focus Topic

Room: 15 - Session 2D-TuA

### Growth of 2D Materials

**Moderator:** Taisuke Ohta, Sandia National Laboratories, Center for Integrated Nanotechnologies

2:20pm **2D-TuA1 A New Approach to the Synthesis of High-quality Graphene on Silicon Carbide**, *Piotr Ciochoń*, *J.J. Kolodziej*, Institute of Physics, Jagiellonian University, Poland

**A new approach to the synthesis of high-quality graphene on silicon carbide**

One of the most widely used methods of graphene synthesis is the graphitization of the (0001) and (000-1) surfaces of silicon carbide crystal. In order to obtain high quality graphene, it is necessary to slow down the excessive sublimation of silicon, observed at temperatures at which graphene ordering occurs. The most widely used method to accomplish this is carrying out the graphitization process in the presence of atmospheric pressure of inert buffer gases, such as argon.

We propose an alternative approach to solve this issue, which relies on exposing SiC surface during thermal annealing to the high-purity beam of silicon, obtained from an external sublimation source. The proposed solution has two advantages over the buffer-gas method. Firstly, it reduces the amount of impurities present near the surface by several orders of magnitude, as compared to even the purest inert gases at the atmospheric pressure. Secondly, it allows for precise control over the process parameters, leading to the possibility of near-equilibrium graphitization.

We have performed a thorough study of the process, systematically varying the parameters, such as graphitization temperature, process time and the silicon flux density and found that the synthesized graphene is characterized by very high degree of crystallographic ordering, low concentration of defects and large size of monocrystalline domains. Varying the process parameters, we were able to control the number of synthesized graphene layers, without the deterioration of overall graphene quality. Moreover, the process has shown a remarkable reproducibility, allowing for proper standardization of the synthesized material, a step considered crucial for the widespread introduction and use of graphene-based devices.

Our method allows for fast, reproducible synthesis of a very high-quality graphene directly on an insulating surface and is perfectly suited for preparing hybrid heterostructures and intercalation of foreign atoms. We have performed preliminary studies of intercalation with Cr atoms, during the graphitization process, as our approach allows to overcome several problems, resulting in unsuccessful past attempts.

2:40pm **2D-TuA2 Cation-Eutectic Transition via Sublattice Melting in CuInP<sub>2</sub>S<sub>6</sub>/In<sub>4/3</sub>P<sub>2</sub>S<sub>6</sub> van der Waals Layered Crystals**, *M.A. Susner*, Air Force Research Laboratory, *M. Chyasnawichyus*, *Q. He*, *B.S. Conner*, *D.A. Cullen*, *P. Ganesh*, *D. Shin*, *J.W. McMurray*, *A. Borisevich*, *M.A. McGuire*, Oak Ridge National Laboratory, *Y. Ren*, Argonne National Laboratory, *Petro Maksymovych*, Oak Ridge National Laboratory

Metal thiophosphate materials family offers a materials toolbox with broad functionality that includes magnetism, ferroelectricity and electron correlations. Here we report on heterostructure engineering of layered ferroelectric CuInP<sub>2</sub>S<sub>6</sub>, which controllably introduces 1D and 2D chemical boundaries into the crystal on bulk scale. Single crystals of mixed Cu<sub>1-x</sub>In<sub>1+x/3</sub>P<sub>2</sub>S<sub>6</sub> spontaneously phase separate into ferroelectric (CuInP<sub>2</sub>S<sub>6</sub>) and paraelectric (In<sub>4/3</sub>P<sub>2</sub>S<sub>6</sub>) chemical domains, providing a new route to functional in-plane heterostructures in layered and 2D materials. We used high temperature x-ray diffraction and in-situ electron microscopy to conclusively demonstrate that this material forms a single phase at high temperature, and

to identify the mechanism by which the phase separation proceeds upon cooling. Above 500 K  $\text{Cu}_{1-x}\text{In}_{1+x/3}\text{P}_2\text{S}_6$  adopts a heavily disordered structure with respect to metal/vacant sites occupying the octahedral sites within a layer, thus indicating high  $\text{Cu}^+$  and  $\text{In}^{3+}$  mobilities. However, the framework of  $\text{P}_2\text{S}_6$  anions remains invariant across this transition. Considering the results of our detailed measurements of the transition temperature as a function of Cu/In ratio, we propose that this transition can be understood as eutectic melting on the cation sublattice, conceptually similar to intermediate temperature behavior of halide superionic conductors. Such a model suggests that the transition temperature for the melting process is relatively low because it requires only a partial reorganization of the crystal lattice. As a result, varying the cooling rate through the phase transition controls the lateral extent of chemical domains over several decades in size, forming an intricate mesh of in-layer heterostructures comprised of domains with distinct cation compositions. Heterostructures can be formed, destroyed, and reformed by thermal cycling. Using this mode of lattice manipulation, we demonstrate that the ferroelectric  $T_c$  can be both increased to a nearly record level (about 20K higher than the pure bulk  $\text{CuInP}_2\text{S}_6$  of 305K) and completely suppressed well below room temperature, without changing the physical sample, chemical composition, or loss of reversibility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

[1] Susner et al., "Metal Thio- and Selenophosphates as Multi-Functional van der Waals Layered Materials", *Advanced Materials*, in press (2017)

[2] Susner et al., Cation-eutectic transition via sublattice melting in  $\text{CuInP}_2\text{S}_6/\text{In}_{4/3}\text{P}_2\text{S}_6$  van der Waals layered crystals, *ACS Nano* in review (2017).

### 3:00pm 2D-TuA3 Direct, Real-Time Observation of Layer-by-Layer Growth of a 2D Semiconductor using *In Situ* X-ray Synchrotron Radiation, H.J. Bullen, R.K. Nahm, S. Vishwanath, G. Xing, James Engstrom, Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. In a number of studies, thin films of these materials are produced by techniques such as exfoliation. While these techniques have been invaluable concerning the measurement of electronic and other important physical properties, growth of thin films of these materials is essential to fully exploit their promise in a variety of devices. In particular, there is a great need to develop an understanding of the growth process such that one can at will deposit an arbitrary number of layers (e.g., 1, 2, 3 etc.) on a variety of possible substrates. Here we report on the metal-organic MBE growth of thin films of  $\text{WSe}_2$  on sapphire substrates using  $\text{W}(\text{CO})_6$  and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of  $\text{W}(\text{CO})_6$  in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence, both *in situ* and in real time. We have examined growth for a variety of conditions, including the flux and incident kinetic energy of the  $\text{W}(\text{CO})_6$ , and the substrate temperature. After a short incubation time, we observe steady-state epitaxial growth of crystalline  $\text{WSe}_2$  thin films. X-ray fluorescence confirms formation of a stoichiometric thin film of  $\text{WSe}_2$ . Perhaps most interestingly, during epitaxial growth we observe strong and sustained oscillations at the "anti-Bragg" condition for X-ray scattering, consistent with layer-by-layer growth. These results enable a direct determination of how each successive layer forms<sup>[1]</sup>, and how these depend on process conditions. Concerning process conditions, we observe a spectacular change in the growth as the incident kinetic energy of the  $\text{W}(\text{CO})_6$  is varied. At sufficiently low values of the incident kinetic energy we observe no growth, while at higher values we observed sustained 2D LbL growth. These results point to the importance of incident kinetic energy in driving the dissociative chemisorption of the  $\text{W}(\text{CO})_6$  precursor.

[1] See, e.g., A. R. Woll, T. V. Desai and J. R. Engstrom, *Quantitative modeling of in situ x-ray reflectivity during organic molecule thin film growth*, *Phys. Rev. B* **84**, 075479/1-14 (2011).

### 3:20pm 2D-TuA4 Crystallization Kinetics of Photonically Annealed 2D Materials, N.R. Glavin, R.A. Vila, R. Kim, R.S. Rao, M.E. McConney, B. Maruyama, L.J. Bissell, Air Force Research Laboratory, R.H. Rai, Air Force Research Laboratory; University of Dayton, Christopher Muratore, University of Dayton

Synthesis of flexible electronic devices using low-cost, naturally abundant materials (e.g.,  $\text{MoS}_2$ ) directly onto inexpensive polymeric materials promises manufacturing of flexible 2D devices at economically viable scales enabling use of their unique physics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic

annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as  $\text{MoS}_2/\text{WS}_2/\text{BN}$  multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices. Detailed kinetic studies of crystal formation were accomplished through high throughput in-situ Raman spectroscopy at different surface temperatures and ambient conditions. With this technique, heterostructures were formed incorporating multiple TMD layers that were annealed simultaneously, and insights into the role of surface diffusion for metal and chalcogen species, and factors dictating activation energy for two-dimensional crystallization will be discussed.

### 4:20pm 2D-TuA7 Intercalation Then Ordering of Oxygen Leading to Isolation Then Etching of Monolayer *h*-BN on Copper, C. Ma, J. Park, Oak Ridge National Laboratory, L. Liu, University of Tennessee, Y.-S. Kim, M. Yoon, Arthur Baddorf, Oak Ridge National Laboratory, G. Gu, University of Tennessee, A.-P. Li, Oak Ridge National Laboratory

The interaction of *h*-BN, the thinnest 2D insulating material, with oxygen is important technologically, but has proven complex. *h*-BN has strong covalent bonds that exhibit great stability and multilayers have been recommended as an oxidation resistant barrier for both metal and graphene substrates. At the same time, oxygen is predicted to form adsorbed chains and then to cut *h*-BN sheets along the chains. We have exposed monolayer *h*-BN on copper substrates to air and then examined the surface with scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) after annealing to 600°C in ultrahigh vacuum. The active adsorbent is identified as oxygen, as expected. More surprising is evidence that oxygen is intercalated between the *h*-BN and copper and forms both quasi-1D and 2D ordered patterns on the predominantly (100) oriented substrate. STM images display double rows of O in hollow sites forming quasi-1D chains preferably along the moiré patterns and, in areas of higher coverage nucleated by steps, a  $p(2\times 2)$ -O superstructure. Efficient O diffusion along moiré channels is supported by first-principles density functional theory (DFT). Despite searches, a  $p(2\times 2)$ O structure on clean Cu(100) has not been observed; instead, higher density  $c(2\times 2)$ O islands are created there. XPS intensities here are consistent with the lower coverage  $p(2\times 2)$ O stabilized by the *h*-BN layer. Intercalated O increases the *h*-BN to Cu distance thereby decreasing the van der Waals interaction. Both STM  $dI/dV$  and DFT reflect this increased isolation by a 1.7 eV increase in the monolayer band gap, governed by a decrease in the contribution of the Cu surface to the density of states.

Intercalated oxygen is ultimately not stable and extended annealing at 600°C etches away the *h*-BN. In contrast to previous models, *h*-BN is removed by oxygen found underneath rather than adsorbed on the surface. Etching occurs along *h*-BN zig-zag edges and leads to finally to complete removal of the film. These new mechanisms observed for oxygen introduction, organization, and etching offer opportunities to better understand the stability of *h*-BN monolayers and to exploit the addition of oxygen to modify electronic properties or for formation of nanoscale structures.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

### 4:40pm 2D-TuA8 Polished Nickel Substrates for Large-area Multilayer Graphene Films, Stefan Lehnardt, J.T. Rowley, K. Larsen, Brigham Young University, J. Abbott, Moxtek, R.R. Vanfleet, R.F. Davis, Brigham Young University

We show that the roughness of polycrystalline nickel has a significant effect upon the homogeneity of large-area multilayer graphene films grown via chemical vapor deposition. Nickel foil serves as a substrate/catalyst for this multilayer graphene growth. By mechanical polishing nickel foils and reducing roughness from ~100 nm to ~10 nm, we have obtained graphene films with fewer defects and greater thickness uniformity. Mechanical properties were determined by bulge testing and bending measurements on microscale cantilevers. Films from polished foils are thinner and show higher burst pressures.

### 5:00pm 2D-TuA9 Heterostructures of Carbon Nanomembranes and Graphene as a Platform for Electrochemical Sensing, D. Kaiser, A. Winter, C. Neumann, Friedrich Schiller University Jena, Germany, A. Centeno, A. Zurutuza, Graphenea, Spain, T. Weimann, Physikalisch-Technische Bundesanstalt, Germany, Andrey Turchanin, Friedrich Schiller University Jena, Germany

Chemical functionalization of single-layer graphene (SLG) is of key importance for applications in functional electronic devices such as, e.g., field-effect transistor (FET) based nanosensors. However, the electronic structure of graphene is typically degraded after the functionalization, which significantly restricts the applications. Here, we employ a route to non-destructive chemical functionalization of graphene with amino terminated 1 nm thick carbon nanomembranes<sup>1</sup> ( $\text{NH}_2$ -CNM) generated via electron beam

induced crosslinking of aromatic self-assembled monolayers. The electrical response of the NH<sub>2</sub>-CNM/SLG heterostructures in electrolyte-gated FETs shows their high electrical capacitance enabling for effective sensor applications. The electrochemical performance of CNM/graphene FETs for detection of pH-values was studied in parallel with their in detail surface science characterization. We show that the high electronic performance of pristine SLG is preserved in the developed amino-terminated hybrids and demonstrate the pH-sensing with excellent sensitivity and reproducibility. Finally, we discuss the perspectives for highly selective biological sensing with the developed device concepts.

[1] A. Turchanin and A. Gözlhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

5:20pm **2D-TuA10 Nucleation of 2D WS<sub>2</sub> by Plasma Enhanced Atomic Layer Deposition from WF<sub>6</sub>, H<sub>2</sub> Plasma and H<sub>2</sub>S – Impact on Grain Size and Charge Transport**, Benjamin Groven, A. Nalin Mehta, University of Leuven, Belgium, Q. Smets, T. Schram, H. Bender, W. Vandervorst, I. Radu, M. Caymax, M. Heyns, A. Delabie, IMEC, Belgium

To exploit the semiconductor properties of two-dimensional (2D) transition metal dichalcogenides in ultra-scaled nano-electronic devices across large area substrates, these materials need to be deposited with a highly crystalline structure and a controlled number of monolayers by manufacturable deposition techniques. Where the majority of the 2D materials in literature are grown by Chemical Vapor deposition (CVD), Atomic Layer Deposition (ALD) is investigated here as an alternative deposition technique. In ALD, (sub-)monolayer growth control is possible as the deposition is based on self-limiting surface reactions. In addition, due to the relatively low deposition temperature, the 2D materials can be grown directly on temperature sensitive structures at Back-End-Of-Line (BEOL) compatible deposition temperatures. As such, a material transfer from the growth to the target substrate can be avoided.

In Atomic Layer Deposition (ALD), the structure of 2D materials is determined by the nucleation mechanisms. However, the nucleation mechanisms of 2D materials by ALD have so far not yet been investigated. In this work, we investigate the nucleation behavior of WS<sub>2</sub> from a recently reported Plasma-Enhanced (PE)ALD process from WF<sub>6</sub>, H<sub>2</sub>S and H<sub>2</sub> plasma [1]. We show how the crystallinity and domain size of these layers depends on the starting substrate and the deposition temperature, and how they influence the semiconductor properties of WS<sub>2</sub>. WS<sub>2</sub> is grown on 300 mm Si substrates covered with either 30 nm amorphous Al<sub>2</sub>O<sub>3</sub> or 90 nm thermally grown SiO<sub>2</sub>.

At 300 °C, the growth of WS<sub>2</sub> is strongly enhanced on the Al<sub>2</sub>O<sub>3</sub> surface. The high nucleation density of  $(2.2 \pm 0.1) \cdot 10^{14} / \text{cm}^2$  promotes fast closure of the first WS<sub>2</sub> layer. On the other hand, the combination of the high nucleation density with lateral and vertical growth contributions limits the crystal domain size to 5-30 nm. By choosing a substrate that has a lower reactivity towards the PEALD precursors, e.g. SiO<sub>2</sub>, the nucleation density decreases to  $(2.0 \pm 0.1) \cdot 10^{11} / \text{cm}^2$ . An even lower nucleation density of  $(6 \pm 1) \cdot 10^{10} / \text{cm}^2$  is obtained on SiO<sub>2</sub> by increasing the deposition temperature to 450 °C due to the increasing mobility of the ad-atoms on the surface. By lowering the reactivity of the H<sub>2</sub> plasma to further delay nucleation, the WS<sub>2</sub> crystals grow primarily in a lateral direction, which further increases the crystal grain size to 250 nm. Despite the low deposition temperatures, the WS<sub>2</sub> behaves as a semiconductor in back-gated transistors, that show an  $I_{\text{max}}/I_{\text{min}}$  ratio of at least  $10^5$  [2].

[1] B. Groven et al., *Chem. Mater.*, 2017, 29 (7), pp 2927–2938

[2] T. Schram, Q. Smets et al. VLSI satellite workshop 2017 (accepted)

5:40pm **2D-TuA11 Surface Intercalation of Two Disparate Metals in Graphite: Copper and Dysprosium**, Ann Lü-Rosales\*, P.A. Thiel, Iowa State University and Ames Laboratory

In this study, we use STM to investigate the intercalation of atomic metals, copper (Cu) and dysprosium (Dy), in the surface of graphite that is pre-treated with Ar<sup>+</sup> bombardment.

Surface intercalated Dy rafts have a characteristic height of  $0.61 \pm 0.03$  nm, with structured moiré patterns atop faceted rafts. DFT calculations on intercalated Dy rafts support our experimental observation: instead of a dilute,  $(\sqrt{3} \times \sqrt{3})R30^\circ$  arrangement of Dy atoms as in the well-known stage-1 Dy graphite intercalation compound (GIC), our Dy rafts are dense and are composed of three contiguous layers of Dy sandwiched between graphitic layers.

In the case of Cu, for which no bulk GIC's are known, we achieve surface intercalation of Cu in ion-bombarded graphite. Spanning temperatures of 600 – 900 K, the morphology of intercalated Cu responds sensitively. At 600 – 800 K, intercalated Cu forms faceted islands that are variable in heights,

ranging from 1.7 nm to as tall as 35 nm. At 850 K, intercalated Cu no longer forms faceted islands; instead, round clusters ranging from ~0.3 nm to 10 nm tall are present. At 900 K, small and round features ~0.3 nm tall prevail. Larger clusters are presumably removed by desorption. High resolution imaging atop a Cu island sheds light on the number of carbon overlayers and shifting in the stacking sequence of carbon lattice, potentially due to strain as a result of intercalation.

Relative to known bulk GIC's, our work shows that metals on graphite surfaces adopt configurations that are different in two ways. First, the metals form dense intercalated surface islands; and second, metals which do not intercalate in the bulk can do so on the surface. Surface intercalation of other metals can be envisioned.

This work is supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division through the Ames Laboratory, which is operated by Iowa State University under contract # DE-AC02-07CH11358.

## Magnetic Interfaces and Nanostructures Division Room: 11 - Session MI+2D+AC+NS-TuA

### Spin-Orbit Phenomena at Surfaces and Interfaces

Moderators: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Axel Hoffmann, Argonne National Laboratory

2:20pm **MI+2D+AC+NS-TuA1 Coherent Control over Spin-polarized Dirac Surface State in Topological Insulators**, Kenta Kuroda, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

A number of challenging efforts have been recently made for a coherent control of highly spin-polarized Dirac surface states in various topological insulators, suggesting ultrafast optospintronic devices. However, these attempts generally neither realized a selective photoexcitation of the surface state, since the optical response is typically governed by the bulk properties, nor do they exclusively probe the excitation of the surface state, because the applied techniques are not surface sensitive.

In my talk, I will report that the difficulty can be overcome by direct band mapping of a photoexcitation in the Dirac surface state with time-resolved two-photon photoemission spectroscopy combined with ultrashort tunable pump pulses in mid-infrared regime. It is revealed that the mid-infrared excitation permits a direct population of the unoccupied Dirac-cone owing to a novel optical coupling across the Dirac point. In addition, the direct optical transition induces a pronounced asymmetry of the transient surface population in *k*-space which indicates an excitation of a net spin-polarized photocurrent even with linear pump polarization [Phys. Rev. Lett. **116**, 076801 (2016)]. Moreover, the pump polarization can control the asymmetric population, i.e. the surface photocurrent, through the coherent optical transition of the surface Dirac-cone [Phys. Rev. B **95**, 081103(R) (2017)]. By observing the decay of the asymmetric population, the ultrafast dynamics of the photocurrent in the surface Dirac-cone is directly investigated. Our discovery promises important advantages of photoexcitation by mid-infrared pulses for optospintronic applications.

3:00pm **MI+2D+AC+NS-TuA3 Enhancement of Voltage-Controlled Magnetic Anisotropy Through Metallic Insertion at the CoFeB|MgO Interface**, Kevin Fitzell, X. Li, C.T. Karaba, A. Buditama, G. Yu, K. Wong, University of California at Los Angeles (UCLA), D. Wu, UCLA; Fudan University, Republic of China, N. Altieri, C. Grezes, UCLA, N. Kioussis, CSU, Northridge, S.H. Tolbert, UCLA, Z. Zhang, Fudan University, Republic of China, J.P. Chang, P.K. Amiri, K.L. Wang, UCLA

Paramount to the continued scaling of MRAM devices is a comprehensive understanding and control of the factors affecting the interfacial phenomena that occur at the CoFeB|MgO interface, from which the perpendicular magnetic anisotropy (PMA) of the CoFeB originates. Efficient manipulation of this PMA using an applied voltage, known as the voltage-controlled magnetic anisotropy (VCMA) effect, offers significant energy savings over electric-current-controlled alternatives such as STT-RAM. *Ab initio* studies in the literature on Fe/MgO interfaces revealed a dependence of the VCMA effect on the oxidation state of interfacial Fe atoms<sup>1</sup> and on the addition of various heavy metal insertion layers<sup>2</sup> at the CoFeB/MgO interface. While this effect of metallic insertion layers at the CoFeB/MgO interface has not been extensively studied experimentally, inserting a thin Mg layer at the CoFeB/MgO interface has been shown in the literature to improve the (001) texture of the MgO, the tunneling magnetoresistance (TMR) ratio of the MTJ,

\* NSTD Student Award Finalist

and the thermal stress stability of the CoFeB layer's PMA.<sup>3,4</sup> What is lacking in the literature, however, is experimental work studying the dependence on the VCMA effect of Mg insertion layers at the CoFeB/MgO interface.

In this work, the impact of several types of metallic insertion layers (Ta, Pt, and Mg) at the CoFeB/MgO interface on the VCMA characteristics and other magnetic properties is studied. For the case of Mg insertion, four different regimes of materials properties were observed, corresponding to the oxidation state at the CoFeB/MgO interface. Inserting an ultrathin Mg layer of 0.1–0.3 nm yielded a VCMA coefficient of ~100 fJ/V×m, representing more than a factor of 3 improvement over average values of ~30 fJ/V×m reported in Ta/CoFeB/MgO-based structures. Ultrathin Ta and Pt insertion layers also showed a small improvement, yielding VCMA coefficients around 40 fJ/V×m. Electrical, magnetic, and synchrotron-based X-ray diffraction results reveal that a 1.1–1.3 nm Mg insertion layer gives rise to the highest perpendicular magnetic anisotropy and saturation magnetization, as well as to the best CoFe and MgO crystallinity; Mg insertion layers thicker or thinner than this give rise to either under- or over-oxidation of the CoFeB/MgO interface. These results demonstrate that precise control over the oxidation level at the CoFeB/MgO interface is crucial for the development of electric-field-controlled perpendicular magnetic tunnel junctions with low write voltage.

3:20pm **MI+2D+AC+NS-TuA4 THz Radiation Generated from Interfacial Rashba Spin-orbit Coupling**, M.B. Jungfleisch, Argonne National Laboratory, Q. Zhang, Argonne National Laboratory, W. Zhang, Oakland University, J.E. Pearson, H. Wen, Axel Hoffmann, Argonne National Laboratory

Electromagnetic terahertz (THz) radiation is a versatile tool for a wide variety of sensing technologies ranging from security systems to medical applications. Commonly THz radiation is generated using semiconducting materials and using their inherent charge dynamics. Recently, it was also demonstrated that optical excitation of fast spin current pulses in magnetic materials may generate strong broadband THz radiation from transverse spin transport phenomena, known as spin Hall effects. These experiments rely on a bulk conversion of spin currents into charge current, which then subsequently generate the THz radiation. Here we investigate whether interfacial spin-orbit coupling phenomena may also be an efficient source for generating THz radiation. For this purpose we combine a bilayer of Ag and Bi, which is known to have strong Rashba-type spin-orbit coupling at its interface with a magnetic CoFeB layer. Upon optical excitation we also observe in this system THz radiation. Additional experiments with individual Ag and Bi layers show that this radiation originates from interfacial spin galvanic effects. Furthermore, we demonstrate that the amplitude of the THz radiation varies with the helicity of the incident optical light pulse. These observations open up new perspectives for the development of ultrafast spintronic devices.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Lithographic patterning was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357).

4:20pm **MI+2D+AC+NS-TuA7 Spin-orbit Coupled d-electron Surface States of Delafossite Oxides**, Phil King, University of St Andrews, UK

INVITED

The ABO<sub>2</sub> family of delafossite oxide metals has recently found renewed prominence due to their remarkable transport properties. The Pd- and Pt-based cobaltates are the most conductive oxides known, with room-temperature resistivities lower per carrier even than copper metal [1,2]. Meanwhile, giant low-temperature mean-free paths of up to 10<sup>5</sup> lattice spacings make hydrodynamic effects of the electron fluid observable in mesoscopic samples [3] and lead to a curious negative longitudinal magnetoresistance [4]. This is all underpinned by extremely broad bandwidths of the bulk electronic structure around the Fermi level, dominated by Pd/Pt-derived carriers that behave remarkably like free electrons [2], in part mediated by an unusual interplay with correlations which renders the Co block insulating. The crystal structure is polar, however, opening the potential for their surface electronic structures to be dramatically different to that of the bulk [5,6]. Here, we will show how these surfaces support strongly spin-split electronic states, and discuss the intriguing interplay of spin-orbit coupling and electronic interactions that they host.

Key collaborators on this work include Veronika Sunko (St Andrews and Max-Planck Institute for Chemical Physics of Solids, Dresden), Federico Mazzola (StA), and Helge Rosner, Pallavi Kushwaha, Seunghyung Khim, and Andy Mackenzie (MPI-CPFS).

[1] Hicks *et al.*, Phys. Rev. Lett. 109 (2012) 116401

[2] Kushwaha *et al.*, Science Adv. 1 (2015) e1500692

[3] Moll *et al.*, Science 351 (2016) 6277

[4] Kikugawa *et al.*, Nature Commun. 7 (2016) 10903

[5] Kim *et al.*, Phys. Rev. B 80 (2009) 035116

[6] Noh *et al.*, Phys. Rev. Lett. 102 (2009) 256404

5:00pm **MI+2D+AC+NS-TuA9 Understanding the Interfacial Interaction and Isotope Effects in Organic Spin Valve Structures**, Alexandra Steffen, N. Herath, J. Keum, H. Zhang, K. Hong, J. Jakowski, J. Huang, J. Browning, C.M. Rouleau, I.N. Ivanov, V. Lauter, Oak Ridge National Laboratory

Spin-dependent phenomena, such as the extended spin relaxation time and spin diffusion length due to the very weak spin-orbit coupling found in organic spin valves (OSV), are of interest from the view of both fundamental research and development of low power spintronic devices.

While deuteration is widely used for contrast variation measurements under the assumption that the deuterated structure shows identical characteristics in comparison to the protonated version, recently, strong isotopic effect on optoelectronic properties was reported and a remarkable reduction in the open circuit voltage was found [1].

In OSV systems, the interfacial properties are crucial for the understanding of the origin of the macroscopic properties. Still, to identify the exact behavior of the interfaces remains challenging, especially for buried soft matter/hard matter interfaces. Here, we utilize via Polarized Neutron Reflectometry to study depth-resolved the magnetic and chemical structure.

Our system under investigation are prototype spintronic devices with LSMO/polymer/Co trilayer structure, where polyfluorene (PFO) is selected as an optimal 'hole' conducting polymer through the model pre-screening based on the electron affinity and electron's effective mass values obtained from theoretical calculations. Using the exceptional syntheses and deuteration capabilities we have recently completed syntheses of four PFO isotopes, i.e., protonated (P), main-chain deuterated (MD), side-chain deuterated (SD) and fully deuterated (FD) PFOs. By creating such modified polymers, the subatomic, intermolecular and interfacial interactions are modified and characteristics like the  $\pi$ - $\pi$  interaction become tunable. For neutron scattering experiments, the nuclear cross-section varies with the isotopic substitution, thus via changing the contrast with chain-specific deuteration, different parts of a sample are investigated individually.

While our main goal is the understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus on the details of the structural and magnetization profiles on both LSMO/polymer and polymer/Co interfaces and their impact on the coupling between magnetic layers. We will present the results obtained via Polarized Neutron Reflectometry and discuss the interpretation of the depth-resolved magnetometry study.

[1] Ming Shao *et al.*, The isotopic effects of deuteration on optoelectronic properties of conducting polymers. *Nature Communications*, 5:3180, January 2014.

5:20pm **MI+2D+AC+NS-TuA10 Dispersion and Spin Structure of Conduction Bands of Single-layer TMDC's on Au(111)**, Philipp Eickholt\*, M. Holtmann, Westfälische Wilhelms-Universität Münster, Germany, C.E. Sanders, M. Dendzik, M. Bianchi, P. Hofmann, Aarhus University, Denmark, M. Donath, Westfälische Wilhelms-Universität Münster, Germany

In the field of 2D materials, single-layer transition metal dichalcogenides, especially MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub>, play an important role. Due to their exceptional optical and electronic properties, they are promising materials for optoelectronic applications [1]. The key to understand the material properties is a profound knowledge of the electronic structure. While the occupied electronic structure was investigated in a number of studies, the crucial information about the dispersion and spin structure of the conduction bands is still missing.

Spin- and angle-resolved inverse photoemission (SRIPE) [2] is the ideal technique to study dispersion and spin structure of the unoccupied electronic bands. In this talk, we present a SRIPE study of the conduction bands of single-layer WS<sub>2</sub> [3] and MoS<sub>2</sub> [4] grown on Au(111).

The focus of the presentation will be on the lowest conduction band near the K valley, which is decisive for the optoelectronic properties of the materials. The results will be discussed in consideration of a recent pump-probe (TR-ARPES) experiment [5], which determined the band gap of the "pumped" system.

[1] D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012)

- [2] S.D. Stolwijk *et al.*, Rev. Sci. Instrum. **85**, 013306 (2014)  
 [3] M. Dendzik *et al.*, Phys. Rev. B **92**, 245442 (2015)  
 [4] A. Bruix *et al.* Phys. Rev. B **93**, 165422 (2016)  
 [5] A. Grubišić Cabo *et al.*, Nano Lett. **15**, 5883 (2015)

5:40pm **MI+2D+AC+NS-TuA11 Unraveling the Spin Structure of Unoccupied States in Bi<sub>2</sub>Se<sub>3</sub>**, *Markus Donath, C. Datzler, A. Zumbütle*, Westfälische Wilhelms-Universität Münster, Germany, *J. Braun*, LMU München, Germany, *T. Förster, A.B. Schmidt*, Westfälische Wilhelms-Universität Münster, Germany, *J. Mi, B. Iversen, P. Hofmann*, Aarhus University, Denmark, *J. Minár*, University of Pilzen, Czech Republic, *H. Ebert*, LMU München, Germany, *P. Krüger, M. Rohlfiing*, Westfälische Wilhelms-Universität Münster, Germany

In topological insulators, spin-orbit coupling leads to the emergence of metallic topological surface states crossing the fundamental band gap. The optical control of spin currents in topological surface states opens new perspectives in (opto-) spintronics. To understand these processes, a profound knowledge about the dispersion and the spin polarization of both the occupied and the unoccupied electronic states is required. We present a joint experimental and theoretical study on the unoccupied electronic states of the topological insulator Bi<sub>2</sub>Se<sub>3</sub> [1]. We discuss spin- and angle-resolved inverse-photoemission results in comparison with calculations for both the intrinsic band structure and, within the one-step model of (inverse) photoemission, the expected spectral intensities. This allows us to unravel the intrinsic spin texture of the unoccupied bands at the surface of Bi<sub>2</sub>Se<sub>3</sub>.

- [1] Datzler *et al.*, Phys. Rev. B **95**, 115401 (2017)

## Sustainability Focus Topic

**Room: 5 & 6 - Session SU+2D+MS+NS-TuA**

## Membranes, Thin Films, and Sensors

**Moderators:** Keith Brown, Boston University, Roya Maboudian, University of California at Berkeley

2:20pm **SU+2D+MS+NS-TuA1 Protecting Food and Water Quality: Considerations for Materials Innovation**, *Susan Duncan*, Virginia Polytechnic Institute and State University **INVITED**

Innovation in materials and membranes provides opportunity for enhancing water and food safety, diversifying and expanding water and food sources, protecting nutrient quality and bio-availability, and improving human health and well-being. Food and water are transitioned from their original sources into resources for animal feed and human food through production, processing, packaging, and distribution/retail stages. Throughout these stages, membranes and materials for physical and chemical separations, microbiological control, analysis and measurement, capture and containment are required.

Synergistic partnerships, among scientific disciplines and between private-public entities, encourage innovation in the design and applications of materials and membranes for discoveries and advancements in water and food processing and packaging. The objective of this discussion is to showcase the engagement of chemists, engineers, and food scientists in approaching and resolving challenges relating to water and food processing, safety, and quality and the relationship to the consumer. Three featured examples, relating to membranes and materials, include:

**Aquaculture:** Recirculating water for the purpose of raising fish has high economic and global impact by increasing sustainable supply of high quality food proteins for feeding the growing global population. Challenges include the need for removing biosolids, small molecular weight molecules, and bacteria that influence fish health and quality of the fish as a food source.

**Water Safety from Source and Supplier to the Consumer:** Protecting public health is the primary role of water treatment. Changes in water disinfectant treatment, e.g. chlorine to chloramine, affect material stability, safety and performance and can lead to significant economic impacts and consumer concerns.

**Food Packaging Functionality:** Protecting food and beverage freshness from processing to purchase requires understanding of the food system, the process, and storage conditions. Innovative materials that interfere with light energy can protect beverage and food quality for retaining freshness and nutrient retention for enhancing human health.

Expanding our scientific continuum from molecule to materials through process, package and consumer perspective enriches and guides scientific discovery.

3:00pm **SU+2D+MS+NS-TuA3 Real-time Detection of Water Contaminants Using a Graphene-based Field-Effect Transistor Sensing Platform**, *Junhong Chen*, University of Wisconsin - Milwaukee **INVITED**

The National Academy of Engineering identified “providing access to clean water” as one of the top 10 grand challenges for engineering in the 21<sup>st</sup> century. A central requirement for safe drinking water is the availability of low-cost and real-time water quality monitoring. Current detection methods for critical analytes in water are often too expensive or unsuitable for in-situ and real-time detection (*an unmet need*). As a result, there is a lack of water quality monitoring along the water distribution line and at the point of use, which is inadequate because of potential deterioration in water quality within water distribution systems (e.g., Flint Water Crisis). This talk will unveil a powerful approach to real-time water sensors through a graphene-based field-effect transistor platform. The working principle of the sensor is that the conductivity of 2D nanomaterial channel (usually measured in resistance) changes upon binding of chemical or biological species to molecular probes anchored on the graphene surface. As such, the presence and the concentration of analytes, such as heavy metals, bacteria, and nutrients, can be rapidly determined by measuring the sensor resistance change. The talk will introduce the performance of the sensor for detection of various water contaminants and focus on the molecular engineering aspects of the sensor device through both theoretical and experimental approaches. The talk will end with a brief introduction on the translation of the platform technology from concept to prototype product through partnership with industries.

5:00pm **SU+2D+MS+NS-TuA9 Nanocellulose Thin Films and Nanocellulose Aerogels**, *Kenneth Carter*, University of Massachusetts - Amherst, *A. Chang, K.L. Martin, Y. Li*, University of Massachusetts – Amherst **INVITED**

Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. We have developed a new method for the preparation of well-dispersed cellulose nanofibrils and nanocrystals. Advantageously, the method does not require the use of harsh acids and excludes the use of catalytic oxidants such as 2,2,6,6-tetramethyl-1-piperidine-N-oxyl (TEMPO). Furthermore, the nanofibrils and nanocrystals produced by the method are easily re-dispersible and give stable aqueous dispersions. Transparent, robust nanocellulose thin films were prepared with outstanding anti-fogging properties. Most recently, nanocellulose was used to prepare aerogel/foam materials using a new fabrication method. The aerogels are mechanically stable and robust. Our new aerogel fabrication process obviates the need to use freeze-drying or low pressure solvent removal. We will present data on new nanocellulose aerogels with densities ranging from 5-100 mg/cm<sup>3</sup>.

5:40pm **SU+2D+MS+NS-TuA11 Fabrication and Characterization of Thermal Treated Si/Si+Ge Thin Films For Energy Harvesting**, *S. Budak, Z. Xiao, Michael Howard, B. Rodgers, M. Alim*, Alabama A&M University

Thermoelectric thin film devices were prepared from the alternating nanolayers of Si and Si+Ge to form the Si/Si+Ge thin films structures using DC/RF magnetron sputtering system. Fabricated thermoelectric devices were treated at different temperatures for an hour for each case to form quantum (nano) structures in the alternating nanolayers of Si and Si+Ge to increase both the Seebeck coefficients and the electrical conductivity and decrease the thermal conductivity. The prepared Si/Si+Ge thin film thermoelectric devices were characterized using the Seebeck coefficient measurement; the four probe van der Pauw resistivity measurement and the laser thermal conductivity systems for in-plane geometries. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). Thermal treatment showed positive effects on the thermoelectric properties of Si/Si+Ge thin films on the selected temperatures. The findings will be presented during the meeting.

### Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

6:00pm **SU+2D+MS+NS-TuA12 Thermoelectric Properties of Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> Thin Films Annealed at Different Temperatures**, *S. Budak, Z. Xiao, M. Howard, Breonna Rodgers, M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> thin films using DC/RF magnetron sputtering system. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity

system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM/EDS).

**Acknowledgement**

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

# Wednesday Morning, November 1, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+EM+SS+TF-WeM

## 2D Materials Growth and Fabrication

**Moderator:** Aleksandra Radenovic, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

8:00am **2D+EM+SS+TF-WeM1 Chemical Bath Deposition of Phase Selective MoS<sub>2</sub> on Templated Surfaces, Jenny Hedlund, A.V. Walker, University of Texas at Dallas**

Transition metal dichalcogenides (TMDs) have a wide range of physical properties, and consequently have applications in nanoelectronics and biosensors. While TMD materials have been well studied, a simple method for two-dimensional large area thin film deposition of these materials has yet to be achieved. Chemical bath deposition (CBD) is a robust method by which to grow uniform thin films, and offers many advantages over other techniques including low deposition temperatures ( $\leq 50^\circ\text{C}$ ), synthetic flexibility, and it is inexpensive. In this work, CBD is used to deposit large-area ultra-thin molybdenum disulfide (MoS<sub>2</sub>), a group VI TMD, and the resulting deposits are investigated by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS). These TMDs are most commonly found to possess trigonal prismatic crystalline structure (2H phase) and therefore are semiconductors. Although less widely studied, TMDs can also possess octahedral crystallinity to form the 1T phase. The 1T phase exhibits different properties to the 2H phase, and has applications in sensing, metal contacts and catalysis. By using substrates that mimic the TMD crystalline structure for deposition we have shown that MoS<sub>2</sub> can be deposited with large-area crystallites observed. SEM images of deposition performed on highly oriented pyrolytic graphite show large area flakes,  $\sim 100\ \mu\text{m}$  in diameter. Smooth thin films were also deposited on sapphire, and functionalized self-assembled monolayers (SAMs). XPS results show that Mo 3d and S 2s peaks are present in the expected positions and ratios. We further demonstrate that the deposited MoS<sub>2</sub> phase is likely determined by the surface chemistry of the substrate. Using Raman spectroscopy measurements, the thickness and phase of the film are elucidated. CBD of MoS<sub>2</sub> was further characterized using TOF SIMS to elucidate the reaction mechanisms as well as the stability of the deposited film.

8:20am **2D+EM+SS+TF-WeM2 Atomic Layer and Metalorganic Chemical Vapor Deposition of MoS<sub>2</sub> and WS<sub>2</sub> from bis(tert-butylimido)-bis(dialkylamido) Compounds, Berc Kalanyan, J.E. Maslar, W.A. Kimes, B.A. Sperling, NIST, R. Kanjolia, EMD Performance Materials**

Layered 2D transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness-dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires vapor-phase deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a desirable route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting surface chemistry. However, since ALD conditions are only met at relatively low deposition temperatures, most ALD films are amorphous. Some consider this a useful feature of ALD, since film growth rate and structural development can be decoupled by separating the deposition and crystallization steps. In contrast, metalorganic chemical vapor deposition (MOCVD) enables direct growth of crystalline films, but requires careful process control and precursor selection to achieve the required level of thickness control. The tradeoffs between direct CVD growth and post-sulfurization and annealing of amorphous/metallic films is the focus of this work.

In this paper, we present a comparison of process characteristics and film properties, including growth rate, thickness, morphology, composition, and crystallinity, as a function of two deposition routes: ALD and MOCVD. We deposited thin films using (N<sup>t</sup>Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>M and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C for ALD and 400°C to 900°C for pulsed MOCVD on SiO<sub>2</sub>/Si substrates. Precursor saturation conditions were evaluated using in situ infrared flow measurements and ex situ X-ray photoelectron spectroscopy. As-deposited and sulfur-annealed films were further evaluated using X-ray diffraction, optical spectroscopies, and microscopy. As-grown ALD films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in higher growth rates, which also introduced a weak CVD component to the growth. Deposition rates were  $<1.0\ \text{\AA}/\text{cycle}$  at 350°C. As-deposited films were successfully annealed to 2H-MoS<sub>2</sub> under a sulfur atmosphere, which

also removed residual nitrogen. As-grown MOCVD films were polycrystalline 2H-MoS<sub>2</sub> at 600°C. Pulsed injections of precursor enabled Å-level control over aggregate film thickness. For both processes, wafer-scale growth and uniformity in a perpendicular flow reactor were demonstrated on 50 mm substrates. We will also present process characteristics for the analogous WS<sub>2</sub> route and discuss initial data from MoS<sub>2</sub>/WS<sub>2</sub> nanolaminates.

8:40am **2D+EM+SS+TF-WeM3 Epitaxial Growth of Atomically Thin Transition Metal Dichalcogenides and their Electronic Structures, Sung-Kwan Mo, Lawrence Berkeley National Laboratory** **INVITED**  
Transition metal dichalcogenides (TMDCs) is a versatile material platform with a variety of electrical, optical, and topological properties that can be controlled through thickness, strain, field, and other perturbations. In this talk, I will first discuss the growth of atomically-thin TMDC films, such as MoSe<sub>2</sub>, WSe<sub>2</sub>, WTe<sub>2</sub>, NbSe<sub>2</sub>, and TaSe<sub>2</sub>, with a layer-by-layer thickness control, using molecular beam epitaxy. Then, I will present how we investigate the electronic structures of these films using angle-resolved photoemission spectroscopy and scanning tunneling microscopy.

9:20am **2D+EM+SS+TF-WeM5 Terminations and Treatments of Silicon Carbide Surfaces to Promote Epitaxial Hexagonal Boron Nitride Deposition by Chemical Beam Epitaxy, Daniel Pennachio, N.S. Wilson, A.P. McFadden, T. Brown-Heft, University of California at Santa Barbara, K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr., U.S. Naval Research Laboratory, C.J. Palmström, University of California at Santa Barbara**

This work examines the epitaxial deposition of single-crystal hexagonal boron nitride (h-BN) on silicon carbide substrates through the use of surface treatments which promote suitable nucleation and growth. Silicon carbide, 6H-SiC(0001), was chosen as a candidate substrate due to its market availability, high crystalline quality, temperature stability, and potential coincident lattice match to h-BN. Boron nitride was deposited in ultra-high vacuum (UHV) environments by chemical beam epitaxy (CBE) on SiC substrates through thermal decomposition of borazine at high temperatures. Different SiC surface reconstructions reached through exposure to elemental silicon and subsequent *in-vacuo* annealing were examined for their effect on h-BN nucleation and epitaxial arrangement. Along with reconstructions produced through UHV annealing, CVD-grown epitaxial graphene on 4H-SiC was also utilized as a growth surface. Growth past full single atomic layer coverage of sp<sup>2</sup>-bonded material (either h-BN deposited layers or graphene substrates) proved difficult with the accessible temperature range and precursor flux. Various surface treatment approaches were investigated to promote additional layer growth.

Deposited h-BN films on the SiC reconstructed surfaces were found to be near-stoichiometric and of single- to few-atomic layer thickness, as determined by *in-situ* x-ray photoelectron spectroscopy (XPS) B1s:N1s peak area ratios and substrate peak attenuation. Progression of *in-situ* reflection high-energy electron diffraction (RHEED) during h-BN deposition provides evidence of a difference in film nucleation between the Si-rich (3x3) and the C-rich SiC surface reconstructions: while the (3x3) reconstruction quickly transitioned to a (1x1) reconstruction upon precursor dosing, the C-rich reconstruction persisted despite thicker depositions. XPS of the C-rich surface showed a higher binding energy shoulder of the C1s peak, indicative of sp<sup>2</sup>-hybridized bonding in a graphene-like buffer layer at the surface. Triangular nuclei seen by scanning electron microscopy after deposition on the C-rich SiC surface suggests epitaxial arrangement to this buffer layer. *In-situ* scanning probe microscopy and *ex-situ* transmission electron microscopy were performed to acquire additional information on film morphology. The influence of different surface treatments for increasing the thickness of h-BN growth will be presented.

9:40am **2D+EM+SS+TF-WeM6 Photo-Chemical Modification of Monolayer Transition Metal Dichalcogenides, Tariq Afaneh, P.K. Sahoo, H.R. Gutierrez, University of South Florida**

Fabrication of in-plane 2D heterostructures is a crucial step to advance in the development of a truly 2D optoelectronics. Different approaches have been attempted, including in situ sequential growth of two different materials and post-growth modification of the chemical composition in a 2D monolayer. In this work, we studied a post-growth technique that exploits the radiation-matter interaction under a controlled atmosphere. Using a homemade sealed mini-chamber with a quartz optical viewport, a laser beam (532 nm) was focused onto the sample, consisting on MoSe<sub>2</sub> or WSe<sub>2</sub>, while keeping a reactive sulfur-rich atmosphere within the chamber. The spatially localized photo-chemical conversion was in situ monitored by mapping the temporal evolution of the Raman active modes. The process can be tuned thereby choosing appropriate laser power, exposure time, and reactive gas environment. The complete or partial conversion was further confirmed by



collecting the photoluminescence spectra at the desired exposed sites. The time-dependent intensities of the Raman peaks were fitted to exponentially decaying functions. Depending on the reaction parameters, two different processes with distinct time constants can be identified. The following mechanisms for the photo-conversion are proposed: (i) creation of Se vacancies in the TMD materials due to the energy absorbed from the laser radiation, (ii) cracking of sulfur containing molecules from the gas environment and subsequent incorporation of the sulfur atoms into the Se vacancy sites. The optimization of this process will allow to develop techniques based on photo-induced chemical reactions for local doping, alloying and the fabrication of in-plane TMD heterostructure.

11:00am **2D+EM+SS+TF-WeM10 Bottom-up synthesis of Graphene Nanomembranes with Tunable Porosity**, *Christof Neumann*, Friedrich Schiller University Jena, Germany, *M. Füser*, Goethe University Frankfurt, Germany, *M. Mohn*, Ulm University, Germany, *D. Kaiser*, Friedrich Schiller University Jena, Germany, *A. Götzhäuser*, Bielefeld University, Germany, *U. Kaiser*, Ulm University, Germany, *A. Terfort*, Goethe University Frankfurt, Germany, *A. Turchanin*, Friedrich Schiller University Jena, Germany

The potential of atomically thin materials like graphene or carbon nanomembranes (CNMs) [1] for separation or ultrafiltration technologies is based on their negligible thicknesses enabling the ballistic transport of atoms and molecules through the nanomembranes. For such implementations, large scale production of perforated nanomembranes with well-defined sizes of nanopores has to be established. Here we present a scalable method to produce atomically thin graphene nanomembranes with tunable porosity using aromatic self-assembled monolayers (SAMs) as molecular precursors. We employ N-containing 4-(1H-pyrrol-1-yl)thiophenol, 4-(2,5-dimethyl-1H-pyrrol-1-yl)thiophenol and 4-(pyrimidin-2-yl)phenylthiol SAMs on polycrystalline copper foils to convert them into CNMs via low energy electron irradiation induced crosslinking and then to pyrolyze CNMs into nanoporous graphene sheets in vacuum. We characterize the formed supported and suspended graphene nanosheets by different complementary spectroscopy and microscopy techniques including X-ray photoelectron (XPS) and Raman spectroscopy, atomic force (AFM), helium ion (HIM) and high-resolution transmission electron microscopy (HRTEM) as well as by electric transport measurements. We demonstrate that the pore size and the graphene crystallinity can be adjusted by the production parameters and discuss the mechanisms.

[1] A. Turchanin and A. Götzhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

11:20am **2D+EM+SS+TF-WeM11 Cu Single Crystal Substrates for Growth of CVD Graphene**, *Tyler Mowll*, University at Albany, SUNY, *Z.R. Robinson*, SUNY Brockport, *C.A. Ventrice, Jr.*, SUNY Polytechnic Institute

To provide a systematic study of the CVD graphene growth process, a study of the growth of graphene on single crystal Cu substrates, with terminations along the (100), (110), and (111) planes, was performed. Synthesis was performed in an ultra-high vacuum (UHV) chamber using a modified setup to allow growth at pressures as high as 1 Torr. Ethylene was used as the precursor gas. To control Cu sublimation at the elevated growth temperatures, an Ar overpressure was used. This arrangement allowed for the preparation of clean Cu surfaces by sputtering and annealing the Cu crystals in UHV, followed by graphene growth at low pressure, and in-situ analysis with low energy electron diffraction. It was found that surface termination plays a strong role in the rotational alignment of the nucleating graphene grains and the decomposition rate of the ethylene. It was observed that single-domain epitaxy is possible on Cu(111) when the ethylene pressure is 5 mTorr or less. However, growth on both Cu(100) and Cu(110) result in a minimum of two domains. In addition, ex-situ EELS is currently being performed on well-ordered epitaxial graphene films grown on Cu(111) and Cu(100) to determine the effect of the graphene-Cu interaction on the electronic properties of the graphene.

11:40am **2D+EM+SS+TF-WeM12 Paper and Circuits, only Atoms Thick**, *Jiwoong Park*, University of Chicago **INVITED**

2D layered materials are like paper: they can be colored, stitched, stacked, and folded to form integrated devices with atomic thickness. In this talk, I will discuss how different 2D materials can be grown with distinct electrical and optical properties (coloring), how they can be connected laterally to form patterned circuits (stitching), and how their properties can be controlled by the interlayer rotation (twisting). We will then discuss how these atomically thin papers and circuits can be folded to generate active 3D systems.

## MEMS and NEMS Group

Room: 16 - Session MN+2D-WeM

### 2D NEMS

**Moderators:** Zenghui Wang, Case Western Reserve University, Zhu Diao, Halmstad University/Stockholm University

8:00am **MN+2D-WeM1 Micro-patterned Graphene Temperature Sensors on Different Substrates**, *B. Davaji*, Marquette University, Cornell University, *H.D. Cho*, Dongguk University, *Jong-Kwon Lee*, National Nanofab Center in Korea, *T.W. Kang*, Dongguk University, *C.H. Lee*, Marquette University

Since the performance of electronic devices suffers from elevated temperatures as a result of self-heating, outstanding thermal properties of graphene are considered to be suitable for both instrumentation and integrated microelectronic applications [1]. Also, recently developed techniques for fabricating complex graphene structures in micro/nano scale [2, 3] make graphene a great candidate for temperature sensor applications due to its excellent electrical properties, outstanding mechanical strength, and high thermal conductivity.

In this study, micro-fabricated single-layer graphenes on a SiO<sub>2</sub>/Si, a SiN membrane, a suspended architecture, and a spatially nano-modulated Si substrate are presented for their use as temperature sensors. These graphene temperature sensors act as resistance temperature detectors, showing a quadratic dependence of resistance on the temperature. The observed resistance change of the graphene temperature sensors are explained by the temperature dependent electron mobility relationship ( $\sim T^4$ ) and electron-phonon scattering. The transient response analysis of the graphene temperature sensors on different substrates shows that the graphene sensor on the SiN membrane exhibits the highest sensitivity due to low thermal mass, whereas the sensor on SiO<sub>2</sub>/Si reveals the lowest one. In addition, the graphene on the SiN membrane reveals the fastest response, as well as better mechanical stability in comparison with the suspended graphene sensor. Therefore, we can expect that the graphene temperature sensors with an extremely low thermal mass will be used in various applications requiring high sensitive and fast operation.

#### References

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8:20am **MN+2D-WeM2 Characterizing the Resonant Behavior and Quality Factors of 3C-SiC Diaphragms Using Frequency Analysis and the Ring-Down Technique**, *Yongkun Sui*, *H. Chong*, *K. Shara*, *C.A. Zorman*, Case Western Reserve University

Silicon carbide (SiC) has become a mainstream material for microelectromechanical systems (MEMS) due to its unique combination of outstanding electrical, mechanical and chemical properties, making it the preferred choice for applications in harsh environments where Si is not well suited. SiC is an attractive material for MEMS that utilize mechanical transduction due to its high Young's modulus, mechanical strength and chemical inertness. The cubic polytype of SiC (3C-SiC) is particularly attractive for resonant sensing applications because SiC diaphragms can readily be fabricated from thin films by Si bulk micromachining.

This abstract reports the findings of a study to characterize the resonant behavior of MEMS-based single crystalline 3C-SiC diaphragms. The 1 x 1 mm<sup>2</sup> diaphragms consisted of 3C-SiC films that were heteroepitaxially grown on Si by APCVD and created by conventional bulk micromachining. The diaphragms were excited into resonance under vacuum using a piezoelectric PZT crystal and their vibratory behavior was assessed using a custom-built optical interferometer.

Over 20 resonant peaks were observed from a 250 nm-thick diaphragm for frequencies up to ~2 MHz. Quality factors were initially determined by analyzing the full-width-at-half-maximum of particular resonant peaks from the frequency spectrum. Although the fundamental mode exhibited a quality factor of ~3000, at least 3 other modes had high Q's of >20,000, with the highest being over 119,000. For those high quality factor resonance modes, the vibration energy took ~1 s to fully dissipate. As such, the frequency response had to be measured in a relatively slow manner otherwise the residual energy would propagate, resulting in a broadened peak. The ring-down test, which specifically characterizes the vibration energy dissipation

rate, was used to measure the high quality factors. The highest Q at (2,3) mode was found to be 195,981 using ring-down test compared to 119,200 from the FWHM method. The resonance modes of the SiC diaphragm showed a non-linear Duffing behavior when the drive voltage exceeded 200 mV. The resonance peaks exhibited jump discontinuities and one of the half-power points ceased to be experimentally visible. In the nonlinear regime, quality factors measured by ring-down test differ only 1% from those in the linear region measured by both the FWHM and ring-down techniques.

**8:40am MN+2D-WeM3 Ion Radiation Effects in Silicon Carbide (SiC) Crystal Probed by Multimode Diaphragm Resonators, Hailong Chen, V. Pashaei, Case Western Reserve University, W. Liao, C.N. Arutt, Vanderbilt University, H. Jia, Case Western Reserve University, M.W. McCurdy, Vanderbilt University, C.A. Zorman, Case Western Reserve University, R.A. Reed, R.D. Schrimpf, M.L. Alles, Vanderbilt University, P.X.-L. Feng, Case Western Reserve University**

Radiations effects from energetic particles (ions) and electromagnetic waves (photons) on electronics (e.g., MOSFETs and ICs) have been widely investigated for applications in radiative harsh environments including space and nuclear reactors [1]. Radiation effects in mechanical domain, however, remain largely unexplored due to challenges in capturing and detection [2]. Meanwhile, most of preliminary studies on radiation effects in mechanical domain have been limited to Si structures and devices [3-4], while those on more intriguing radiation-durable materials such as SiC have not been investigated yet.

Here we report on experimental investigation and analysis of energetic ion radiation effects on silicon carbide (SiC) crystal, by exploiting a novel scheme of 4 vertically stacked resonant micromechanical SiC diaphragms. The SiC diaphragms are fabricated using a standard photolithographic and wet etching process to form resulting diaphragms (1 mm × 1 mm × 2.1 μm). An S-series Pelletron system is employed to irradiation oxygen ions into the SiC diaphragms (14.3MeV, 8h radiation, corresponding to a total fluence of  $5.6 \times 10^{15}/\text{cm}^2$ ). Before and after radiation, multimode resonances are characterized in vacuum by using an ultrasensitive optical interferometry system. We have observed as large as ~9% frequency shifts (the largest value to date) in the multimode resonances of the 3rd diaphragm (counting from top in the stack) where most ions are expected to stop, as well as obvious quality (Q) factor degradation, which result from ionizing and displacement radiation damage. The 1st and 2nd diaphragms, which ions have mostly penetrated, exhibit moderate multimode frequency downshift of ~2% owing to displacement damage, while the 4th diaphragm shows the least frequency shift ~0.1%. The diaphragm stack exhibits outstanding capability for probing radiation damages in MEMS, not only able to capture the radiation events obviously but also help analyze different amount and types of damages induced in each stacking layer. Combining the data with a mixed elasticity model (that takes into account both flexural rigidity and pre-tension effects), we find: (i) the diaphragms operate in the *transition* regime (between 'plate' and 'membrane' but closer to the latter). (ii) after radiation behavior moves further towards the 'plate' regime, suggesting reduction in *built-in tension* and possible reduction in Young's modulus as well.

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**9:00am MN+2D-WeM4 High-Aspect Ratio, Multi-Electrode, Carbon Nanotube Array, Berg Dodson, G. Chen, R.R. Vanfleet, R.F. Davis, Brigham Young University**

We demonstrate a carbon nanotube based, high aspect ratio (~1 mm tall and 20 μm diameter posts) multi-electrode array with individually addressable electrodes. The mechanical robustness and electrical conductivity of the carbon nanotubes make them a good candidate for the multi-electrode array. The electrode is made out of CNT posts which were grown on a patterned conductive substrate and kept vertically aligned with supporting hedges. The supporting hedges were subsequently removed to leave an isolated CNT post array. The fabrication method makes the structure compatible with a variety of surface coatings, including carbon, metals, and ceramics. Good electrical connection is made to individual elements of the array despite the insulating alumina barrier that is used between the substrate and CNT forests.

**11:00am MN+2D-WeM10 Interferometric Motion Detection in Atomic Layer 2D Nanoelectromechanical Systems (NEMS), Zenghui Wang, University of Electronic Science and Technology of China, China, P.X.-L. Feng, Case Western Reserve University**

Atomic layer crystals have emerged as a new class of two-dimensional (2D) materials, exhibiting great promises for both fundamental research and technological applications. Their outstanding mechanical properties make these materials ideal for constructing novel 2D nanoelectromechanical systems (NEMS), providing opportunities for coupling their material properties across multiple information-transduction domains, at scales down to individual atomic layers. One particularly interesting prototype of 2D NEMS is 2D nanomechanical resonators. While various electrical, mechanical, and optical motional signal transduction schemes have been employed for 2D NEMS resonators, laser optical interferometry [1][2] clearly stands out as one of the most important and widely used techniques. To date, it is the only technique capable to measure the completely undriven thermomechanical motions in these 2D nanostructures.

Toward pushing the ultimate limits, it is highly desirable to quantitatively understand the detection efficiency and its dependence on the device parameters and interferometric conditions. Here, we present a systematic study [3] of the intrinsic motion responsivity in 2D NEMS using a Fresnel-law-based model, analyzing the dependences of motion responsivity upon parameters in device structure, probing wavelength, and type of 2D material. We find that the best responsivity is achieved as the vacuum gap varies (with crystal thickness) around integer multiples of half of the probing wavelength. The optimized device thickness depends on both the type of crystal and probing wavelength. Specifically, when using 633nm He-Ne laser, the ~300nm-SiO<sub>2</sub>-on-Si substrate commonly used in 2D research offers close-to-optimal motion responsivity for several 2D crystals over a wide range of thickness, provided that the oxide is fully removed underneath the 2D layer. We further show that different type of 2D layered materials exhibit different patterns in the same parameter space due to their different band structure and dielectric constants.

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**11:20am MN+2D-WeM11 NEMS on Flexible Substrates for Strain Engineering in Sensing Applications, Swapnil More, Indian Institute of Science, India**

Although nanoelectromechanical systems (NEMS) utilizing 2D material are potent instruments for ultra-sensitive mass spectroscopy, the onset of nonlinearities severely reduces their dynamic range. However, strain tuning of dynamic range is possible if the strain is introduced by methods other than electrostatic gating. Here, we present a method for the fabrication of nanoelectromechanical resonators (NEMRs) from 2D materials on flexible substrate, which allows straining devices through substrate bending, which is independent of electrostatic excitation of the resonator. This device platform can be a basis for studying dynamic range of NEMRs as a function of strain in the resonating membrane, along with studying new novel concepts for sensors involving strain engineering. With the advent of new 2d materials having exotic strain dependent properties, strain engineering opens whole new set of opportunities for the sensing technologies employing NEMS, other than strain tunable dynamic range.

**11:40am MN+2D-WeM12 Parametric Amplification in MoS<sub>2</sub> Drum Resonator, Parmeshwar Prasad\*, N. Arora, A.K. Naik, Indian Institute of Science, India**

Transition metal dichalcogenide (TMDC) materials offer an alternative to carbon based materials, due to their unique mechanical, electrical and optical properties [1]. Molybdenum disulphide (MoS<sub>2</sub>) is one such material which is being explored for NEMS applications. It has ultra-low mass density of 3.3 fg/μm<sup>2</sup> and high Young's modulus 0.3 TPa. Furthermore, its semi-conducting property allow its mechanical motion to be transduced electrically. NEMS devices based on 2D materials perform exceptionally well in terms of quality factor at low temperatures. Quality factors (Q) as high as 10<sup>5</sup> have been observed at cryogenic temperatures[2]. However, at room temperatures quality factors are typically pegged at 100. Low quality factor

of these resonators make them difficult to transduce the motion of these resonators and thus hinder applications as potential ultra-sensitive detectors. In this paper, we amplify the motion of these resonators by parametric amplification. We report enhancement of mechanical response in MoS<sub>2</sub> drum resonator using parametric amplification and achieve ~ 10dB gain. We also show quality factor enhancement in the resonator with parametric amplification at 397 K. The signal enhancement is similar to the recently reported NEMS devices [2]. However, the amplification is significantly lower as compared to the reported MEMS devices [3]. We investigate the effect of Duffing (cubic) non-linearity in the current work and show that it plays significant role in the maximum achievable gain from NEMS devices using parametric amplification. The experiments are performed using direct capacitive measurement technique on near insulating ~ 1GΩ device. This shows the ability to perform electrical capacitive actuation and detection technique in very high resistance NEMS devices.

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#### 12:00pm MN+2D-WeM13 Anisotropic Thermal Conductivity of Suspended Black Phosphorous Probed by Opto-thermomechanical Resonance Spectromicroscopy, *Arnob Islam\**, *P.X.-L. Feng*, Case Western Reserve University

Two-dimensional (2D) black phosphorus (P) exfoliated from its layered bulk crystals has attracted great attention due to its unique in-plane anisotropic properties along armchair (AC) and zigzag (ZZ) directions [1-2]. Probing the anisotropic properties in the black P is important for both exploring fundamental science and engineering device performance. Here, we employ 2D nanoelectromechanical systems (NEMS) platform to study anisotropic thermal conductivity ( $k$ ) of black P.

In this study, for the first time, we use thermomechanical motion with localized laser heating (Fig. 1a) (*opto-thermomechanical spectromicroscopy*) in combination with finite element modeling (FEM) to precisely determine anisotropic  $k_{AC}$  and  $k_{ZZ}$  of black P. We fabricate a black P circular drumhead resonator (thickness of  $t \sim 80$ nm and diameter of  $d \sim 9\mu\text{m}$ ) using a dry-transfer method [3]. Before resonance measurement, polarized reflectance measurement is performed to determine the crystal orientation of the black P flake (Fig. 1b) [4]. We then employ a 633nm laser (laser power of  $P=1.6\text{mW}$ , spot size of  $1\mu\text{m}$ ) to photothermally heat up the device and interferometrically detect Brownian motion. We obtain the fundamental mode frequency at  $f_{\text{res}} \sim 9\text{MHz}$  when the laser is located on the center of the device. We move the laser spot location along AC/ZZ on the resonator, and track  $f_{\text{res}}$  along the path. We find that measured  $f_{\text{res}}$  values are higher when laser spot is moving in AC direction ( $f_{\text{res,AC}}$ ) than that in ZZ direction ( $f_{\text{res,ZZ}}$ ) (Fig. 1c) at same distance from the center. This can be attributed to anisotropic  $k_{AC}$  and  $k_{ZZ}$ , which dictates different temperature distribution on the device as the laser is moving along AC/ZZ, providing uneven biaxial thermal expansion thus frequency shift.

We employ FEM simulation to model the coupling between thermal transport from optothermal heating and resonance characteristics of the black P drumhead resonator. By fitting the modeling to the experimental results, we are able to determine anisotropic thermal conductivities along AC/ZZ orientations ( $k_{AC}=15\text{Wm}^{-1}\text{K}^{-1}$  and  $k_{ZZ}=55\text{Wm}^{-1}\text{K}^{-1}$ ) (Fig. 1c and 1d), which are consistent with  $k_{AC}$  and  $k_{ZZ}$  obtained by other methods [2].

#### References:

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## Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room: 9 - Session SA+2D+AC+MI-WeM

### Recent Advances of Diffracting/Scattering and Spectroscopic Methods for Correlated and 2D Materials

**Moderators:** Hans-Peter Steinrück, University Erlangen-Nuernberg, Germany, Kristina Edström, Uppsala University, Sweden

#### 8:00am SA+2D+AC+MI-WeM1 Studies of Surfaces and Catalysis in real time with X-ray Free Electron Laser, *Anders Nilsson*, Stockholm University, Sweden **INVITED**

In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales. Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers LCLS (Linac Coherent Light Source) at SLAC National Accelerator Laboratory) will be presented. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

#### 8:40am SA+2D+AC+MI-WeM3 New Generation RIXS of 3d-TM Oxides, *Giacomo Ghiringhelli*, Politecnico Milano, Italy **INVITED**

Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital ( $dd$  or  $ff$ ) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer.

I will review some of the results obtained in the first year of operations of ID32, with a special focus on cuprate superconductors studied at the Cu L<sub>3</sub> edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [2] and single layer Bi2201. Finally the feasibility of high resolution RIXS in standing wave geometry has been successfully demonstrated, adding depth control on this bulk sensitive technique.

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[2] H. Miao, J. Lorenzana, G. Seibold, Y.Y. Peng, A. Amorese, F. Yakhou-Harris, K. Kummer, N. B. Brookes, R. M. Konik, V. Thampy, G. D. Gu, G. Ghiringhelli, L. Braicovich, M. P. M. Dean, [<https://arxiv.org/abs/1701.00022>]

9:20am **SA+2D+AC+MI-WeM5 Resonant Inelastic X-ray Scattering on Low-Dimensional Correlated Transition Metal Oxides and Oxide Heterostructures**, *Thorsten Schmitt*, Paul Scherrer Institut, Switzerland **INVITED**

Resonant inelastic X-ray scattering (RIXS) is a powerful bulk-sensitive photon-in / photon-out spectroscopic probe of the electronic structure of condensed matter with atomic and orbital sensitivity. It is a unique tool for studying excitations from the electronic ground state in correlated transition-metal oxides, being directly sensitive to lattice-, charge-, orbital- and spin-degrees of freedom. In this talk, we report RIXS investigations of the  $\text{LaTiO}_3$  layers in  $(\text{LaTiO}_3)_n/(\text{LaAlO}_3)_5$  superlattices undergoing a transition from  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$  oxidation state upon reducing  $n$  and thickness as well as temperature-driven metal-insulator transitions in thin films of  $\text{CaVO}_3$ .

$(\text{LaTiO}_3)_n/(\text{LaAlO}_3)_5$  superlattices (SL) composed of a band-insulator ( $\text{LaAlO}_3$ ) and a Mott-insulator ( $\text{LaTiO}_3$ ) present an enhanced insulating character when  $n$  is reduced. We prepared a set of SLs ( $n=10, 5$  and  $2$  unit cells) and investigated these with X-ray absorption spectroscopy (XAS) and RIXS. XAS shows a clear change in the Ti valence going progressively from the nominal  $\text{Ti}^{3+}$  ( $3d^1, n=10$  u.c.) for bulk  $\text{LaTiO}_3$  to an almost pure  $\text{Ti}^{4+}$  ( $3d^0, n=2$  u.c.). RIXS reveals two spectral developments when reducing the  $\text{LaTiO}_3$  thickness  $n$ : 1) reduction of intra- $t_{2g}$  / intra- $e_g$  splitting and increase of  $t_{2g}$  to  $e_g$  separation and 2) increase of the charge transfer excitation spectral weight. The changes in the energy of the orbital levels observed as a function of  $n$  reveal a clear change of the local  $\text{TiO}_6$  distortion. We suggest that an inverse Jahn-Teller effect, inducing the octahedra to assume higher symmetry, is responsible for the observed orbital energy shifts. This peculiar effect is partially caused by strain, triggering a  $3d^1 \rightarrow 3d^0$  electron transition at the interfacial Ti sites.

Bulk  $\text{CaVO}_3$  is a correlated paramagnetic metal. Thin films of  $\text{CaVO}_3$  undergo a metal-insulator transition (MIT) when the thickness is reduced below ca.  $20$  u.c.. Our XAS and RIXS measurements at the V L-edge across this dimensionality driven MIT in  $\text{CaVO}_3$  reveal a large transfer of spectral weight from fluorescent to Raman modes upon entering the insulating state. We observe a large reduction in the charge excitation bandwidth and V-O covalence across the thickness and temperature-driven MIT. Further analysis of the charge modes suggests a bandwidth-controlled MIT, assisted by the presence of strong correlations.

11:00am **SA+2D+AC+MI-WeM10 Doping of Graphene Exploited with Spectromicroscopy**, *Carla Bittencourt*, University of Mons, Belgium **INVITED**

Limitations in characterisation and theoretical modelling tools have been a major obstacle for the engineering of novel functional materials with properties enhanced by their nanoscale morphology, because detailed understanding of the structure-property-operando relationships are required. In this perspective technology has entered in a period of convergence between theory and characterisation tools, traditional spectroscopic techniques are being combined with microscopy to characterise individual nano-objects. In this context advances in the design and fabrication of x-ray focusing systems allow modifying conventional X-ray spectroscopies using synchrotron light to be used to study individual nanostructures and selected regions of a nanoscale sample. These spectroscopies are amongst the most powerful tools in material science providing elemental, electronic, structural and chemical information. Recent trends include in-operando analysis of individual nanostructures.

In my talk I will report recent results obtained using spectromicroscopy techniques to study the doping of suspended graphene flakes. The nitrogen doping of suspended graphene was performed via ion implantation. We will show that inclusion of up to  $20$  at.% nitrogen can be reached, while maintaining a  $sp^2$ -network. The evolution of nitrogen species: pyridinic, graphitic, and pyrrolic, at different doping stages and annealing temperatures is observed by scanning X-ray photoelectron microscopy (SPEM). Variations in the ratio between  $sp^2$  nitrogen species is observed for increasing treatment time; thermally heating the doped carbon nanostructure results in quenching of the  $sp^3$  component, suggesting the graphitic nitrogen as the most thermal stable species. The effect of the interaction of molecular oxygen with nitrogen doped graphene will be discussed.

11:40am **SA+2D+AC+MI-WeM12 Multi-modal and Multi-dimensional Synchrotron Investigation of Functional Materials**, *Karen Chen-Wiegart*, Stony Brook University/Brookhaven National Laboratory **INVITED**

Multi-modal and multi-dimensional characterization at synchrotrons can provide unprecedented information for complex, heterogeneous materials system. A multi-modal approach combines multiple synchrotron techniques to gain complementary information. Furthermore, with imaging techniques specifically, multi-dimensional imaging includes techniques such as tomography, spectroscopic microscopy, or in *situ/operando* imaging. These capabilities are particularly powerful when used to study complex structures with morphological and chemical heterogeneity. This talk will address the

applications in energy storage and conversion materials, including Li-ion batteries, Li-S batteries, and solid-oxide fuel cells. Other examples, including nano-/meso-porous metals, cultural heritage and surface treatment on metals will also be briefly discussed.

# Wednesday Afternoon, November 1, 2017

## 2D Materials Focus Topic

Room: 16 - Session 2D+EM+MN+NS-WeA

## 2D Device Physics and Applications

**Moderator:** Humberto Gutierrez, University of South Florida

### 2:20pm 2D+EM+MN+NS-WeA1 Capacitance-voltage Characteristics of Graphene-gate MOS Devices: The Effect of Graphene Quantum Capacitance, Ruixue Lian, A. Ural, University of Florida

There has been significant research interest in graphene for electronics applications, due to its good electrical conductivity, high optical transparency, mechanical flexibility, and two-dimensional structure. However, the potential of graphene as a channel material replacing silicon is limited due to the absence of a bandgap. On the other hand, graphene is an excellent candidate as a transparent, conductive, and flexible electrode for electronic and optoelectronic devices.

Unlike conventional metals, whose Fermi level is typically pinned at the surface, the Fermi level and hence workfunction of graphene can be tailored by electrostatic gating, chemical doping, or surface engineering. As a result, graphene is also a promising candidate as the gate electrode in metal-oxide-semiconductor (MOS) devices, particularly when transparency or workfunction tunability is a requirement.

In real graphene sheets, charged impurities cause electron-hole puddles and random local electrostatic potential fluctuations (statistically described by a Gaussian distribution), which leads to a modified density of states (DOS). In this work, using this modified DOS, we numerically compute the quantum capacitance of graphene as a function of the graphene electrostatic potential at different temperatures and strengths of the potential energy fluctuations. We compare the exact results to various approximations made in the literature when fitting experimental data. We find that the largest discrepancy between the exact results and the approximations occurs near the Dirac point.

In capacitance-voltage (C-V) characterization of graphene-gate MOS devices, what is measured is not the quantum capacitance versus the graphene potential, but the total gate capacitance versus the gate voltage. We numerically compute the gate voltage as a function of the graphene potential and the resulting C-V characteristics at different temperatures, strengths of the potential energy fluctuations, and equivalent oxide thicknesses. We also consider the effect of series and parallel parasitic impedance to the overall shape of the C-V curves. Furthermore, we numerically compute the full C-V characteristics at different values of the equivalent oxide thickness, silicon doping density, and Dirac voltage of graphene. Finally, we fit our recent experimental C-V data with these theoretical calculations to extract the strength of the potential energy fluctuations and the parasitic impedances.

These results provide important insights into the effect of the graphene quantum capacitance on the C-V characteristics of MOS devices and the potential of graphene as a gate electrode in future MOS technology.

### 2:40pm 2D+EM+MN+NS-WeA2 *in-situ* Electrical Characterization of Surface Functionalization and Gate Dielectric Deposition Processes on 2D Transition Metal Dichalcogenides Transistors, Antonio T. Lucero, J.B. Lee, L. Cheng, H.S. Kim, S.J. Kim, J. Kim, University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are a subject of intense research for use as future, low-power semiconductors. The successful fabrication of TMD based transistors requires a scalable dielectric deposition process. Atomic layer deposition (ALD) is commonly used to grow high-k gate dielectrics, though deposition of thin, pin-hole free dielectrics is challenging due to the chemically inert basal plane of most TMD materials. To overcome this limitation, surface functionalization processes have been developed to improve ALD nucleation.

In order to elucidate the effects of surface functionalization and subsequent ALD on the electrical characteristics of TMD transistors we use an *in-situ* electrical characterization system to measure the electrical properties of TMD transistors at various steps during the deposition process. MoS<sub>2</sub> backgated transistors are loaded into an ultra-high vacuum (UHV) cluster tool where samples can be transferred under UHV conditions between various chambers. The cluster tool is equipped with a thermal ALD chamber, a hollow cathode plasma enhanced ALD chamber, a plasma enhanced chemical vapor deposition chamber, and a UHV electrical probe station. Results for ozone, nitrogen radical, and nitrogen plasma functionalization will be presented. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

### 3:00pm 2D+EM+MN+NS-WeA3 High-K Gate oxide by Low Temperature ALD Technique for 2D Materials and Inert Metal Surfaces, Il Jo Kwak, J.H. Park, University of California at San Diego, S. Fathipour, A. Seabaugh, University of Notre Dame, C.S. Pang, Z. Chen, Purdue University, A.C. Kummel, University of California at San Diego

2D materials such as TMDs (Transition Metal Dichalcogenides), Graphene and BN have attracted great attention as new channel materials for future devices due to their excellent electronic and optical properties. For such devices, sub nanometer thick and defect free gate oxide is an essential part. However, due to the inert surface of the materials, high K oxide such as Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> selectively nucleates on defect sites or step edges. Therefore, for successful integration, preparation of uniform and insulating gate oxides are a matter of importance. In this study, Al<sub>2</sub>O<sub>3</sub> was deposited on 2D materials surface by low temperature ALD using trimethylaluminum (TMA) and H<sub>2</sub>O without any seeding layer or surface treatments. Using short purge time between two precursor pulses at 50C, a CVD component was induced to provide uniform nucleation sites on the surface. The CVD component generates subnanometer AlO<sub>x</sub> particles [s1] [file:///C:/Users/kwak1/Downloads/2017\_AV\_S\_abstract\_bilayer\_oxide.docx#\_msocom\_1] on the surface which provide uniform nucleation sites. In order to obtain lower EOT layer, 10 cycles of Al<sub>2</sub>O<sub>3</sub> ALD was deposited at 50C as a seeding layer and 40 cycles of HfO<sub>2</sub> ALD was deposited with Tetrakis(dimethylamido) hafnium (TDMAH) and H<sub>2</sub>O at 250C. The same oxide was deposited on a SiGe substrate to compare the oxide characteristics. After ALD, MOSCAPs were fabricated to measure electrical properties. AFM measurement revealed that uniform and defect free oxide layers were nucleated on the surfaces. Capacitance-voltage measurement showed that Cox of the bilayer oxide was 2.5 uF/cm<sup>2</sup> and the gate leakage current of the oxide was about 10<sup>-5</sup> A/cm<sup>2</sup> which was comparable to the oxide on a SiGe substrate. Identical bilayer oxide layer was deposited on a dual gated WSe<sub>2</sub> FETs. Top gate oxide leakage of the device was about 10<sup>-6</sup> A/cm<sup>2</sup>. In order to assess the quality of the oxide, a benchmarking study of current density versus EOT of 2D semiconductor FET devices and Si based devices was investigated. The study showed that record-low EOT (1.2 nm) and leakage current (10<sup>-8</sup> μA/μm<sup>2</sup>) comparable to the best Si devices with La<sub>2</sub>O<sub>3</sub> gate oxide by Iwai *et al* was achieved by the WSe<sub>2</sub> FET. This technique was also applied to initiate nucleation [s2] [file:///C:/Users/kwak1/Downloads/2017\_AV\_S\_abstract\_bilayer\_oxide.docx#\_msocom\_2] on inert metal surfaces which are important for logic memory devices including selectors. Using the bilayer oxide, insulating oxide was prepared on Au electrodes of a MOSFET device. The leakage current of the oxide was as low as 10<sup>-7</sup> A/cm<sup>2</sup>.

### 3:20pm 2D+EM+MN+NS-WeA4 Exploration and Comparison of Optoelectronic Properties of MoS<sub>2</sub> Monolayers with Multilayer Flakes and Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> Ternary Compounds, Sourav Garg, J. Waters, A. Mollah, S. Kim, P. Kung, University of Alabama

2D transition metal dichalcogenide (TMDC) semiconductors, including MoS<sub>2</sub>, WS<sub>2</sub>, and more recently ternary compounds, exhibit exceptional structural, electrical and optical properties that make these materials of great interest for nano-optoelectronic devices. For example, unlike graphene, TMDCs have a bandgap, which has the remarkable characteristic of becoming direct when the material is in monolayer form, while it is indirect when the material is composed of multiple layers.

Here, we report the synthesis of monolayer MoS<sub>2</sub>, WS<sub>2</sub>, ternary Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> ternary compounds and MoS<sub>2</sub>/WS<sub>2</sub>-based heterostructures, by chemical vapor deposition (CVD) process at temperatures in the range 950-1000 C, without the use of seeds to avoid contamination. The material was extensively characterized using micro-Raman spectroscopy, micro-photoluminescence, and electron microscopy.

Using such large area CVD grown materials, large-area MoS<sub>2</sub> photoconductive detector devices were fabricated using conventional photolithography to realize of interdigitated metal fingers. The electrical and spectral photoresponse from monolayer and multilayer MoS<sub>2</sub> have been compared, in terms of responsivity and specific detectivity. The monolayer devices exhibited high photoconductive gain and detectivity near 10<sup>12</sup> Jones, which was also found to be higher than in the case of multilayer MoS<sub>2</sub> devices. The rise and decay time of passivated monolayer devices was investigated and shown to be much faster than the unpassivated devices.

4:40pm **2D+EM+MN+NS-WeA8 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers investigated by Impedance Spectroscopy.** *Paul Penner, E. Marschewski, X. Zhang*, Bielefeld University, Germany, *T. Weimann, P. Hinze*, Physikalisch-Technische Bundesanstalt, Germany, *A. Beyer, A. Götzhäuser*, Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous study of molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaIn) top-electrodes<sup>1</sup> and conductive probe atomic force microscopy (CP-AFM). Here we investigate the dielectric properties of pristine SAMs and CNMs with an EGaIn top electrode by impedance spectroscopy. Analysis and comparison of the tunneling resistance and capacitance density of pristine and cross-linked SAMs revealed a thickness dependent capacitance associated with the monolayer as well as a thickness independent capacitance. We adopted an equivalent circuit to take into account the contribution of the interfacial capacitance as well as the oxide layer of the EGaIn top electrode. The obtained tunneling decay constant remains unaffected after electron irradiation, which exhibits a value of about  $0.5 \text{ \AA}^{-1}$  for both systems. A determination of dielectric constants of SAMs and CNMs from the impedance spectra will also be analyzed and discussed. Furthermore we characterize stacks of CNMs sandwiched with graphene and other 2D materials.

<sup>1</sup> P. Penner, X. Zhang, E. Marschewski, et. al, J Phys Chem C 2014, 118, 21687.

5:00pm **2D+EM+MN+NS-WeA9 2D Crystals for Next-Generation Ultra Energy-Efficient Electronics.** *Kaustav Banerjee*, University of California at Santa Barbara

**INVITED**

I will highlight the prospects of two-dimensional (2D) materials for innovating energy-efficient transistors, sensors, and interconnects targeted for next-generation electronics needed to support the emerging paradigm of the *Internet of Things*. More specifically, I will bring forward a few applications uniquely enabled by 2D materials and their heterostructures that have been demonstrated in my lab for realizing ultra-energy-efficient electronics. This will include the world's first 2D-channel band-to-band tunneling transistor that overcomes a fundamental power consumption challenge in all electronic devices since the invention of the first transistor in 1947 (Nature 2015), as well as a breakthrough interconnect technology based on doped-graphene-nanoribbons, which overcomes the fundamental limitations of conventional metals and provides an attractive pathway toward a low-power and highly reliable interconnect technology for next-generation integrated circuits (Nano Letters 2016). I will also bring forward a new class of ultra-sensitive and low-power sensors as well as area-efficient and high-performance passive devices, both enabled by 2D materials, for ubiquitous sensing and connectivity to improve quality of life.

## 2D Materials Focus Topic

Room: 15 - Session 2D-WeA

### Properties and Characterization of 2D Materials

Moderator: Tien-Ming Chuang, Academia Sinica, Taiwan

2:20pm **2D-WeA1 Multi-scale Mechanics of Graphene Oxide.** *Changhong Cao, M. Daly, C.V. Singh, Y. Sun, T. Filleter*, University of Toronto, Canada

The mechanical behavior of graphene oxide is length scale dependent: orders of magnitude different between the bulk forms and monolayer counterparts. Understanding the underlying mechanisms plays a significant role in their versatile application. A systematic multiscale mechanical study from monolayer to multilayer, including the interactions between layers of GO, can provide fundamental support for material engineering. In this talk, an experimental coupled with simulation approach will be introduced studying the multiscale mechanics of graphene oxide (GO).

GO is a layered nanomaterial comprised of hierarchical units whose characteristic dimension lies between monolayer GO (0.7 nm-1.2 nm) and bulk GO papers ( $\geq 1 \mu\text{m}$ ). Mechanical behaviors of monolayer GO and GO nanosheets (10 nm-100 nm) were comprehensively studied by our group. Monolayer GO was measured to have an average strength of 24.7 GPa, orders of magnitude higher than previously reported values for GO paper and approximately 50% of the 2D intrinsic strength of pristine graphene. The huge discrepancy between the strength of monolayer GO and that of bulk GO paper motivated the study of GO at the intermediate length scale (GO nanosheets). Experimental results showed that GO nanosheets possess high strength in the gigapascal range. Molecular Dynamic simulations showed that

the transition in the failure behavior from interplanar fracture to intraplanar fracture was responsible for the huge strength discrepancy between nanometer scale GO and bulk GO papers. Additionally, the interfacial shear strength between GO layers was found to be a key contributing factor to the distinct mechanical behavior among hierarchical units of GO. The understanding of the multiscale mechanics of GO is transferrable in the study of other 2D materials.

2:40pm **2D-WeA2 Modification of Density of States in Iron Chloride Intercalated Epitaxial Graphene with Electric Bias.** *K.D. McAllister, A.P. Sharma*, Clark Atlanta University, *K. Shepperd, E.H. Conrad*, Georgia Institute of Technology, *Michael Williams*, Clark Atlanta University

Epitaxial semi-metallic graphene on the carbon face of silicon carbide has mixed phase AA and AB stacking orders. Iron chloride intercalated graphene is characterized, by contrast, with AA stacking order. The high electronegativity of the iron chloride spacing layers between the graphene bilayer results in hole-doping of the graphene. Ultraviolet photoemission spectroscopy is used to investigate the electronic structure modifications of stage-1 and stage-3 iron chloride intercalated bi-layer graphene with the application of an external electric field normal to the surface. The dominant features of the study are the modification of the work function and the density of states with the applied electric field and staging order of the intercalant. In particular, the p-type carriers of the stage-1 system are switched to n-type behavior with increasing field strength in agreement with recent models.

3:00pm **2D-WeA3 Anisotropic MoS<sub>2</sub> Nanosheets Grown on Self-Organized Nanopatterned Substrates.** *Francesco Buatier de Mongeot*, *Buatier de Mongeot, Carlo Mennucci*, Università di Genova, Italy, *C. Martella, E. Cinquanta, A. Lamperti*, IMM-CNR, Agrate Brianza (MB), Italy, *E. Cappelluti*, Istituto dei Sistemi Complessi (ISC)-CNR U.O.S. Sapienza Roma, Italy, *A. Molle*, IMM-CNR, Agrate Brianza (MB), Italy

Manipulating the anisotropy in 2D nanosheets is a promising way to tune or trigger functional properties at the nanoscale. Here, a novel approach is presented to introduce a one-directional anisotropy in MoS<sub>2</sub> nanosheets via chemical vapor deposition (CVD) onto rippled patterns prepared on ion-sputtered SiO<sub>2</sub>/Si substrates. The optoelectronic properties of MoS<sub>2</sub> are dramatically affected by the rippled MoS<sub>2</sub> morphology both at the macro- and the nanoscale. In particular, strongly anisotropic phonon modes are observed depending on the polarization orientation with respect to the ripple axis. Moreover, the rippled morphology induces localization of strain and charge doping at the nanoscale, thus causing substantial redshifts of the phonon mode frequencies and a topography-dependent modulation of the MoS<sub>2</sub> workfunction, respectively [1].

Additionally the uniaxial morphological modulation of the MoS<sub>2</sub> nanosheets induces a strong dichroism in their optical extinction spectra which is particularly pronounced in correspondence to the C-exciton.

This study paves the way to a controllable tuning of the anisotropy via substrate pattern engineering in CVD-grown 2D nanosheets.

[1] C.Martella et al. Adv. Mater. 2017, 1605785

3:20pm **2D-WeA4 The Potential for Fast van der Waals Computations for Layered Materials using a Lifshitz Model.** *Yao Zhou, L.A. Pellochoud, E.J. Reed*, Stanford University

Computation of the van der Waals (vdW) interactions plays a crucial role in the study of layered materials. The adiabatic-connection fluctuation-dissipation theorem within random phase approximation (ACFDT-RPA) has been empirically reported to be the most accurate of commonly used methods, but it is limited to small systems due to its computational complexity. Without a computationally tractable vdW correction, fictitious strains are often introduced in the study of multilayer heterostructures, which, we find, can change the vdW binding energy by as much as 15%. In this work, we employed for the first time a defined Lifshitz model to provide the vdW potentials for a spectrum of layered materials orders of magnitude faster than the ACFDT-RPA for representative layered material structures. We find that a suitably defined Lifshitz model gives the correlation component of the binding energy to within 8–20% of the ACFDT-RPA calculations for a variety of layered heterostructures. Using this fast Lifshitz model, we studied the vdW binding properties of 210 three-layered heterostructures. Our results demonstrate that the three-body vdW effects are generally small (10% of the binding energy) in layered materials for most cases, and that non-negligible second-nearest neighbor layer interaction and three-body effects are observed for only those cases in which the middle layer is atomically thin (e.g. BN or graphene). We find that there is potential for particular combinations of stacked layers to exhibit repulsive three-body van der Waals effects, although these effects are likely to be much smaller than two-body effects.

4:20pm **2D-WeA7 Tip Enhanced Optical Spectroscopy: A Unique Tool to Address Nanoscale Heterogeneity in 2D Materials**, *Andrey Krayev*, AIST-NT Inc., *M. Chaigneau*, Horiba Scientific, France, *V. Zhizhimontov*, *A.E. Robinson*, AIST-NT Inc

Raman spectroscopy has proved to be an indispensable tool for characterization of both carbon-based 2D materials, such as graphene or graphene oxide, and TMDCs, providing information on: number of layers, distribution of defects, type of structure and (in case of TMDCs) excitonic behavior. Despite the wealth of the information Raman spectroscopy can provide about the structure of 2D materials, its spatial resolution is limited to approximately 300-500nm, depending on the wavelength of the excitation laser; in many cases this is insufficient for precise characterization of spatial distribution of the variations of structural and the related electronic and optoelectronic properties. Hyperspectral imaging using tip enhanced optical spectroscopy (TEOS), which includes tip enhanced Raman spectroscopy (TERS) and tip enhanced photoluminescence spectroscopy (TEPL), can dramatically improve the spatial resolution of both Raman and PL optical microscopy, providing this much-needed sensitivity.

TERS characterization of graphene and graphene oxide, both pristine and functionalized, reveals a dramatic increase in Raman response at folds and wrinkles in the flakes, as well as over the patterns imprinted in the flakes using an ultrasharp single crystal diamond probe. Interestingly, the wrinkles in graphene oxide flakes exhibit increased conductivity compared to flat areas of the flake, a rather unexpected discovery; as graphene oxide in its normal state is a dielectric, increased thickness of the material might have been expected to result in worse conductivity.

TERS and TEPL analysis of as-grown WS<sub>2</sub> demonstrated significant heterogeneity of the flakes. In an approximately 100nm-wide band adjacent to the flake edges we see both decreased, blue-shifted intensity of the photoluminescence and also increased intensity of the TERS signal; this can be attributed to decreased density of the charge carriers in the vicinity of the edges resulting in increased efficiency of Raman scattering and decreased concentration of trions, which have red-shifted PL relative to regular uncharged excitons.

TERS and correlated surface potential imaging of the WS<sub>2</sub> flakes exfoliated to gold revealed significant nanoscale (from tens to low hundreds of nanometer) variations in intensity of the major Raman bands across the flake. A high resolution map of the photoluminescence distribution extracted from the TERS map of the WS<sub>2</sub> flake clearly delineates that portion of the flake that is single layer. Correlation of the TERS hyperspectral image Raman band intensity with the distribution of surface potential may be diagnostic of TMDC doping level and of the exact sign of the charge carriers.

4:40pm **2D-WeA8 Lithium-Free Covalent Chemical Functionalization of Two-Dimensional Molybdenum Disulfide**, *X.S. Chu*, *A. Yousef*, *D.O. Li*, *A.A. Tang*, *A. Debnath*, *D. Ma*, *A.A. Green*, Arizona State University, *E.J.G. Santos*, Queen's University Belfast, UK, *Qing Hua Wang*, Arizona State University

Two-dimensional transition metal dichalcogenides like molybdenum disulfide (MoS<sub>2</sub>) are generating significant excitement due to their unique electronic, chemical, and optical properties. Chemical functionalization is crucial for tuning their properties for use in many applications. Previous methods to covalently functionalize the basal planes of TMDCs require using harsh lithium compounds for intercalation, exfoliation, and phase change from semiconducting to metallic. Here, we demonstrate the direct covalent functionalization of unmodified semiconducting MoS<sub>2</sub> using aryl diazonium salts without lithium treatments. Our approach preserves the structure and semiconducting nature of MoS<sub>2</sub>, results in covalent C-S bonds, and is applicable to MoS<sub>2</sub> derived from mechanical exfoliation, chemical vapour deposition, and liquid phase dispersion. We use density functional theory including van der Waals interactions to determine the reaction mechanism, and support it by scanning probe microscopies. The flexibility of this covalent chemistry is exploited to tether active proteins to MoS<sub>2</sub>, suggesting future biological applications.

5:00pm **2D-WeA9 Spatially Resolved Modification of Graphene's Band Structure by Surface Oxygen Atoms**, *C. Harthcock*, *A. Jahanbekam*, *Y. Zhang*, *David Y. Lee*, Washington State University

We report the spatially resolved modification of the topography and electronic properties of monolayer graphene by low dosage of atomic oxygen in the nm-scale. Using an ultra-high vacuum scanning tunneling microscope, we show that surface O-atoms, even at a low coverage of O/C = ~1/150, form random surface distributions and clusters of various sizes. Using scanning tunneling spectroscopy, oxygen adsorbates are observed to be p-type dopants, which leads to site-dependent partial and full band modifications up to a gap of few hundred meV. The degree of band gap opening and the number of O-atom induced charge-holes per area are inversely proportional to the distance between the position at which each STS spectrum is collected and the location of the nearest adsorbate. However, the number of holes contributed per

oxygen atom was found to be a site-independent constant of 0.15±0.05. For a small population of adsorbates taller than 4Å, the graphene energy bands are no longer resolved; instead STS measurements show very spatially localized but high density of states over a wide energy range, which indicates sole tunneling contribution from the cluster of electron-rich O-atoms and a complete decoupling from the graphene bands

5:20pm **2D-WeA10 Enabling Atmospheric Pressure Photoelectron Imaging and Spectroscopy using Graphene**, *H.X. Guo*, National Institute of Standards and Technology, *E. Strelcov*, NIST Center for Nanoscale Science and Technology / University of Maryland, *A. Yulaev*, University of Maryland, *Ivan Vlassiuk*, Oak Ridge National Laboratory, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

We report on recent progress in ambient pressure XPS (APXPS) spectroscopy and electron microscopy of liquid and gaseous samples enabled by electron transparent and molecular impermeable graphene membranes. Single and bilayer graphene membranes are sufficiently transparent to few hundred eV photoelectrons generated by synchrotron or laboratory x-ray sources what makes this experimental platform to be an inexpensive alternative to current differentially pumped APXPS systems. We demonstrate the capabilities of this approach on model liquids and electrochemical cells using a wide array of spectroscopy (AES, XPS, NEXAFS) and imaging (SEM, PEEM) techniques. We also discuss the limitations of this approach and lines of its future development

5:40pm **2D-WeA11 Direct Write Mask Free Fabrication of Semiconductor 2D Architectures on Different Substrates using Aqueous Inks**, *Irma Kuljanishvili*, *D. Alameri*, *R. Dong*, Saint Louis University, *L.E. Ocola*, Argonne National Laboratory

Low dimensional semiconductor materials with different sized band-gaps such as 2D atomic crystals, for example WS<sub>2</sub> or MoS<sub>2</sub> layered van der Waals materials, or 1D nanowires (NWs) and nanoribbons such as ZnO, or semiconducting carbon nanotubes (CNTs), have drawn significant attention due to their unique physical, chemical, mechanical properties, and other just to name a few. Low dimensional materials when assembled in vertical or lateral arrangements often lead to the largely enhanced properties, and new functionalities. While the preparation of layered architectures usually involves multi-step fabrication processes it also relies on mask assisted lithographic processes.

Here we present controlled selective preparation of 1D and 2D nanostructures of MoS<sub>2</sub>, WS<sub>2</sub> and ZnO in the variety of geometric assemblies by employing parallel direct write patterning (DWP) of aqueous ink precursors on substrates at predefined locations. In a two-step process (1<sup>st</sup> patterning and 2<sup>nd</sup> growth) our unconventional fabrication approach enables simple and flexible production of hetero-structures and other architectures based on "mix and match" principle in precisely controlled fashion. Location specific synthesis of materials also provides access to as-grown interfaces and rapid testing of materials quality, crystallinity and chemical composition which was confirmed by various characterization methods (Raman Spectroscopy, PL, AFM, XRD etc)

Acknowledgement

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6:00pm **2D-WeA12 Band Gap Tuning of MBE Grown WSe<sub>2</sub> via Solution Treatment of Ammonium Sulfide (NH<sub>4</sub>)<sub>2</sub>S and Ozone (O<sub>3</sub>)**, *Jun Hong Park*, Institute for Basic Science (IBS), Ewha Womans University, Republic of Korea, *I.J. Kwak*, University of California at San Diego, *A. Rai*, *S.K. Banerjee*, University of Texas at Austin, *A.C. Kummel*, University of California at San Diego

Transition metal dichalcogenides (TMDs) have been extensively studied because of their unique electronic and optical properties. In addition, having the non-zero band gap, they can be directly integrated in logic devices. However, it is of crucial importance to tune the band gap and Fermi level positions of TMDs effectively to enhance the ON/OFF current ratio. In this study, the band gap of WSe<sub>2</sub> was engineered using a (NH<sub>4</sub>)<sub>2</sub>S solution and a gaseous O<sub>3</sub> treatment. Prior to the chemical treatments, the surface of MBE (molecular beam epitaxy) grown WSe<sub>2</sub> was studied using STM (scanning tunneling microscopy). Large grains of WSe<sub>2</sub> about 100 nm were observed. The band gap of monolayer (ML) WSe<sub>2</sub> was about 2.1 eV in STS (scanning tunneling spectroscopy), consistent with previous STM studies. A bare WSe<sub>2</sub> sample was emerged in ammonium sulfide solution (40% (NH<sub>4</sub>)<sub>2</sub>S(aq)) at 300K. Afterward, the sulfur treated (ST) WSe<sub>2</sub> sample was transferred to a UHV scanning tunneling microscopy (STM) chamber to observe the effect of the treatment on the band gap. The STM imaging revealed that new electronic states were generated by ST across the entire WSe<sub>2</sub> surface, with asymmetric bias dependence. In STS, band gap of the ST WSe<sub>2</sub> was reduced to 1.2 eV, while Fermi level was pinned near the valence band. A WSe<sub>2</sub> field

effect transistor (FET) was fabricated to show the effect of ST on electrical properties. Electrical measurement showed that ST of monolayer WSe<sub>2</sub> transistors increased ON states current by two order of magnitude in the p-branch, while ON state current in n-branch was increased by an order of magnitude which is consistent with the (NH<sub>4</sub>)<sub>2</sub>S decreasing the band gap and inducing p-type doping. The band gap was also tuned by ozone (O<sub>3</sub>) treatment at room temperature. A MBE grown WSe<sub>2</sub> was inserted in a vacuum chamber. O<sub>3</sub> gas was prepared by UV lamp excitation of a continuous O<sub>2</sub> flow into the chamber at 300 K for 2 min. After dosing O<sub>3</sub> gas for 2 min, the band gap of the WSe<sub>2</sub> was about 1.3 eV, while Fermi level was near conduction band indication (n-type). As exposure time of O<sub>3</sub> increased to 6 min, the band gap of ML WSe<sub>2</sub> was decreased to 1.1eV and the formation of WOx was observed on the ML terraces. Therefore, O<sub>3</sub> had the opposite behavior of (NH<sub>4</sub>)<sub>2</sub>S since O<sub>3</sub> treatment maintained n-type doping while shrinking the band gap.

## Applied Surface Science Division

### Room: 13 - Session AS+2D+NS+SA-WeA

#### 2D, 3D and nD Imaging of Surfaces, Buried Interfaces and Nanostructures

**Moderators:** Michael Brumbach, Sandia National Laboratories, Kathryn Lloyd, DuPont

2:20pm **AS+2D+NS+SA-WeA1 Laser-SNMS Imaging of Organic and Biological Systems in Two and Three Dimensions.**, *Bonnie June Tyler, A. Pelster, M. Heeger, H.F. Arlinghaus*, Universität Münster, Germany

The introduction of commercial large argon gas cluster ion sputter sources has enabled routine molecular depth profiling and 3D imaging of organic materials with ToF-SIMS. 3D molecular imaging has been demonstrated for a wide variety of organic and biological systems. Despite these advances, sensitivity and quantitation continue to limit applications of the technique for many important systems such as pharmaceuticals. Laser post-ionization of sputtered neutral species is one potential solution to the problems of both low sensitivity and matrix effects.

In this work, we have compared ToF-SIMS and Laser-SNMS for 2D and 3D imaging of several organic systems, including biological samples, pharmaceuticals, and polymeric materials [1-3]. Sample analysis and sputtering were performed using combinations of Bi<sub>3</sub><sup>+</sup> and Ar<sub>n</sub><sup>+</sup> ions. Laser post-ionization was performed using either a 157 nm excimer laser or a 195 nm excimer laser. For organic molecules, superior results are obtained using the shorter wavelength laser at lower power density whereas higher power density with the longer wavelength laser is superior for elemental analysis. Increases in ion yield of as much as 4 orders of magnitude have been observed for both elemental and molecular species.

ToF-SIMS and Laser-SNMS show complementary strengths. For high intensity ion signals, ToF-SIMS allows for faster data acquisition. Laser-SNMS, on the other hand, reduces artefacts from topography and matrix effects and enhances measurement efficiency. Higher efficiency reduces the amount of matter that must be sputtered to obtain a given signal, which facilitates measurement of lower concentrations with higher ultimate spatial resolution.

[1] Nees, R. et al., *Biointerphases*, 2016. 11(2): p. 02A305.

[2] Pelster, A., et al., *Analytical Chemistry*, 2016. 88(19): p. 9638-9646.

[3] Pelster, A., et al., *Biointerphases*, 2016. 11(4): p 041001.

2:40pm **AS+2D+NS+SA-WeA2 Distribution of Surfactants and Polymer in a Coating using GCIB-SIMS**, *Michaeleen Pacholski, Z. Qu, W. Ouyang*, The Dow Chemical Company

Water-based coatings are commonly composed of a latex polymer with additional formulation ingredients such as surfactants, defoamers, etc. The distribution of the additives can have a large role in product performance affecting properties such as adhesion, gloss, water whitening, cohesion, etc. Using GCIB-SIMS profiling the distribution of the additives throughout a film can be shown to relate to the particle size and expected film formation theoretical results. The data from this study show, for the first time, that polymer, surfactant and salts can be monitored as a function of film depth with superior sensitivity and specificity to previous literature studies.

3:00pm **AS+2D+NS+SA-WeA3 Correlation of Morphological and Hyperspectral Characterization Techniques for Nanoelectronic and Energy Applications**, *Jean-Paul Barnes, A. Priebe, G. Goret, I. Mouton, A. Grenier, G. Audoit, P. Bleuet, Y. Mazel, E. Nolot*, Univ. Grenoble Alpes, CEA, LETI, France, *S. Legendre, A.L. Tempez*, Horiba France S.a.s., France, *R. Estivill, M. Juhel*, STMicroelectronics, France, *S. Duguay, F. Vurpillot, D. Blavette*, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, France

**INVITED**

The integration of a growing variety of materials in increasingly complex structures drives the need to correlate characterization techniques. In this presentation we will discuss the advantages of correlating pairs of techniques such as focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) and X-ray computed nanotomography (CNT); atom probe tomography (APT) and electron tomography (ET); and TOF-SIMS depth profiling and plasma profiling time-of-flight mass spectrometry (PPTOFMS).

FIB-TOF-SIMS tomography extends the capacity of TOF-SIMS instruments to analyze large heterogeneous samples of several tens of microns in size as well as porous samples or those with strong surface topography. Standard depth profiling is often not possible as the depth scale information is rapidly lost in such samples. Examples include copper pillars used in 3-D integration in nanoelectronics and solid oxide fuel cells (SOFCs) which have a complex porous multilayer (sandwich) structure. Whilst FIB-TOF-SIMS provides unique information on the sample chemical composition, there may be morphological artefacts such as curtaining. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in an SEM. We have developed a method to analyze the same object by both techniques by using novel sample preparation protocols [1].

The correlation of morphological with hyperspectral data can also be applied to APT and ET. APT is increasingly used for the analysis of semiconductor devices because of its unique ability to measure composition in 3D at the atomic scale with high sensitivity. However the APT data sets are often distorted and care must be taken in quantifying composition. The morphological information obtained from analyzing the APT tip beforehand by ET can be used to optimize the parameters when reconstructing the APT data.

PPTOFMS is a rapid depth profiling technique that uses a plasma to etch away the sample and analyze the composition as a function of depth. Unlike SIMS based techniques, the ionization takes place in the plasma and the ratio of ions extracted from the plasma is directly representative (within a factor of 2-3) of the sputtered sample composition. However, the sensitivity and depth resolution are worse than for TOF-SIMS. Combining PPTOFMS with TOF-SIMS depth profiling enables the standard-free quantification and rapid sample screening capabilities of the PPTOFMS to be combined with the sensitivity and high depth and lateral resolution of TOF-SIMS [3].

[1] A. Priebe et al. *Ultramicroscopy*. 173 (2017):10-13.[2] A. Grenier et al *APL* 106, 213102 (2015). [3] A. Tempez et al., *J. Vac. Sci. Technol. B* (2016) 34

4:20pm **AS+2D+NS+SA-WeA7 Insights into Corrosion and Radiation Damage Processes Through 2D and 3D Imaging at the Nanoscale**, *Karen Kruska, D.K. Schreiber, D.J. Edwards, Z. Zhai, M.J. Olszta, I. Arslan, M.A. Conroy, C. Wang, R.J. Kurtz, S.M. Bruemmer*, Pacific Northwest National Laboratory

**INVITED**

There is an increasing demand for characterization of materials for nuclear reactors with advanced microscopy techniques. Intelligent materials selection requires a fundamental mechanistic understanding of environmental and irradiation damage processes at the nanoscale.

Current and future nuclear power generating systems require materials that can withstand extreme environments. Long-term resistance to environmental degradation is critical for light water reactors as evidenced by stress corrosion cracking concerns in structural alloys for both primary and secondary systems. Resistance to radiation damage further challenges material selection in current and advanced reactors with unique issues for plasma facing components in tokamak-style fusion energy systems where materials must tolerate extended neutron (14 MeV) and He<sup>+</sup> ion (3.5 MeV) irradiation at extreme temperatures (up to 1300 K). Accumulation of metallic fission products in LWR fuels may cause cracking and has been linked to cladding erosion.

2D analytical electron microscopy techniques have and continue to provide key insights into the evolution of local microstructure and chemistry. More recently, these traditional 2D imaging techniques have been complemented by novel 3D imaging methods, including serial sectioning using a focused ion beam, electron tomography and atom probe tomography. When paired with 2D imaging methods, the 3D microscopy provides deeper insights into the hierarchy of the degradation and damage processes, improved statistical relevance and a greater sensitivity to highly localized effects that were not apparent from 2D imaging alone. Going one step further, dynamic processes (such as oxidation and vacancy injection) can be directly imaged by in situ



and operando techniques in transmission electron microscopy. Each technique has its own set of strengths and weaknesses, and in this talk we will emphasize how combining these complementary techniques provides a more comprehensive understanding of material degradation than could be obtained from any individual imaging method.

5:00pm **AS+2D+NS+SA-WeA9 XPS Spectroscopic Imaging of 2D-Materials**, *Olivier Renault*, CEA-Leti, France, *H. Kim*, EPFL, France, *D. Ferrah*, UCI, France, *N. Fairley*, Casa Software, France, *M. Gay*, CEA-Leti, France, *M. Frégnaux*, UVSQ, France, *A. Kis*, EPFL, France

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as MoS<sub>2</sub>, WSe<sub>2</sub>, ...) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and kPEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS<sub>2</sub> [3-4], including also novel materials and 2D heterostructures.

This work was performed at the Platform For Nano-Characterization of CEA-MINATEC.

- [1] H. Kim, O. Renault *et al.*, *Appl. Phys. Lett.* **105**, 011605 (2014).
- [2] M. Frégnaux, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 465-469.
- [3] D. Ferrah, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 451-455.
- [4] H. Kim, M. Frégnaux, A. Kis, O. Renault, *et al.*, *Phys. Rev. B* **34**, 081401 (R) (2016).

5:20pm **AS+2D+NS+SA-WeA10 Carboxylic Acid Headgroups – Towards a New Standard in SAMs**, *Anna Krzykawska*, Jagiellonian University, Poland, *J. Ossowski*, *T. Żaba*, *P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) prepared from biphenyl-substituted molecules chemisorbed on the Ag(111) substrate via an -SH or -COOH headgroup were characterized using scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). The objective of this work was to determine which of these headgroups, -SH or -COOH, will provide better 2D ordered SAMs. Importantly, to make such comparison valuable, i.e., to correlate the reduction in the concentration of surface defects with the particular headgroup, we need to compare the two systems, which are chemical analogues, and it would be desired that both systems form SAMs of similar packing density. Only under such conditions can the difference in intermolecular interactions in both systems be minimized to determine the role of headgroup bonding to the substrate in the 2D structural ordering of the resulting SAMs. Our results<sup>1</sup> obtained for monolayers meeting the above criteria show that SAMs with carboxylic headgroups can form, at room temperature and within a very short time of just a few minutes well-ordered 2D structures on Ag(111) with surprisingly large domains. In contrast, the thiol analogue formed at the same temperature reveals poor 2D ordering, with approximately 30 times smaller structural domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 300 times longer incubation process of the thiol analogue. We also demonstrate that formation of the thiol analogue at elevated solution temperature (60°C) can significantly increase the size of its domains, which is, however, still approximately 5 times smaller in comparison to the carboxylic analogue formed at room temperature. Moreover, the structure of the carboxylic analogue on Ag(111) also shows better 2D order compared with the former data obtained for the thiol analogue SAMs formed on the Au(111) substrate at room temperature. Only the formation of thiol analogue SAMs at elevated solution temperature (60°C) on the Au(111) substrate with 300 times longer formation time provides comparable 2D ordering to that obtained at the room temperature for the carboxylic analogue SAMs on the Ag(111) substrate.

Our results indicate, therefore, that SAMs based on carboxylic head group can be considered an interesting alternative for the current standard based on

the sulfur headgroups, particularly when 2D ordering, SAM fabrication time and stability in the ambient conditions are of great importance.

## References

- [1] A. Krzykawska, J. Ossowski, T. Żaba and P. Cyganik, *Chem Comm* **2017** accepted

5:40pm **AS+2D+NS+SA-WeA11 2-D and 3-D Characterization of Functionalized Nanostructured Carbons**, *Chilan Ngo*, *D.R. Diercks*, *M.B. Strand*, *M.J. Dzara*, *J. Hagen*, *S. Pylypenko*, Colorado School of Mines

Low cost, versatility, and a broad range of properties make carbon a widely studied material with numerous practical applications. Functionalization/doping with heteroatoms is an effective method to tailor the composition and structure of carbon, in order to adjust its properties for various applications. Significant efforts have been dedicated to elucidation of the composition, structure and properties of doped carbon materials, however atomic scale visualization of high-surface area carbons in 3-D has not been achieved. Here, by utilizing a combination of techniques, we focus on understanding the 2-D and 3-D distribution of nitrogen and iron dopants in high-surface area carbons. Information on surface composition evaluated using X-ray photoelectron spectroscopy (XPS) is complemented by 2-D bulk measurements using energy dispersive X-ray spectroscopy (EDS) through transmission electron microscopy (TEM). 3-D distribution of dopants is studied using atom probe tomography (APT), providing novel insight into the properties of high-surface area carbon materials. This type of investigation necessitated the fabrication of a diverse set of materials with defined shape and morphology, along with variation in the distribution of nitrogen and iron species relative to each other. Nitrogen-doped carbon nanospheres (NCs) were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different dopant concentrations and varied relative distribution of nitrogen functionalities. Iron- and nitrogen-doped nanospheres (FeNCs) were prepared by two routes. For the first set of materials, addition of an iron-containing precursor to the NC synthesis was done prior to hydrothermal treatment, to incorporate Fe throughout the bulk of the nanosphere. The second set is expected to deposit iron only on the surface of the carbon, and is prepared by addition of the iron precursor after the NC pyrolysis, followed by a second pyrolysis. A dual-beam focused-ion beam scanning electron microscope (FIB/SEM) was used to isolate nanospheres into a workable APT tip. Combination of 2-D and 3-D analysis are expected to further the understanding of N-doped carbon materials and N-containing Pt-group metal free catalysts employed in a variety of important catalytic reactions. This work also serves as a foundation to prepare model high-surface area materials that are compatible with *in situ* liquid and electrochemistry TEM techniques, to allow further investigations of these catalytically active materials under conditions relevant to their applications.

6:00pm **AS+2D+NS+SA-WeA12 Characterization of Natural Photonic Crystals in Glitterwing (*Chalcopteryx rutilans*) Dragonfly Wings using 3D TOF-SIMS**, *Ashley Ellsworth*, *D.M. Carr*, *G.L. Fisher*, Physical Electronics, *W.W. Valeriano*, *R.R. de Andrade*, *J.P. Vasco*, *E.R. da Silva*, *A.B.M. Machado*, *P.S.S. Guimarães*, *W.N. Rodrigues*, Universidade Federal de Minas Gerais, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) dragonfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for dragonflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The variation of the local color was related to the number and thickness of the layers which varied across the wing. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. The experimental reflectance was calculated and fitted through the transfer matrix method for the structure obtained from the electron microscopy images. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can now be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C<sub>60</sub><sup>+</sup> and large cluster Ar<sub>n</sub><sup>+</sup>. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals.

- [1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from [http://www.fisica.ufmg.br/posgrad/Dissertacoes\\_Mestrado/decada2010/wesley-valeriano/WesleyWalisonValeriano-diss.pdf](http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wesley-valeriano/WesleyWalisonValeriano-diss.pdf).

**Materials and Devices for Quantum Information Processing**

**Moderators:** Rachael Myers-Ward, U.S. Naval Research Laboratory, Steven Vitale, MIT Lincoln Laboratory

2:20pm **EM+2D+MI+MN-WeA1 Controlling the Valley Degree of Freedom in 2D Transition Metal Dichalcogenides**, *Tony Heinz*, Stanford University / SLAC National Accelerator Laboratory **INVITED**

Monolayer transition metal dichalcogenide crystals in the MX<sub>2</sub> family with M = Mo, W and X = S, Se have been shown to provide attractive possibilities for access to the valley degree of freedom both optically and through the valley Hall effect. In this paper we will summarize recent advances in the electrical and optical control of the valley degree of freedom in this class of materials.

The optical selection rules in the transition metal dichalcogenide monolayers permit selective creation of excitons in either the K or K' valley through the use of circularly polarized light. Excitons consisting of coherent superpositions of both valleys can also be produced through excitation with linearly polarized light. While these results have already been demonstrated experimentally, to date there has been no report of an approach to *manipulate* the valley exciton pseudospin after its creation. In this paper we present our recent use of the optical Stark effect to dynamically modify the valley pseudospin. The approach is based on selectively altering the energy of one valley vis-a-vis the other through application of a sub-gap optical pulse with circular polarization. This perturbation leads to a rapid rotation of the exciton valley pseudospin, as revealed by a change in the polarization state of the exciton emission.

In a second line of investigation, we have applied to spin-valley Hall effect in transition metal dichalcogenide monolayers to produce spatially separated regions with enhanced valley (and spin) populations. This is achieved by running a current through a hole-doped monolayer and relying on the anomalous velocity terms to separate the holes spatially. The resulting spin-valley spatial profile has been directly imaged on the micron scale and characterized using measurements based on the optical Kerr effect. The magnitude of this spin-valley imbalance and its dependence on doping and bias fields have been investigated and compared with theoretical predictions.

3:00pm **EM+2D+MI+MN-WeA3 VOI-based Valleytronics in Graphene**, *Yu-Shu Wu*, National Tsing-Hua University, Taiwan, Republic of China **INVITED**

Electrons in gapped graphene carry a unique binary degree of freedom called valley pseudospin, in association with the two-fold valley degeneracy at the Dirac points (K and K') of Brillouin zone. Such pseudospin carries an intrinsic angular momentum and responds to external electromagnetic fields in ways similar to those of an ordinary electron spin [1,2]. We examine the response and address the important issue of valleytronics - the electrical manipulation of valley pseudospin. A unified methodology called VOI based valleytronics will be presented, which exploits the valley-orbit interaction (VOI) between an in-plane electric field and a valley pseudospin for the implementation of valleytronics. Based on the VOI mechanism, a family of fundamental structures have been proposed with important device functions, such as valley qubits, valley filters, and valley FETs [3]. We will report recent theoretical developments in these structures.

[1] Rycerz et al., *Nat. Phys.* **3** (2007), 172.

[2] Xiao et al., *Phys. Rev. Lett.* **99**, (2007), 236809.

[3] Wu et al., *Phys. Rev. B* **84**, (2011), 195463; *ibid B* **86** (2012), 165411; *ibid B* **88** (2013), 125422; *ibid B* **94** (2016), 075407.

4:20pm **EM+2D+MI+MN-WeA7 Creating Quantum Technologies with Spins in Semiconductors**, *B.B. Zhou, David Awschalom*, University of Chicago **INVITED**

There is a growing interest in exploiting the quantum properties of electronic and nuclear spins for the manipulation and storage of information in the solid state. Such schemes offer fundamentally new scientific and technological opportunities by leveraging elements of traditional electronics to precisely control coherent interactions between electrons, nuclei, and electromagnetic fields. Although conventional electronics avoid disorder, recent efforts embrace materials with incorporated defects whose special electronic and nuclear spin states allow the processing of information in a fundamentally different manner because of their explicitly quantum nature [1]. These defects possess desirable qualities – their spin states can be controlled at and above room temperature, they can reside in a material host amenable to microfabrication, and they can have an optical interface near the telecom

bands. Here we focus on recent developments that exploit precise quantum control techniques to explore coherent spin dynamics and interactions. In particular, we manipulate a single spin in diamond using all-optical adiabatic passage techniques [2], and investigate the robustness of the acquired geometric (Berry) phase to noise as well as novel strategies to overcome traditional speed limits to quantum gating. Separately, we find that defect-based electronic states in silicon carbide can be isolated at the single spin level [3] with surprisingly long spin coherence times and high fidelity, can achieve near-unity nuclear polarization [4] and be robustly entangled at room temperature [5]. Finally, we identify and characterize a new class of optically controllable defect spin based on chromium impurities in the wide-bandgap semiconductors silicon carbide and gallium nitride [6].

[1] D.D. Awschalom, L.C. Bassett, A.S. Dzurak, E.L. Hu and J.R. Petta, *Science* **339**, 1174 (2013).

[2] C. G. Yale, F. J. Heremans, B. B. Zhou, et al., *Nature Photonics* **10**, 184 (2016); B. B. Zhou et al., *Nature Physics* **13**, 330 (2017).

[3] D. J. Christle, A. L. Falk, P. Andrich, P. V. Klimov, et al., *Nature Materials* **14**, 160 (2015); D. J. Christle et al., arXiv:1702.07330 (2017).

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[6] W. F. Koehl et al., Editors Suggestion, *Phys. Rev. B* **95**, 035207 (2017).

5:00pm **EM+2D+MI+MN-WeA9 Diamond as an Electronic Material: Opportunities and Challenges**, *Steven Vitale, J.O. Varghese, M.F. Marchant, T. Wade, M.W. Geis, T.H. Fedynyshyn, D.M. Lennon, M.A. Hollis*, MIT Lincoln Laboratory

Diamond possesses extraordinary semiconductor properties including carrier mobility, saturation velocity, and thermal conductivity which far exceed those of silicon and essentially all other semiconductor materials. In spite of these incredible qualities diamond has not yet become a mainstream transistor material, for two primary reasons. First, existing small single-crystal substrates have not been able to take advantage of commercial microelectronics processing equipment and growth of wafer-scale single-crystal diamond has not been vigorously pursued. Second, deep donor and acceptor levels in diamond imply that the impurity ionization fraction is quite low at room temperature which results in low carrier density in conventional FET architectures.

However the situation has changed dramatically in the past few years. Plasma-enhanced CVD promises to create large-wafer single-crystal diamond through mosaic or novel catalytic growth.<sup>1</sup> Additionally, the discovery of the diamond surface FET has addressed the problem of low carrier density.<sup>2</sup> Together, these advancements may allow development of practical diamond transistors with unparalleled performance for high-power, high-frequency applications. Many unit process and process integration challenges remain to develop diamond surface FETs into commercial technology. This paper will report on the state of the art in diamond surface FET technology and will examine current unmet needs.

We have developed diamond surface FETs with current densities in excess of 100 mA/mm. This is enabled by a novel surface activation process using a high concentration of NO<sub>2</sub> in air to react with a hydrogen-plasma-treated diamond surface. The electron accepting nature of the modified surface abstracts an electron from the diamond, resulting in a 2D hole gas (2DHG) in the diamond. We measure a hole mobility of 30-130 cm<sup>2</sup>/V-s and a repeatable surface resistance of ~ 1.5 kΩ sq<sup>-1</sup> using this technique. 2DHG formation has been demonstrated using other surface moieties as well, including photoacid radical generators and trinitrotoluene. Pros and cons of these different surface adsorbates will be discussed. The performance of Au, Mo, Pt, Al, Pd, Ti, Cr contacts, as well as combinations of these metals will be presented, with a record-low diamond contact resistance of 0.6 ohm-mm and good ohmic behavior.

<sup>1</sup> M. Schreck, et al, *Sci. Rep.* **7**, 44462 (2017).

<sup>2</sup> M. Kasu, *Japanese Journal of Applied Physics* **56**, 01AA01 (2017).

5:20pm **EM+2D+MI+MN-WeA10 Studies on Influence of Processing on Optical Characteristics of Electron Irradiated 4H-SiC Nanostructures**, *Shojan Pavunny*, ASEE Research Fellow at U.S. Naval Research Laboratory, *H. Banks*, NRC Research Fellow at U.S. Naval Research Laboratory, *P.B. Klein*, U.S. Naval Research Laboratory, *K.M. Daniels*, NRC Research Fellow at U.S. Naval Research Laboratory, *M.T. DeJarlid*, ASEE Research Fellow at U.S. Naval Research Laboratory, *E.R. Glaser*, *S.G. Carter*, *R.L. Myers-Ward*, *D.K. Gaskill*, U.S. Naval Research Laboratory

Spin-coherent single silicon defect centers (*V<sub>Si</sub>*) in wide bandgap silicon carbide polytypes have recently drawn great research interest for future applications in information technologies such as scalable quantum computing, sensing and metrology. Identification of these deep defects,

gaining a thorough knowledge of their characteristics, active control of their concentrations, isolation of single spin defects and understanding the effects of semiconductor processing on their properties are crucial challenges for the realization of SiC based quantum electronic and integrated photonic devices. These color centers coupled to photonic crystal cavities (PCC) have the capability of high efficiency emission of zero phonon lines which can significantly improve the performance of on-chip photonic networks and long-distance quantum communication systems, as compared to conventional solid-state emitters. Here we investigate the impact of fabrication process on the photoluminescence properties of PCCs realized using three techniques: hydrogen implantation to form thin SiC layers on an oxide layer that can be easily etched away to form an air gap under the PCC, wafer bonding and mechanical thinning of the SiC, also on an oxide layer, and selective electrochemical anodization of an n-p epitaxial SiC structure to form an air gap. We also comment upon the impact of electron irradiation for these three fabrication techniques.

5:40pm **EM+2D+MI+MN-WeA11 Ab Initio Simulations of Point Defects in Solids Acting as Quantum Bits**, *Adam Gali*, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary **INVITED**  
Luminescent and paramagnetic point defects in insulators and semiconductors may realize quantum bits that could be the source of next generation computers and nanoscale sensors. Detailed understanding of the optical and magnetic properties of these defects is needed in order to optimize them for these purposes.

In this talk I show our recent methodology developments in the field to calculate the ground and excited state of point defects and to determine their Auger-rates, hyperfine tensors and electron spin – electron spin couplings, and intersystem crossing rates. We show recent results on the nitrogen-vacancy center in diamond as well as divacancy and other defects in silicon carbide that we have found a very promising alternative to the well-established nitrogen-vacancy center for integration of traditional semiconductor and quantum technologies into a single platform.

## Advanced Surface Engineering Division

**Room: 11 - Session SE+2D+NS+SS+TF-WeA**

### Nanostructured Thin Films and Coatings

**Moderators:** Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB<sub>2</sub> Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc**, *Johanna Rosen*, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB<sub>2</sub> coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to  $\geq 42$  GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of B<sup>+</sup> ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly Ar<sup>+</sup> ions.

Finally, we also present results from TiB<sub>2</sub> synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films**, *Lirong Sun*, General Dynamics Information Technology, *N.R. Murphy*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an O<sub>2</sub>/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions (M<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (*iSE*). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of Zr/Al<sub>2</sub>O<sub>3</sub>(0001): Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al<sub>2</sub>O<sub>3</sub> Interfaces**, *K. Tanaka*, *J. Fankhauser*, University of California at Los Angeles, *M. Sato*, Nagoya University, Japan, *D. Yu*, *A. Aleman*, *A. Ebnonnasir*, *C. Li*, University of California at Los Angeles, *M. Kobashi*, Nagoya University, Japan, *M.S. Goorsky*, *Suneel Kodambaka*, University of California at Los Angeles

Zr thin films are grown on Al<sub>2</sub>O<sub>3</sub>(0001) substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere at temperatures T<sub>s</sub> between 600 °C and 900 °C. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 °C  $\leq$  T<sub>s</sub> < 750 °C, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At T<sub>s</sub>  $\geq$  750 °C, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/Al<sub>2</sub>O<sub>3</sub> interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing T<sub>s</sub>. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the Al<sub>2</sub>O<sub>3</sub> substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Nanocrystalline Films for Extreme Environment Applications**, *Anil Battu*, *S. Manandhar*, *C.V. Ramana*, University of Texas at El Paso

Recently, gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping Ga<sub>2</sub>O<sub>3</sub> with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content  $\leq$  4 at% retains the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> phase, higher Mo content induces amorphization. Molybdenum incorporation into  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elastic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship is established in Mo incorporated Ga<sub>2</sub>O<sub>3</sub> films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films**, *David Adams, M.J. Abere, C. Sobczak, D.E. Kittell, C.D. Yarrington, C.B. Saltonstall, T.E. Beechem*, Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates  $> 1 \times 10^7$  K/s. Equimolar designs are characterized by a substantial heat of formation,  $\sim 100$  kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LLRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, *Samir Aouadi*, University of North Texas, *C. Muratore*, University of Dayton, *A.A. Voevodin*, University of North Texas **INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, *Nicolas Argibay, T.A. Furnish, T.F. Babuska, C.J. O'Brien, J.F. Curry, B.L. Nation, A.B. Kustas, P. Lu, M. Chandross, D.P. Adams, M.A. Rodriguez, M.T. Dugger, B.L. Boyce, B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction ( $\mu \sim 0.2-0.3$ ) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, *Daniel Edström, D. Sangiovanni, L. Hultman, I. Petrov, J. Greene, V. Chirita*, Linköping University, University of Illinois at Urbana-Champaign  
Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic  $d-t_{2g}$  metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness  $> 50\%$  higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

**KEYWORDS:** nitrides, carbides, toughness, hardness, ductility.

# Thursday Morning, November 2, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+MI-ThM

### Novel Quantum Phenomena in 2D Materials

Moderator: Kai Xiao, Oak Ridge National Laboratory

8:00am **2D+MI-ThM1 Quantum Plasmonics with 2D Materials**, *Dmitri Voronine*, University of South Florida

Quantum plasmonics effects were previously investigated in coupled metallic nanostructures with sub-nanometer gaps leading to large electron tunneling contributions. Two-dimensional transition metal dichalcogenides are promising materials with interesting optoelectronic, catalytic and sensing applications which may be integrated with plasmonic nanostructures and used in the quantum plasmonics regime. Their nanoscale optical characterization using tip-enhanced photoluminescence (TEPL) and tip-enhanced Raman scattering (TERS) spectroscopies provides detailed local structure-function information which is not available using far-field diffraction-limited techniques. Nanoscale optical imaging provides an improved understanding of the optoelectronic properties of edge states, defects and grain boundaries. Here we report nanoscale TEPL and TERS characterization of monolayer and few-layer 2D materials such as MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub> and their alloys and heterostructures with subdiffraction spatial resolution due to the strong signal enhancement via surface plasmon confinement of the nano-size metallic tip. We investigate the limits of signal enhancement on various substrates by varying the tip-sample gap and reveal quantum plasmonic behavior for sub-nanometer gaps. We show that quantum plasmonics provides a new mechanism of the generation and control of excitons and trions in 2D materials via electron tunneling. We investigate various quantum plasmonics regimes with picometer-scale indentation control. These results may be used for improving the nano-optical properties of 2D materials and for designing novel quantum optoelectronic devices.

8:20am **2D+MI-ThM2 Investigation and Manipulation of One-Dimensional Charge Density Waves in MoS<sub>2</sub>**, *Wouter Jolie, C. Murray, J. Hall*, Institute of Physics II, University of Cologne, Germany, *F. Portner*, Institute for Theoretical Physics, University of Cologne, Germany, *B. Pilić*, Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Zagreb, Croatia, *N. Atodiressei*, Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich, Germany, *M. Kralj*, Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Zagreb, Croatia, *A. Rosch*, Institute for Theoretical Physics, University of Cologne, Germany, *C. Busse*, Institut für Materialphysik, Westfälische Wilhelms-Universität Münster, Germany, *T. Michely*, Institute of Physics II, University of Cologne, Germany

Grain boundaries in monolayer transition metal dichalcogenides (TMDC) are predicted to host one-dimensional metallic states embedded in an otherwise insulating layer. As was shown recently for MoSe<sub>2</sub> [1,2], these states may be electronically unstable, undergoing a Peierls transition which leads to a charge density wave (CDW) at low temperatures.

We investigate epitaxial monolayer-MoS<sub>2</sub> on graphene on Ir(111) with scanning tunneling microscopy and spectroscopy (STM/STS). We find a large bandgap in MoS<sub>2</sub> showing that it is well decoupled from the substrate. The MoS<sub>2</sub> islands feature long, straight, highly symmetric twin boundaries. Along these we measure a small bandgap together with periodic beatings in the local density of states, both characteristic of CDWs. We investigate different types of line defects in MoS<sub>2</sub> and find correspondingly different CDWs. These quasi-freestanding wires offer an opportunity to study the simple yet rich physics of CDWs, not often seen in true 1D form experimentally. Specifically, we investigate their properties based on symmetry analysis, the impact of point defects, temperature-dependence, phase-behavior and their response to doping.

[1] S. Barja, S. Wickenburg, Z.-F. Liu, Y. Zhang, H. Ryu, M.M. Ugeda, Z. Hussain, Z.-X. Shen, S.-K. Mo, E. Wong, M.B. Salmeron, F. Wang, M.F. Crommie, D.F. Ogletree, J.B. Neaton, A. Weber-Bargioni, *Nat. Phys.* **12**, 751-756 (2016)

[2] Y. Ma, H.C. Diaz, J. Avila, C. Chen, V. Kalappattil, R. Das, M.-H. Phan, T. Čadež, J.M.P. Carmelo, M.C. Asensio, M. Batzill, *Nat. Commun.* **8**, 14231 (2017)

8:40am **2D+MI-ThM3 Configuring Electronic States in an Atomically Precise Array of Quantum Boxes**, *Seyedeh Fatemeh Mousavi, S. Nowakowska, A. Wäckerlin*, University of Basel, Switzerland, *I. Piquero-Zulaica*, Materials Physics Center, San Sebastián, Spain, *J. Nowakowski*, Paul Scherrer Institut (PSI), Switzerland, *S. Kawai*, University of Basel, Switzerland, *C. Wäckerlin*, Paul Scherrer Institut (PSI), Switzerland, *M. Matena, T. Nijs, S. Fatayer, O. Popova, A. Ahsan, T. Ivas, E. Meyer*, University of Basel, Switzerland, *M. Stöhr*, University of Groningen, Netherlands, *J.E. Ortega*, Materials Physics Center, San Sebastián, Spain, *J. Björk*, Linköping University, Sweden, *L.H. Gade*, Universität Heidelberg, Germany, *J. Lobo-Checa*, Universidad de Zaragoza, Spain, *T.A. Jung*, Paul Scherrer Institut (PSI), Switzerland

Quantum boxes (QBs) [1] have been arranged in extended 2D arrays by the self-assembled formation of a porous on-surface coordinated network [2]. Xe atoms were used as an adsorbate for their well-defined interaction with the surface state electrons of Cu(111), which is dominated by Pauli repulsion. The electronic states contained in these arrays can be configured by the localized perturbation by the targeted filling level of the individual QBs with Xe atoms after Xe repositioning, each quantum box exhibits maximal 12 filling levels, which incrementally perturb the quantum box state(s) via Pauli repulsion. It is shown that specific filling patterns of the network of the QBs which are coupled in an inherently precise way by self assembly [3] specifically perturb, and thus modify the localized and delocalized quantum box states (QBSs). In particular the energy levels of the QBSs is modulated also it is demonstrated that the inter-box coupling can be sustained or significantly weakened by an appropriate arrangement of empty and filled boxes. We gain unprecedented insight into the physics of interacting quantum states on the local level as well as in their cooperative interaction by using complementary scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission spectroscopy (ARPES) measurements. Our approach establishes that such self-assembled two-dimensional quantum box architectures may serve as nanoscale analog of breadboards that are commonly employed in electronic circuitry and guide towards the fabrication of quantum devices.

#### References

[1] S. Nowakowska et al., Nature Communications | 6:6071 | DOI: 10.1038/ncomms7071

[2] J. Lobo Checa et al., Science 325, 17, 300ff (2009)

[3] S. Nowakowska et al, small, 2016; DOI: 10.1002/sml.201600915..

9:00am **2D+MI-ThM4 A Quantum Berry Phase Switch in Circular Graphene Resonators**, *Daniel Walkup\**, *F. Ghahari, C. Gutiérrez, NIST/CNST, J.F. Rodriguez-Nieva*, Harvard University, *Y. Zhao, J. Wyrick, F.D. Natterer, W.G. Cullen*, NIST/CNST, *K. Watanabe, T. Taniguchi*, National Institute for Materials Science, Japan, *L.S. Levitov*, MIT, *N.B. Zhitenev, J.A. Stroscio*, NIST/CNST

In graphene and other 2D Dirac materials, the band structure has the property that momentum-space paths enclosing the Dirac point pick up a Berry phase of  $\pi$ . In a uniform magnetic field, this leads to a special quantization rule and an N=0 Landau level at the Dirac point. In a circular graphene resonator, weak magnetic fields can tune the quantized electron orbits between states with Berry phases of zero and  $\pi$ , leading to a discontinuous jump in the quantum energy level as a function of applied field. Here we report scanning tunneling microscopy and spectroscopy (STM/S) studies of circular resonators fabricated in p-n junction rings in graphene/hBN backgated devices. We observe direct signatures of a Berry-phase-induced switching of the resonator states measured with scanning tunneling spectroscopy as a function of magnetic field. The telltale signature is a sudden and large increase in the energy of angular-momentum states in the graphene p-n junction resonators when a small critical magnetic field is reached, in agreement with theoretical calculations of Dirac potential wells.

9:20am **2D+MI-ThM5 Nanostructured Graphene: A Platform for Fundamental Physics and Applications**, *Anti-Pekka Jauho*, Technical University of Denmark, Denmark **INVITED**

Despite of its many wonderful properties, pristine graphene has one major drawback: being a semimetal it does not have a band gap, which complicates its applications in electronic devices. Many routes have been suggested to overcome this difficulty, such as cutting graphene into nanoribbons, using chemical methods or periodic gates, and - which is the paradigmatic example of this talk - by making regular nanop perforations, also known antidot lattices [1]. All these ideas work beautifully in theory, but realizing them in the lab

\* NSTD Postdoc Finalist

is very difficult because fabrication steps inevitably induce disorder and other nonidealities, with potentially disastrous consequences for the intended device operation. In this talk I introduce these ideas and review the state-of-the-art both from the theoretical and the experimental points of view. I also introduce some new ideas, such as triangular antidots [2], and nanobubbles formed in graphene [3]. Our simulations, relying on advanced numerical techniques, show that it may be possible to generate very high quality spin- and valley polarized currents with these structures – something that has not yet been achieved in the lab. Importantly, our simulations involve millions of atoms which is necessary in order to address structures feasible in the lab.

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[2] S. S. Gregersen et al., "Nanostructured graphene for spintronics", *Phys. Rev. B*, vol. 95, 121406(R), March 2017

[3] M. Settnes et al., "Graphene Nanobubbles as Valley Filters and Beam Splitters", *Phys. Rev. Lett.* vol. 117, 276801, December 2016

11:00am **2D+MI-ThM10 Anomalous Kondo Resonance Mediated by Graphene Nanoribbons**, *Yang Li*, Ohio University and Argonne National Laboratory, *A. Ngo*, Argonne National Laboratory, *K.Z. Latt*, Ohio University, *B. Fisher*, Argonne National Laboratory, *S.W. Hla*, Argonne National Laboratory and Ohio University

Atomically precise graphene nanoribbons (AGNR) are formed by one dimensional graphene sheets of carbon atoms and they can exhibit semiconducting characteristics with varying bandgaps. For the device and sensor applications, it is important to explore AGNR heterostructures. Here, we form molecular heterostructures using magnetic molecules and on-surface synthesized AGNRs on a Au(111) surface. Then the electronic and spintronic properties of the AGNR-magnetic molecule-Au(111) heterostructures are investigated by using scanning tunneling microscopy, tunneling spectroscopy and atomic/molecular manipulation schemes at 5 K substrate temperature in an ultrahigh vacuum environment. Although the AGNRs on Au(111) surface have a semiconducting characteristic with a large bandgap, we discover the unexpected Kondo resonance on molecules adsorbed on AGNRs. Interestingly, the observed Kondo temperatures of the molecules appear the same as the ones adsorbed on AGNRs and Au(111) surface including the atomic scale differences due to adsorption site. The experimental results are explained by density functional theory and numerical renormalization group theory calculations. We acknowledge the support of DOE SISGR grant: DE-FG02-09ER16109.

11:20am **2D+MI-ThM11 Valley Photoluminescence Polarization in Monolayer WSe<sub>2</sub>**, *Aubrey Hanbicki*, *M. Currie*, Naval Research Laboratory, *G. Kioseoglou*, University of Crete, *A.L. Friedman*, *B.T. Jonker*, Naval Research Laboratory

Monolayer materials such as WS<sub>2</sub> or WSe<sub>2</sub> are direct gap semiconductors with degenerate, yet inequivalent  $k$ -points at  $K$  and  $K'$ . The valence band maxima for  $K$  and  $K'$  have spin states of opposite sense enabling one to selectively populate each valley independently with circularly polarized light. Subsequent valley populations can be determined via the polarization of emitted light. Optical emission is dominated by neutral and charged exciton (trion) features, and changes in emitted polarization provide insight into the fundamental processes of intervalley scattering. We measure the circularly polarized photoluminescence of WSe<sub>2</sub> monolayers as a function of excitation energy for both continuous-wave (cw) and pulsed laser excitation sources. Using cw excitation, the temperature dependence of the depolarization of the trion follows the same trend as that of the neutral exciton and involves collisional broadening. However, the initial polarization of the trion is nearly twice the polarization of the neutral exciton at low temperature. When a pulsed laser is used as the excitation source, the initial polarization of the neutral exciton increases and becomes very similar to the trion. We propose either an up-conversion process or screening from the instantaneously large carrier density generated by the pulsed excitation to explain these data. The difference in polarization behavior is linked to the different way energy is deposited in the system during these measurements. We also discuss changes in the photoluminescence induced by pulsed laser excitation.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

11:40am **2D+MI-ThM12 Imaging Superconducting Topological Surface States in Non-centrosymmetric PbTaSe<sub>2</sub>**, *Tien-Ming Chuang*, Academia Sinica, Taiwan, Republic of China **INVITED**

The search for topological superconductors (TSCs) is one of the most exciting subjects in condensed matter physics. TSCs are characterized by a full superconducting gap in the bulk and topologically protected gapless surface (or edge) states. Within each vortex core of TSCs, there exist the zero energy Majorana bound states, which are predicted to exhibit non-Abelian

statistics and to form the basis of the fault-tolerant quantum computation. So far, no stoichiometric bulk material exhibits the required topological surface states (TSSs) at  $E_F$  combined with fully gapped bulk superconductivity. Here, we use spectroscopic-imaging scanning tunneling microscopy to study the atomic and electronic structures of the non-centrosymmetric superconductor, PbTaSe<sub>2</sub>. Our results demonstrate PbTaSe<sub>2</sub> as a promising candidate as a 2D TSC.

# Thursday Afternoon, November 2, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+AS+SS-ThA

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

Moderator: Aubrey Hanbicki, Naval Research Laboratory

### 2:20pm 2D+AS+SS-ThA1 Electron Irradiation-induced Defects and Phase Transformations in Two-dimensional Inorganic Materials, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN, transition metal dichalcogenides (TMDs) and silica bilayers were manufactured. All these systems contain defects and impurities, which may govern the electronic and optical properties of these materials, calling upon the studies on defect properties. In my talk, I will present the results [1-6] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in collaboration with several experimental groups. I will further dwell on the signatures of defects in Raman spectra and discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. I will also present the results [7] of our theoretical studies of electron-beam induced phase transformations in 2D TMDs when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the TMD monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample.

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### 2:40pm 2D+AS+SS-ThA2 Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111), Luca Bignardi, P. Lacovig, M. Dalmiglio, Elettra-Sincrotrone Trieste, Italy, F. Orlando, Paul Scherrer Institut (PSI), Switzerland, A. Ghafari, Helmholtz-Zentrum Berlin, Germany, L. Petaccia, Elettra-Sincrotrone Trieste, Italy, A. Baraldi, University of Trieste, Italy, R. Larciprete, Istituto dei Sistemi Complessi - CNR, Italy, S. Lizzit, Elettra-Sincrotrone Trieste, Italy

In this contribution I will provide a description of the oxygen intercalation at the strongly interacting graphene on Ni(111) and of the role of rotated graphene domains in triggering the intercalation. The system was studied by a combination of high-resolution x-ray photoelectron spectroscopy (HR-XPS), photoelectron diffraction (XPD) and angle-resolved photoemission (ARUPS) performed with synchrotron radiation. The HR-XPS measurements provided a full characterization of the interface at each stage of the intercalation, revealing the formation of an oxide layer between graphene and the metal substrate. The ARUPS data showed that the oxide layer efficiently decouples graphene from the substrate, restoring the Dirac cone and providing a slight n-doping. The C1s XPD measurements revealed that the graphene domains not aligned with the Ni substrate are the first to be intercalated with oxygen. At the same time, these domains are also preferential regions under which the oxygen is retained during the deintercalation process.

### 3:00pm 2D+AS+SS-ThA3 Atomic Structure of Defect and Dopants in 2D Semiconductor Monolayer MoS<sub>2</sub> and WS<sub>2</sub>, Jamie Warner, University of Oxford, UK

INVITED

Defects impact the properties of materials and understanding their atomic structure is critical to their interpretation and behaviour. I will discuss how aberration corrected TEM can be used to resolve the detailed structure of Sulfur vacancies and grain boundaries in CVD grown MoS<sub>2</sub> and WS<sub>2</sub>. I will present our latest results on detecting single Cr and V impurity dopants that substitute Mo and W sites. Electron energy loss spectroscopy is used to map out the spatial position and confirm the contrast profiles from HAADF STEM images. Single Pt atoms are added to the surface of MoS<sub>2</sub> and we study the dynamics of hopping between S vacancies. Finally I will discuss in situ observations of Pt nanocrystal formation on MoS<sub>2</sub> using high temperature annealing.

### 4:00pm 2D+AS+SS-ThA6 Interaction of an Energetic Ar Molecular Cluster Beam with Graphene, Songkil Kim, A.V. Levlev, J. Jakowski, I. Vlasiouk, M.J. Burch, C.C. Brown, A. Belianinov, B.G. Sumpter, S. Jesse, O.S. Ovchinnikova, Oak Ridge National Laboratory

Manipulation of low dimensional nanomaterials provides intriguing opportunities to design new functional materials as well as to develop next-generation device applications. To manipulate properties of low dimensional nanomaterials, extensive study has been conducted so far for interaction of energetic particles with low dimensional nanomaterials. However, most of the research has been focused on utilizing electron or light/heavy ion beams to study irradiation effects on alternation of structural, mechanical and electrical properties of nanomaterials. In this study, we investigated the effect of Argon molecular cluster beam irradiation on both defect formation and removal of organic contaminants on graphene. An Argon cluster beam was generated using the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) combined with Atomic Force Microscopy (AFM). The ToF-SIMS allows for conducting in-situ monitoring of defect formation as well as organic contaminants removal. This leads to accomplishments of a high degree of controls over modification of graphene. A systematic study has been conducted to provide in-depth understanding about defect formation of graphene by synergistic theoretical and experimental approaches. Raman spectra clearly indicate that suspended graphene is more susceptible to Ar cluster beam irradiation than supported graphene on a SiO<sub>2</sub>/Si substrate under the same irradiation conditions. The underlying mechanisms for the experimentally observed phenomena are demonstrated by theoretical analysis using the first-principles molecular dynamics calculations.

This work was supported by the Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

### 4:20pm 2D+AS+SS-ThA7 Efficient and Low-Damage N-doping of Graphene by Nitrogen Late-Afterglow Plasma Treatment, Xavier Glad, G. Robert-Bigras, P. Levesque, R. Martel, L. Stafford, Université de Montréal, Canada

Graphene already shows promises for the next generation of electronics and optoelectronics devices and other applications where a band gap or magnetic response is necessary [1]. The availability of versatile processing techniques is thus crucial to the development of these graphene-based technologies. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. In this work, we explore the potential of the late afterglow of a microwave N<sub>2</sub> plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils.

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/C = 29%) while RS assessed an uncommonly low damage generation (D/G ratio below 0.4) for such incorporation.

XPS, RS and ultraviolet photoelectron spectroscopy (UPS) were also performed on the sample after transfer to an Si/SiO<sub>2</sub> substrate via the PMMA method [2]. The results show a strong decrease of the N content (N/C = 6%) which is attributed to the desorption of out-of-plane adsorbed N due to the transfer. RS and UPS techniques both support an n-doping which is associated to the different aromatic N-incorporations deconvoluted from the high resolution XPS spectra.

The low ion density (< 10<sup>7</sup> cm<sup>-3</sup>) and the high density of reactive neutral (> 10<sup>14</sup> cm<sup>-3</sup>) and metastable species (> 10<sup>10</sup> cm<sup>-3</sup>) of the nitrogen late-afterglow in our conditions [3] are believed to be the key of such efficient and low-defect N-incorporation in graphene.

[1] Vashist SK, Luong JH (2015) *Carbon* 84 519-550.

[2] Suk JW, Kitt A, Magnuson CW *et al.* (2011) *ACS Nano* 5(9):6916-6924.

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### 4:40pm 2D+AS+SS-ThA8 Exploring the Electronic Signature of Disordered Monolayer MoS<sub>2</sub>, Chinedu Ekuma, D. Gunlycke, Naval Research Laboratory

Atomic defects in two-dimensional semiconductors could be used to induce insulator-metal transitions (IMT), making it possible to have both insulating and metallic behavior in different regions of a single seamless material. Using a first-principles-based many-body typical medium dynamical cluster approach [1], we explore the electronic signature in monolayer MoS<sub>2</sub> resulting from atomic defects. Analyzing the typical (geometric) density of states, which unlike the arithmetic density of states, is able to discern

localized and delocalized states, our calculations show a correlation-mediated IMT at the experimentally relevant sulfur vacancy concentration  $\sim 10^{13} \text{ cm}^{-2}$ , depending on the strength of the intrinsic electron-electron interactions. We will also discuss the role of atomic defects on the absorption spectra.

[1] C. E. Ekuma, V. Dobrosavljević, and D. Gunlycke, Phys. Rev. Lett. 118, 106404 (2017)

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5:00pm **2D+AS+SS-ThA9 Heterogeneity in 2D Materials: From Localized Defects, Isoelectronic Doping to Macroscopic Heterostructures**, *Kai Xiao, X. Li, M. Mahjouri-Samani, M.-W. Lin, L. Liang, A. Oyedele*, Oak Ridge National Laboratory, *M. Tian*, University of Tennessee, *A.A. Puretzky, J. Idrobe, M. Yoon, B.G. Sumpter*, Oak Ridge National Laboratory, *G. Duscher*, University of Tennessee, *C.M. Rouleau, D.B. Geohegan*, Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces, and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. This talk will discuss the fundamental understanding of the roles of heterogeneity, atomic interface, and disorder in 2D materials and their heterostructures. Through isoelectronic doping in monolayer of  $\text{MoSe}_2$ , the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced due to the decrease of defect-mediated non-radiative recombination. In addition, we demonstrate the non-equilibrium, bottom-up synthesis of single crystalline monolayers of 2D  $\text{MoSe}_{2-x}$  with controllable levels of Se vacancies far beyond intrinsic levels. Both substitutional dopants and vacancies were shown to significantly alter the carrier properties and transport characteristics within a single monolayer (e.g., n- to p-type conduction in W-doped  $\text{MoSe}_2$  and in Se-deficient  $\text{MoSe}_{2-x}$ ). The vertical and lateral 2D heterostructures by controlled assembly and doping will be discussed. In addition, the lattice misfit heterostructures of monolayer  $\text{GaSe}/\text{MoSe}_2$  were synthesized by a two-step chemical vapor deposition (CVD) method. We find the vertically stacked  $\text{GaSe}/\text{MoSe}_2$  heterostructures maintain vdW epitaxy with well-aligned lattice orientation between the two layers, forming an incommensurate moiré superlattice. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can tunably modulate the optical and electrical properties in 2D materials and their heterostructure.

**Acknowledgment:** Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility

5:40pm **2D+AS+SS-ThA11 Evidence of a One-dimensional Metal in Twin-grain Boundaries of  $\text{MoSe}_2$** , *Horacio Coy Diaz, M. Batzill*, University of South Florida

In monolayer van der Waals-materials, grain boundaries become one-dimensional (1D) line defects. Here we show using angle resolved photoemission spectroscopy (ARPES) that twin-grain boundaries in the 2D semiconductor  $\text{MoSe}_2$  exhibit parabolic metallic bands. The 1D nature is evident from a charge density wave transition, whose periodicity is given by  $k_F/p$ , where the Fermi momentum  $k_F$  is determined by ARPES. Most importantly, we provide evidence for spin- and charge-separation, the hallmark of 1D quantum liquids. ARPES shows that the spectral line splits into distinctive spinon and holon excitations whose dispersions exactly follow the energy-momentum dependence calculated by 1D Hubbard model, with suitable finite-range interactions. Our results also imply that quantum wires and junctions can be isolated in line defects in 2D materials, which may enable quantum transport measurements and devices.



# Thursday Evening Poster Sessions

## 2D Materials Focus Topic

Room: Central Hall - Session 2D-ThP

## 2D Materials Poster Session

**2D-ThP1 In-situ Analysis of Electronic Structure of monolayer MoS<sub>2</sub> using Photoemission Spectroscopy and Kelvin probe.** *JaeGwan Chung, U.J. Kim, D. Yun, Y.S. Kim, J. Shin*, Samsung Electronics, Republic of Korea

Although two-dimensional monolayer transition metal dichalcogenides reveal numerous unique features that are inaccessible in bulk materials, their intrinsic properties are often obscured by environmental effects. Among them, work function, which is the energy required to extract an electron from a material to vacuum, is one critical parameter in electronic/optoelectronic devices.

In this study, we systematically measure the electronic structure of monolayered MoS<sub>2</sub> – work function, energy band gap, conduction band and valence band structure by in-situ photoemission spectroscopy (PES), inverse photoemission spectroscopy (IPES), reflective electron energy loss spectroscopy (REELS) and Kelvin Probe (KP) under various ambient condition (air, ultra-high vacuum, oxygen and nitrogen gases). The energy band gap by REELS of monolayer MoS<sub>2</sub> on SiO<sub>2</sub> is 1.7 eV. It shows a increase as compared with the optical band gap of 1.2 eV of Bulk MoS<sub>2</sub> [1]. And also, the valence band offset and conduction band offset of mono layer MoS<sub>2</sub> are shifted higher binding energy side of 0.5 eV. A work function measured by in-situ KP of 4.04 eV in vacuum was converted to 4.47 eV with O<sub>2</sub> exposure, which is comparable with a large variation in graphene. The homojunction diode by partially passivating a transistor reveals an ideal junction with an ideality factor of almost one and perfect electrical reversibility. The estimated depletion width obtained from photocurrent mapping was ~200 nm, which is much narrower than bulk semiconductors. References [1] Y. Zhang, Nature nanotech. **9** 111 (2014).

**2D-ThP2 Reliable Passivation of Black Phosphorus by Thin Hybrid Coating.** *S. Gamage, Alireza Fali, N. Aghamiri*, Georgia State University, *L. Yang, P.D. Ye*, Purdue University, *Y. Abate*, Georgia State University  
**Topic:** 2D materials

Black phosphorus (BP) possesses several extraordinary properties such as layered structure but with a unique puckered single-layer geometry, thickness dependent direct bandgap, high carrier mobility and anisotropic in-plane properties that not shared by other exfoliable materials that are highly desirable from the point of view of fundamental science and modern optoelectronics applications. The excitement about this material has always been accompanied by unreserved skepticism due to its extraordinary degradation under ambient conditions. Here we show ambient degradation of exfoliated BP can be effectively suppressed using thin layer of hybrid MOCVD coating of BN followed by ALD coating of Al<sub>2</sub>O<sub>3</sub>. We have extensively studied the time dependent surface, optical and electrical properties of BP encapsulated by BN and/or Al<sub>2</sub>O<sub>3</sub> using nanoscale infrared imaging and I-V characterizations. Our results show hybrid thin layer (~5 nm) BN/Al<sub>2</sub>O<sub>3</sub> coated BP exfoliated on SiO<sub>2</sub> substrate is protected from degradation in ambient for over 45 days much longer than those coated on BN or Al<sub>2</sub>O<sub>3</sub> layers only as well as those exfoliated on Si substrate. Our theoretical modeling of the experimental degradation growth pattern shows that the influence of neighboring elements on the degradation of a given element is minimal for BP flakes with hybrid coating. Electrical characterization further confirms the effectiveness of BN/Al<sub>2</sub>O<sub>3</sub> as encapsulation layer and gate dielectrics with minor changes after several weeks.

**2D-ThP3 Temperature-dependent Photo-current Behaviors of CVD-grown MoS<sub>2</sub> layers.** *Soyeong Kwon, E. Kim, Y. Cho*, Ewha Womans University, Republic of Korea, *Y. Kim, B. Cho, D.-H. Kim*, Korea Institute of Materials Science, *D.-W. Kim*, Ewha Womans University, Republic of Korea  
MoS<sub>2</sub>, a representative 2D atomically thin semiconductor, has unique optical, electrical, and mechanical properties. There have been intensive research efforts to fabricate MoS<sub>2</sub>-based optoelectronic devices due to its sizable band gap (1.2 ~ 1.8 eV). In this work, we investigated transport behaviors of MoS<sub>2</sub> layers, grown by chemical vapor deposition (CVD), in dark and under illumination of visible light [1,2]. CVD techniques can produce high-quality, large-area MoS<sub>2</sub> thin films with a high throughput. Surface potential maps near the electrode/MoS<sub>2</sub> contacts were obtained using Kelvin probe force microscopy, which clearly showed how the potential gradient near the contacts could affect the collection of the photo-generated carriers. The dark- and photo-current behaviors of the devices in dark and light were measured

while varying the sample temperature (100 ~ 300 K). The temperature dependent current-voltage characteristics helped us to understand the carrier transport mechanism and its roles in the photo-detection of the CVD-grown MoS<sub>2</sub> thin films.

1. Y. Cho et al., *ACS Appl. Mater. Interfaces* **8**, 21612 (2016).

2. Y. Cho et al., *ACS Appl. Mater. Interfaces* **9**, 6314 (2017).

**2D-ThP4 Controlling Charge Density Wave Transition in Monolayer TiSe<sub>2</sub>** *Sadhu Kolekar, M. Batzill*, University of South Florida

Layered transition metal dichalcogenides (TMDCs) have been studied for their charge density wave (CDW) and superconductivity transitions. TiSe<sub>2</sub> is interesting because traditional explanations for CDW formation based on electron phonon coupling described by Fermi surface nesting does not apply. Instead an unconventional excitonic mechanism has been invoked. The well-established dependence of the exciton binding energy on the number of layers in TMDCs implies that the CDW transition in TiSe<sub>2</sub> should also be layer dependent. Furthermore, the dielectric properties of the substrate for monolayer TiSe<sub>2</sub> should exert further control over the excitonic properties and thus the CDW transitions in TiSe<sub>2</sub>. Here we investigate mono- to few-layer TiSe<sub>2</sub> films grown by molecular beam epitaxy on HOPG or MoS<sub>2</sub> substrate by variable temperature scanning tunneling spectroscopy. We show that the band gap opening and CDW transition temperature in monolayer is strongly increased compared to bulk TiSe<sub>2</sub> and correlates with the expected exciton binding energy dependence. Interestingly, we also observe phase coherence peaks in monolayer TiSe<sub>2</sub>. The phase coherence occurs, however, at a much lower temperature than the CDW transition, suggesting that formation of an excitonic condensate is possible but is not essential for CDW formation.

**2D-ThP5 Growth and Characterization of MoTe<sub>2</sub> on GaTe by Molecular Beam Epitaxy.** *Paula Mariel Coelho, M. Batzill*, University of South Florida

MoTe<sub>2</sub> exist in semiconducting (2H) and metallic (1T') polymorphs. The potential for switching between these phases makes it a promising 2D material for phase change applications. In this study we are investigating van der Waals epitaxy of single layer MoTe<sub>2</sub> on different substrates and growth conditions. Specifically, we aim at selectively growing 2H or 1T' phases by molecular beam epitaxy. Using van der Waals substrates with symmetries similar to the 2H or 1T' phases of MoTe<sub>2</sub> we are aiming at obtaining epitaxial single crystalline monolayer materials. Specifically, we propose GaTe to be a suitable substrate for the growth of 1T'-MoTe<sub>2</sub>. We characterize the substrates and MoTe<sub>2</sub>-films *in-situ* by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and angle resolved photoemission spectroscopy (ARPES). Furthermore the thermal stability and phase change behavior of these monolayers are investigated.

**2D-ThP7 Single Layer VSe<sub>2</sub>: A Ferromagnetic 2D Material.** *Manuel Bonilla, S. Kolekar, H. Coy Diaz, Y. Ma, M. Batzill*, University of South Florida

VSe<sub>2</sub> has been proposed to be ferromagnetic in single- to few- layer form. However, the high reactivity of VSe<sub>2</sub> makes mechanical exfoliation to single layers and subsequent magnetic characterization challenging. Here we grow VSe<sub>2</sub> by molecular beam epitaxy in ultra-high vacuum. We characterize the film-growth and materials properties *in-situ* by scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. High quality single- to few- layer materials are obtained, with the well-known charge density wave transition for bulk VSe<sub>2</sub> persisting to monolayer material. For magnetic characterizations we protect the single- to few- layer materials from oxidation by a few nanometer thick selenium capping layer. We observe a strong ferromagnetism for the single layer, which decreases with number of layers. This study shows that VSe<sub>2</sub> single layer is indeed a promising 2D ferromagnetic material, whose magnetic properties can be tuned by the layer thickness.

**2D-ThP8 Surface Functionalization of Few-layer MoS<sub>2</sub> for Atomic Layer Deposition using Gold Chloride Salts.** *Jaron Kropp*, UMBC, *T. Gougousi*, University of Maryland, Baltimore County

Transition metal dichalcogenides such as MoS<sub>2</sub> have attracted much interest in the field of nanoelectronics in recent years. MoS<sub>2</sub> is a layered material with a hexagonal structure similar to graphene. Unlike graphene, however, MoS<sub>2</sub> is a semiconducting material with an indirect band gap of ~1.2 eV in bulk form and a direct band gap of ~1.8 eV in monolayer form. As such, MoS<sub>2</sub> has attracted interest as a possible channel material in field-effect transistors. An important feature of the modern field-effect transistor is the gate dielectric. In the past decade, the electronics industry has transitioned from using native silicon oxide as the gate dielectric to using high-k metal oxides deposited via atomic layer deposition. Field-effect devices fabricated from MoS<sub>2</sub> will thus

require the growth of metal oxides on the MoS<sub>2</sub> surface. Unfortunately, the sulfur-terminated MoS<sub>2</sub> surface is hydrophobic and not conducive to metal oxide film growth using atomic layer deposition. As such, the surface must be functionalized prior to deposition. Here, we report a novel wet chemistry method for functionalization of MoS<sub>2</sub> surfaces using gold chloride salts.

Mechanically exfoliated MoS<sub>2</sub> surfaces are treated by immersion in a solution of HAuCl<sub>4</sub> or AuCl<sub>3</sub> for 5-60 seconds and are subsequently subjected to atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> using trimethylaluminum and water as precursors. We measure the effectiveness of the surface treatment by investigating the post-deposition surface topography using atomic force microscopy. Our hypothesis is that immersion of the MoS<sub>2</sub> surfaces in the gold chloride solution will leave behind adsorbed gold chloride molecules which render the surface hydrophilic and amenable to the growth of metal oxide films. While untreated surfaces show island growth, gold chloride-treated surfaces show more coalesced films. Treatment for at least 30 seconds results in a reduction of the film RMS roughness by a factor of 4 compared to untreated surfaces after deposition of 3 nm (nominal thickness) Al<sub>2</sub>O<sub>3</sub> at 200°C. Film surface coverage improves from 50-60% on untreated surfaces to 80-99% on surfaces treated for 10 seconds and finally to complete film coverage on surfaces treated for 30 and 60 seconds. Surface roughness and coverage is investigated as a function of film thickness and deposition temperature, and provides information on initial growth mechanisms and process conditions for the growth of conformal, high-quality films.

**2D-ThP10 Alternative Pathway to Silicene Synthesis via Surface Relaxation of Hexagonal-MoSi<sub>2</sub> Crystallites, Cameron Volders, E. Monazami, G. Ramalingam, P. Reinke, University of Virginia**

The 2D material community has been dominated by Graphene, however, more recently, different single layer materials have garnered more attention including transition metal dichalcogenides (TMDs), silicene, and germanene. Silicene is particularly intriguing due to its potential for integration into silicon based devices. The most frequently used method for synthesizing silicene has been the deposition of monolayer (ML) amounts of Si onto Ag (111). The resulting layer(s) exhibit a honeycomb symmetry, which have been identified as silicene. An alternative interpretation of the Si-Ag system suggests the formation of 2D Ag-Si surface alloy rather than the formation of a well-defined silicene layer.

Our work will present an approach, which offers an alternative pathway for growing silicene layers, based on the observation of a Silicene-like reconstruction (SLR) on the surface of hexagonal-MoSi<sub>2</sub> crystallites. Scanning Tunneling Microscopy and Spectroscopy were the primary techniques used for this study. H-MoSi<sub>2</sub> crystallites are grown by depositing Mo onto a Si (001) surface followed by annealing. These crystallites are terminated by the (0001) plane which is comprised of Si hexagons with a Mo atom residing in the center. Upon annealing, the Si atoms decouple from the underlying h-MoSi<sub>2</sub> crystallites and a honeycomb pattern with the lateral dimensions of a low-buckled silicene structure is observed.

We first discuss the optimal parameter space where the SLR is consistently reproduced. This regime includes depositing 2-5 MLs of Mo onto a Si (001) substrate and annealing around 650 - 800°C. In this regime the SLR structure is readily observed and the geometrical parameters are nearly identical to that of a ( $\sqrt{3}\times\sqrt{3}$ ) silicene superstructure. Additional features of the SLR such as a well-defined 'rim' structure and defect motif will also be discussed.

The area of the SLR structure is controlled by the surface area of the h-MoSi<sub>2</sub> crystallites, therefore, the second portion of this work will discuss how to control the size and distribution of these crystallites, thus the area of the SLR layer. This becomes critical for future device integration and assessing the detailed bonding structure with AR-UPS.

We would like to thank the Office of Naval Research for supporting this work.

(1) Volders, C.; Monazami, E.; Ramalingam, G.; Reinke, P. Alternative Route to Silicene Synthesis via Surface Reconstruction on h-MoSi<sub>2</sub> Crystallites *Nano. Lett.* **2017**, 17, 299-307.

**2D-ThP11 CVD Grown 2D Metal Carbides using Folded Cu/Metal Foils, Kwonjae Yoo, I.S. Kang, G. Kim, M.S. Hyun, Y.C. Park, National Nanofab Center (KAIST), Republic of Korea, S. Lee, C. Hwang, Korea Research Institute of Standards and Science, Republic of Korea**

Two dimensional (2D) metal carbides (MC) are recently entered in a playground of 2D materials world. Unlike conventional 2D materials, such as graphene and transition metal chalcogenides, they have shown the unique properties of 2D metallic- and superconducting- state. Moreover, their high thermal and chemical stability due to covalent-ionic bonding between metal and carbide atoms can offer a great advantage for harsh environmental sensor applications.

2D MC are obtained by selective extraction method from ternary carbides or by recently chemical vapor deposition (CVD). While monolayer metal

carbides known as MXenes which produced by selective extraction method have shown defects and surface terminations which affect their physical properties, CVD grown monolayer metal carbides such as Mo<sub>2</sub>C, W<sub>2</sub>C are known to have very low defects [1, 2]. This modified CVD method uses Cu foil on molybdenum foil with melted Cu and moly alloy surface near the temperature of the Cu melting point.

Here we present the CVD using Cu foil inside folded Mo foil for growing metal carbides. The folded Mo foil inside CVD quartz tube not only prevents from evaporation of melted Cu, but also provides uniform gas flow. These growth conditions seem to be positive effect on the growth of large area and uniform monolayer metal carbides such as Mo<sub>2</sub>C and W<sub>2</sub>C. We investigated CVD grown monolayer Mo<sub>2</sub>C using electron back scattering diffraction (EDSD), tunneling electron microscopy (TEM), and low temperature electron transport. Growth results depending on Cu crystallographic orientation will be discussed.

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**2D-ThP12 Scanning Tunneling Microscopy and Spectroscopy of Wet Chemically Synthesized Porous Graphene Nanoribbons, Kaitlyn Parsons, A. Radocea, University of Illinois at Urbana-Champaign, M. Pour, University of Nebraska - Lincoln, T. Sun, N. Aluru, University of Illinois at Urbana-Champaign, A. Sinitskii, University of Nebraska - Lincoln, J.W. Lyding, University of Illinois at Urbana-Champaign**

The bottom-up wet chemical synthesis of graphene nanoribbons (GNRs) opens interesting opportunities for tailoring the GNR structure with atomic precision [1]. Atomically precise porous GNRs are a new chemically synthesized variation for which the fabrication procedure yielding multiple pores in a single ribbon and the electronic details of the ribbon have not been reported. In this work, porous GNRs are dry contact transferred in ultrahigh vacuum to clean silicon and III-V semiconducting substrates and examined using UHV scanning tunneling microscopy (STM) and spectroscopy (STS). STM imaging confirms the expected porous structure and indicates a unique electronic feature at the graphene nanopores, and STS measurements indicate a 2.0 eV bandgap. These results are compared to first-principles DFT simulations in which an increased local density of states at the pores is predicted. A GW correction predicts a 3.24 eV bandgap. Illumination of pore effects in GNRs contributes to an increased understanding of the tunability of GNR electronic structure. Porous GNRs have potential applications in molecular filtration, detection and DNA sequencing.

References

- [1] Vo, T. H., Shekhirev, M., Kunkel, D. A., Morton, M. D., Berglund, E., Kong, L., Wilson, P. M., Dowben, P. A., Enders, A., and Sinitskii, A., *Nat. Commun.* 2014, 5, 3189.

**2D-ThP13 Surfactant-Exfoliated 2D Molybdenum Disulphide (2D-MoS<sub>2</sub>): The Role of Surfactant upon the Hydrogen Evolution Reaction, Simon Hutton, Kratos Analytical Limited, UK, S.J. Rowley-Neale, C.E. Banks, Manchester Metropolitan University, UK, C.J. Blomfield, S.J. Coultas, A.J. Roberts, J.D.P. Counsell, Kratos Analytical Limited, UK**

Hydrogen, produced via the electrolysis of water, is a promising alternative to fossil fuels. Hydrogen may be transported in bulk from areas of energy production to areas of energy consumption and used to generate electricity directly in fuel cells. One of the major problems limiting the widespread take-up of hydrogen based technology is the high cost of platinum which is used as a catalytic electrode material in both water electrolysis and fuel cells.[1]

Recent research has focused on finding a more cost effective electrode materials to catalyse the Hydrogen Evolution Reaction (HER). Studies have shown that 2D Molybdenum disulphide (2D-MoS<sub>2</sub>) can be used as an effective electrocatalyst towards the HER.[2] Surfactant (e.g. sodium cholate, SC) mediated aqueous liquid phase exfoliation is a common method of fabricating 2D-MoS<sub>2</sub> nanosheets. This method produces defect free flakes with nanometer lateral size (2D-MoS<sub>2</sub>-SC).

This study investigates the effect of using sodium cholate to produce the 2D nanosheets (2D-MoS<sub>2</sub>-SC) on the electrocatalytic behaviour towards the HER when compared to 2D-MoS<sub>2</sub> produced without a surfactant. The 2D-MoS<sub>2</sub>-SC nanosheet surface was characterised using X-ray photoelectron spectroscopy. Electrocatalytic performance was evaluated by measuring the HER onset potentials, current densities and Tafel values.

**2D-ThP14 Low Damage Layer-controlled Thinning of Black Phosphorus by a Low Energy Ar<sup>+</sup> Ion Beam,** *Jinwoo Park, D.S. Kim, W.O. Lee, M.K. Mun, K.S. Kim, G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

Black phosphorus (BP) is one of the most interested two-dimensional (2D) layered materials due to their unique properties of energy band gap change from 0.3 eV (bulk) to 2.0 eV (monolayer) depending on the number of BP layers for the application of nanoelectronic devices. Currently, for the fabrication of 2D BP materials, a thinning technique from bulk material to 2D material needs to be used while controlling the removed layer thickness. In this study, low-damage layer thinning of BP was performed by using an Ar<sup>+</sup> ion beam method and its BP thinning characteristics were investigated. By using the Ar<sup>+</sup> ion energy of ~ 45 eV, the BP could be thinned with the thinning rate of ~ 5 Å/min down to bilayer without increasing the surface roughness and changing the chemical binding states. Back-gate BP field-effect transistors (FETs) fabricated with a BP thinned to bilayer ~ 10 layers by the Ar<sup>+</sup> ion beam exhibited the electrical characteristics similar to those of pristine BP FETs such as a high-drain current and 7000 on/off ratio suggesting no electrical damage on the BP layers thinned by the low-energy Ar<sup>+</sup> ion beam. Therefore, it is believed that the low energy Ar<sup>+</sup> ion beam technique used in this study can precisely control thickness 2D materials like BP without any damages and can be a promising thinning method for fabricating 2D-based devices.

**2D-ThP15 Controlled Growth of Multilayered Hexagonal Boron Nitride on Ni-Cu Alloys,** *Karthik Sridhara,* Texas A&M University, *B.N. Feigelson, J.K. Hite,* US Naval Research Laboratory, *L.O. Nyakiti,* Texas A&M University Galveston

Hexagonal boron nitride (h-BN) has been frequently studied as a potential substrate and a tunnel dielectric for two-dimensional materials such as graphene and transition metal dichalcogenides. Large area (>1 cm<sup>2</sup>) single and multilayered h-BN films have been successfully grown using chemical vapor deposition (CVD) on various single crystal and polycrystalline transition metal substrates such as Cu, Ni, Pt, and Ag. Of these substrates, polycrystalline Cu followed by polycrystalline Ni are by far the most commonly used substrates for CVD growth. Despite the popularity of polycrystalline Cu and Ni for the growth of h-BN, controlled uniform growth of multilayered (>3 layers) and few-layered (<3 layers) h-BN still remains a challenge.

We propose a method to grow few and multilayered h-BN on nickel-copper (NiCu) alloys, and control the thickness of h-BN by varying the concentration of Cu in NiCu alloy samples. These NiCu alloys are prepared by electroplating Cu onto high purity (99.8%) Ni foils (25 μm) and thermally annealing them at 1030°C for > 3 hours in H<sub>2</sub> environment. The Cu concentration in the alloy can be controlled by the electroplating current density and time to give desired weight percent of Cu deposited on Ni foils. NiCu alloys with four different Cu weight percentages (10%, 20%, 30%, 40%) are prepared using electroplating and thermal annealing procedure. The alloyed foils are subsequently cut into smaller pieces (~1 cm<sup>2</sup>) and are further annealed before h-BN growth. h-BN films are grown on these alloyed samples at 1030°C using borazine as the precursor, with H<sub>2</sub> and N<sub>2</sub> as the carrier gases, and high purity Cu (99.98%) and Ni (99.8%) are used as control samples. We use energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to quantify the Ni and Cu concentration in the alloy. Scanning electron microscopy (SEM) is used to assess the surface morphology of the alloys, and ascertain the crystal size of h-BN films. We use Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) to assess the h-BN film growth. Our preliminary results show that there is an immediate increase in the amount (thickness) of h-BN with the introduction of Cu in the NiCu alloy. We observe a subsequent decrease of h-BN thereafter with increasing Cu concentration in the NiCu alloy samples. We consistently observe that the thickest h-BN films, as calculated by FT-IRRAS peak area, grow on Ni<sub>90</sub>Cu<sub>10</sub> while the thinnest grow on Ni<sub>60</sub>Cu<sub>40</sub>. We also observe that the alloy grain size decreases with increasing Cu concentration. The role of alloy surface morphology and the h-BN growth kinetics will also be discussed.

**2D-ThP16 Metal Oxide/Functionalized Graphene Oxide Composite as Highly Stable Lithium Ion Battery Anode with Enhanced Performance,** *SunSook Lee,* Korea Research Institute of Chemical Technology(KRICT), Republic of Korea, *S. Ji, J.Y. Ju, S-K. Kim, J.K. Kim, S. Choi,* Korea Research Institute of Chemical Technology(KRICT)

Metal-oxide based lithium ion battery(LIB) anodes theoretically should provide high specific capacity, but their disappointing experimentally measured capacity and cycle stability inhibit their commercial usage. Here, we propose a simple method to process Metal oxide/functionalized-graphene-oxide(fGO) composite anode, in which fGO is inserted as the current path that simultaneously enhances the specific capacity to reach near the theoretical capacity and the cyclic stability at least up to 200 cycles for the metal oxide based anodes.

**2D-ThP18 Exploration of Hybrid 2DEG/Ferroelectric Heterostructure Fabrication Methodology,** *Stephan Young, E.J. Moon, R. Doucette, A.N. Caruso,* University of Missouri - Kansas City

The hybrid two-dimension electron gas (2DEG)/ferroelectric (FE) heterostructure system has many promising applications, including field effect transistors and non-volatile memory. Such devices exploit the ambipolar field effect, utilizing the high local electric field produced by the FE substrate to shift the Fermi level in the 2DEG. Thus, controlling magnitude and direction of polarization of the FE can significantly alter conductivity and majority charge carrier in the 2DEG. FE/2DEG hybrid devices are typically fabricated by transferring the 2DEG onto the FE substrate. However, this process often introduces adsorbates onto the surface of the 2DEG and FE, resulting in a poor interface and degrading the electric field at the 2DEG. This problem can be partially mitigated by improving the transfer process, but direct growth is a path to eliminate the problem entirely. This work explores the effect of different transfer processes in comparison to chemical vapor deposition growth of 2DEG's directly on FE substrates. The study aims to elucidate the interfacial interaction between 2DEG's (i.e. transition metal dichalcogenides and graphene) and low-coercivity, high-remnant-polarization perovskite ferroelectrics. Characterization of the 2DEG domain size was completed with atomic force microscopy, the number of layers confirmed with Raman spectroscopy, and the conductivity of each growth was measured.

This work was supported by the Office of Naval Research (ONR) under N00014-16-1-2067.

**2D-ThP20 Effect of Stacking Orientation and Sag on the Strength and Fracture of Graphene Oxide,** *Teng Cui, C.H. Cao, S. Parambath Mundayodan, Y. Sun, T. Filleter,* University of Toronto, Canada

One great challenge in translating the extraordinary mechanical properties of isolated 2D materials to impact real applications is to understand, and bridge the gap, between monolayer and multilayer properties. Bilayer films, as the most fundamental step towards this challenge, require systematic study to unveil the interaction between layers and elucidate the effect on mechanical behavior. Here, bilayer graphene oxide (GO) with different crystalline stacking orientation and sag conditions will be presented, and the resulting effect on the material strength and fracture will be discussed in detail.

Highly oxidized bilayer GO films were prepared on perforated substrates by a solution-based method, from which different interlayer crystalline stacking angle and sagging depth were obtained and characterized. Atomic force microscopy-based mechanical testing revealed higher strength of aligned (small stacking angle) bilayers as compared to misaligned (large stacking angle) counterparts. Further transmission electron microscopy analysis of fracture surface revealed through-film fracture for the aligned case and individual layer cracking for the misaligned case, casting light on the origin of the strength discrepancy. In addition, the suspended GO films present different sagging depth, which in turn is found to effect the load carrying capacity and the fracture behavior significantly. Our results demonstrated that bilayer GO with ~165 nm sag doubles the fracture force as compared to ~ 40 nm sag. A deeper understanding of the configurational effect, e.g., stacking orientation and sagging, on the mechanical behavior will better facilitate engineering GO for various applications at different size scales.

**2D-ThP22 Single Atom Manipulation and Controllable Atom by Atom Assembly in 2D Materials via Scanning Transmission Electron Microscopy,** *Sergei Kalinin, O. Dyck, S. Kim, S. Jesse,* Oak Ridge National Laboratory

Fabrication of structure atom-by-atom has remained one of the longest-held dreams of nanoscience, as a key element of nanotechnology and penultimate step for understanding physics and chemistry on the atomic level. The development of scanning tunneling microscopy (STM) in the early 1980s has demonstrated the potential of an atomically sharp tip to induce atomic motion on a surface, originally perceived to be detrimental to microscope operation. The work by Eigler at IBM in the early 1980s demonstrated that tip induced atomic motion can be used for the assembly of functional atomic structures, an accomplishment believed to be one of the key factors that lead to the nanotechnology revolution of the last decades. However, STM operation necessitates low temperature ultra-high vacuum environments and typically results in structures confined to reactive surfaces. Correspondingly, it took over 20 years to transition from atomic manipulation by STM to viable pathways for single-atom devices. This in turn, necessitates the search for alternative methods for single atom manipulation and atom-by-atom assembly.

Here we demonstrate that the sub-atomically focused beam of a scanning transmission electron microscope (STEM) can be used to controllably manipulate individual dopant atoms in a 2D graphene lattice. We demonstrate the manipulation of adsorbed source materials and the graphene lattice with the electron beam such that individual vacancy defects can be controllably passivated by Si substitutional atoms. We further demonstrate that these Si

defects may be directed through the lattice via e-beam control or modified to form new defects which can incorporate new atoms into the graphene lattice. We further explore the application of beam to probe local dynamics within individual or between adjacent atomic sites. These studies demonstrate the potential of STEM for atom-by-atom nanofabrication and fundamental studies of chemical reactions in 2D materials on the atomic level.

Research supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy (S.V.K.), and by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy (O.D, S.K.,S.J.).

# Friday Morning, November 3, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+MI+NS+SS+TF-FrM

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

**Moderators:** Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

8:20am **2D+MI+NS+SS+TF-FrM1 Electro-optics with 2D Semiconductors and Heterostructures**, *Goki Eda*, National University of Singapore, Singapore **INVITED**

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS<sub>2</sub> and phosphorene exhibit distinctly strong light-matter interaction compared to their bulk counterparts. Excitons and their complexes with giant oscillator strength play a fundamental role in mediating the strong coupling between light and a 2D semiconductor. These excitons are stable at room temperature and make 2D semiconductors attractive for a number of photonic devices including ultra-fast photo-detectors, optical modulators, on-chip photonic circuits, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers<sup>1</sup>. In order for these devices to be integrated for photonic devices, practical schemes for electrical generation, manipulation, and detection of excitons need to be developed. We create artificial quantum wells based on van der Waal heterostructures and investigate the dynamics of 2D excitons under various conditions to achieve the desired photonic functionalities. In this talk, I will start by discussing our findings on the ultrafast dipole-dipole energy transfer processes involving 2D excitons. I will show that exciton-exciton energy transfer in hetero-bilayers is among the fastest measured in nanomaterials<sup>2</sup>. Peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles will also be discussed<sup>3</sup>. Finally, our recent efforts in realizing electro-optical (electroluminescence, electro-absorption, and Pockels effect) devices will be discussed. I will share our views on the potential advantages of 2D semiconductors over other materials and discuss our outlook for further studies.

#### References:

1. F. Xia et al. "Two-dimensional material nanophotonics" Nat. Phot. 8, 899 (2016).
2. D. Kozawa et al. "Efficient interlayer energy transfer via 2D dipole coupling in MoSe<sub>2</sub>/WS<sub>2</sub> heterostructures" Nano Lett. 16, 4087 (2016).
3. W. Zhao et al. "Exciton-plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles" Adv. Mater. 28, 2709 (2016).

9:00am **2D+MI+NS+SS+TF-FrM3 Understanding Variations in Circularly Polarized Photoluminescence in Monolayer Transition Metal Dichalcogenides**, *Kathleen McCreary, M. Currie, A.T. Hanbicki, B.T. Jonker*, Naval Research Laboratory

The unique electronic band structure in monolayer transition metal dichalcogenides (TMDs) provides the ability to selectively populate a desired conduction band valley by exciting with circularly polarized light. The subsequent valley population can be interrogated by measuring helicity-resolved photoluminescence (PL). A high degree of circular polarization has been theoretically predicted for resonant excitation of TMDs, yet rarely observed experimentally. In fact, a wide range of values for the degree of circularly polarized emission ( $P_{\text{circ}}$ ), has been reported for monolayer TMDs, although the reasons for the disparity are unclear. Here we investigate the room-temperature  $P_{\text{circ}}$  in several TMD monolayers synthesized via chemical vapor deposition. The samples include as-grown WS<sub>2</sub>, as-grown WSe<sub>2</sub>, and WS<sub>2</sub> monolayers that have been transferred to a fresh substrate. In each system, a wide range of  $P_{\text{circ}}$  and PL intensity values are observed. There is a pronounced inverse correlation between  $P_{\text{circ}}$  and PL intensity: samples that demonstrate weak PL emission and short exciton relaxation time exhibit a high degree of valley polarization. We attribute these effects to sample-dependent variations in the exciton radiative and non-radiative lifetime components. The short exciton lifetime results in a higher measured polarization by limiting opportunity for depolarizing scattering events. These findings clarify the disparities among previously reported values and suggest a means to engineer valley polarization via controlled introduction of defects and non-radiative recombination sites.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AORD 14IOA018-134141.

9:20am **2D+MI+NS+SS+TF-FrM4 Multi-Junction Lateral 2D Heterostructures of Transition Metal Dichalcogenides**, *Prasana Sahoo*, University of South Florida, *S. Memaran*, Florida State University, *Y. Xin*, National High Magnetic Field Laboratory, *L. Balicas*, Florida State University, *H.R. Gutierrez*, University of South Florida

Here we demonstrate the successful synthesis of lateral in-plane multi-junction heterostructures based on transition metal dichalcogenides (TMD) 2D monolayers. The heterostructures were synthesized using a modified chemical vapor deposition approach. By only controlling the carrier gas composition, it is possible to selectively grow only one TMD at the time. This introduces an unprecedented flexibility in the CVD process and allows a good control of the lateral size of each TMD segment. Heterostructures only containing MoS<sub>2</sub>-WS<sub>2</sub> or MoSe<sub>2</sub>-WSe<sub>2</sub> multiple segments, were fabricated. We also demonstrate the synthesis of heterostructures based on homogeneous TMD ternary alloys (Mo<sub>x</sub>Se<sub>y</sub>-WS<sub>2</sub>Se<sub>z</sub>). Introducing ternary alloys in heterostructures opens the horizon of possible chemical combinations and applications of 2D optoelectronic devices. The band gap modulation as well as spatial chemical distribution were studied by Raman and photoluminescence mapping. The crystalline quality of the heterostructures were characterized within an aberration-corrected scanning transmission electron microscope. Basic devices were also fabricated to study the transport properties across the junctions. Depending of the growing conditions, diffuse and/or sharp seamless interfaces with high-crystalline quality can be produced.

9:40am **2D+MI+NS+SS+TF-FrM5 Novel Electronic, Optoelectronic, and Topological Properties of 2D Materials and Their Heterostructures**, *Xiaofeng Qian*, Texas A&M University **INVITED**

Low-dimensional materials exhibits dramatically distinct properties compared to their 3D bulk counterpart. 2D materials is such a fascinating platform with many exotic physical properties and unprecedented opportunities. In this talk, I will highlight some examples of interesting 2D materials and their heterostructures, including 2D multiferroics, 2D topological insulators and topological crystalline insulators, 2D nanostructured exciton funnels. First, I will present our discovery of 2D multiferroics in semiconducting Group IV monochalcogenide monolayers with giant spontaneous in-plane ferroelectric polarization and ferroelastic lattice strain that are strongly coupled. The multiferroicity and hence anisotropic 2D excitonic responses as well as low domain wall energy and migration barrier suggest their great potentials for tunable multiferroic functional devices such as 2D ferroelectric and ferroelastic memory, 2D ferroelastolectric nonvolatile photonic memory, and 2D ferroelectric excitonic photovoltaics. In the second example, I will highlight our discovery on 2D topological insulators in binary and ternary transition metal dichalcogenides, and topological crystalline insulators in monolayer IV-VI semiconductors. We found electric field, elastic strain, and van der Waals stacking are able to induce topological phase transition (TPT), among which the electric-field induced TPT can be utilized for realizing topological field effect transistor distinctly different from conventional MOSFET. In the third example, I will discuss how macroscopic responses of materials can be tuned and configured by nanostructuring such as inhomogeneous strain engineering and van der Waals Moire patterning. Both nanostructures can modify local atomistic configurations and generate spatially varying electronic structures, thereby introducing novel excitonic photon funneling effect. The latter could be exploited for developing more efficient photovoltaics and light-emitting diodes. Finally, I will highlight relevant experimental progresses as well as some critical challenges and opportunities in 2D materials and their nanostructures.

10:20am **2D+MI+NS+SS+TF-FrM7 Imaging Nanoscale Heterogeneity at the Two-dimensional Semiconductor-Metal Heterointerface by Correlated Scanning Probe Microscopy**, *Deep Jariwala\**, California Institute of Technology, *A. Krayev, E. Robinson*, AIST-NT Inc., *M.C. Sherrott*, California Institute of Technology, *M. Terrones*, Pennsylvania State University, *H.A. Atwater*, California Institute of Technology

Transition metal dichalcogenides (TMDCs) of molybdenum and tungsten have recently attracted significant attention due to their band gaps in visible part of the spectrum for optoelectronic device applications. The ability to isolate these materials down to a monolayer with direct band-gap make TMDCs very attractive alternatives to graphene.

\* NSTD Postdoc Finalist

While a lot of investigation has been devoted to understanding of crystalline and electronic quality of TMDCs in devices, little is known about the spatial distribution of electronic quality and interfaces with metals. Conventional Raman spectroscopy and confocal Raman microscopy have proved to be useful tools in this regard. However, the spatial resolution of these techniques is diffraction limited to a few hundred nanometers only. Tip enhanced Raman scattering (TERS) provides spatial resolution down to few nanometers, along with increased sensitivity due to dramatic enhancement of the Raman signal by the plasmonic tip and is therefore a suitable technique to probe nanoscale heterogeneity in TMDC samples.

Here, we report observation of nanoscale heterogeneity in exfoliated WSe<sub>2</sub> flakes on plasmonic Au and Ag substrates using a combination of spatial mapping with TERS, contact potential difference, topography and conductance measurements. In TERS mapping of exfoliated WSe<sub>2</sub> flakes, we observe the presence of domains with enhanced or depreciated Raman signal compared to adjacent material. We also observe that WSe<sub>2</sub> demonstrates a resonant Raman response with 638nm excitation, the TERS spectra of these domains feature a single peak at around 250 cm<sup>-1</sup>, typical for non-resonant conditions. Distribution of these domains correlates extremely well with surface potential map, non-resonant areas being negatively charged compared to adjacent areas of WSe<sub>2</sub> that demonstrate a resonant Raman response.

We further correlate the TERS maps with concurrently recorded photocurrent maps, where we observe that domains showing both resonant and non-resonant Raman response, generated significant photocurrent, but of opposite polarities. Based on this observation, we conclude that in exfoliated layers of WSe<sub>2</sub>, there exist nanoscale semiconducting domains with opposite doping types when in contact with the underlying metal. This hitherto unobserved heterogeneity is therefore critical to understanding of the metal-two dimensional (2D) semiconductor contact and important for optoelectronic device design and performance. The results presented here show that cross-correlation of TERS with local conductivity, surface potential and photocurrent is a vital characterization technique for nanoscale inhomogeneities in 2D semiconductors and devices.

10:40am **2D+MI+NS+SS+TF-FrM8 Two-dimensional Circuitry Achieved by Defect Engineering of Transition Metal Dichalcogenides.** Michael G. Stanford\*, P.R. Pudasaini, A.N. Hoffman, P.D. Rack, The University of Tennessee Knoxville

Two-dimensional materials, such as transition metal dichalcogenides (TMDs), have demonstrated promising semiconducting properties. The electrical and optical properties of TMDs can be finely tuned by altering material thickness as well as chemical composition. Properties can also be tuned by defect engineering. In this work, a focused He<sup>+</sup> beam as well as a remote plasma source were utilized to introduce defects into TMDs such as WSe<sub>2</sub> and WS<sub>2</sub> with fine control. Scanning transmission electron microscopy reveals that defects introduced into the TMDs range from chalcogen vacancies (0D defects) to 1D defects and extended defect networks. Tailoring defect concentration enables tunability of the electronic properties with insulating, semiconducting, and metallic behavior each obtainable. By tuning electronic properties, we demonstrate direct-write logic gates such as resistor loaded inverters with a voltage gain of greater than 5. We also demonstrate the fabrication of edge-contacted field effect transistors by defect engineering homojunctions between metallic and semiconducting WSe<sub>2</sub> with on/off ratios greater than 10<sup>6</sup>. Defect engineering of TMDs enables the direct-write of complex devices into single flakes toward the goal of atomically thin circuitry.

11:00am **2D+MI+NS+SS+TF-FrM9 Scanning Tunneling Microscopy and Spectroscopy Studies of Atomically Precise Graphene Nanoribbons on Semiconducting Surfaces.** Ximeng Liu, A. Radocea, T. Sun, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, M. Pour, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, N. Aluru, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, A. Sinitskii, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, J.W. Lyding, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign

Graphene nanoribbons (GNRs) with atomically smooth edges, controllable geometry and therefore tunable electronic band gaps have ignited enormous interest due to their high potential for future electronic devices. Among different techniques for GNR characterization, scanning tunneling microscopy and spectroscopy (STM/STS) provide both topographic details and local electronic structure with atomic resolution. Large-scale production of two different kinds of chevron-type GNRs (the double-wide (w) GNRs and the extended chevron (e) GNRs) was realized by a solution synthesis method

[1]. Dry contact transfer technique [2] was implemented for depositing the solution-synthesized GNRs onto clean InAs (110) and hydrogen-passivated Si(100) semiconducting surfaces under ultrahigh vacuum conditions. For both GNRs, their structures were confirmed by high resolution STM imaging. The band gap of the eGNRs was determined to be 2.6eV via STS. For the wGNRs, detailed analysis and mapping of the electronic density of states both spatially and energetically was carried out with STS and current imaging tunneling spectroscopy. We found that the electron orbital shapes at the GNR edges are different from those at the centers, in agreement with computational simulations. The measured band gap of the wGNRs was only 2eV, which may result in a great improvement in conductivity. In addition, these GNRs are found to be transparent to the substrate when scanned at a small tip-sample separation, indicating a strong interaction when GNRs are pushed towards the substrate.

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11:20am **2D+MI+NS+SS+TF-FrM10 Perfectly Perforated Monolayer WSe<sub>2</sub>.** Kirby Smithe, C. Bailey, Stanford University, A. Kravayev, AIST-NT Inc., E. Pop, Stanford University

One of many prospective applications of 2D transition metal dichalcogenides (TMDs) is catalytic splitting of water for hydrogen generation. Strain in TMD layers, chalcogen atom vacancies, and increased length of the edges of TMD flakes all play an important role in increased catalytic activity, with the latter being the most effective way for improving performance. One possible way to achieve increased ratios of edge length to surface area is to use small flakes, preferably a few hundred nm across. Unfortunately, such small flakes are difficult to manipulate, and the structure of such flakes should also differ from the perfect structure of the inner areas of larger flakes<sup>1</sup>. Here we report that WSe<sub>2</sub> monolayers, grown by chemical vapor deposition (CVD) on Si/SiO<sub>2</sub> and transferred from the original substrate by means of dissolving the sacrificial SiO<sub>2</sub> layer, contain a significant concentration of perfect triangular holes. The result is confirmed by correlating the data of topography, the surface potential, friction and tip enhanced Raman spectroscopy (TERS) characterization of transferred flakes. The ratio of edge length to surface area in such perforated flakes could be up to 3 to 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain that is also beneficial for hydrogen catalytic activity. The perfect triangular shape of the holes suggests high quality of the atomic structure of the hole edges, which also implies that the perforated flakes can be used as templates for growth of distributed in-plane heterostructures of different TMDs.

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\* National Student Award Finalist

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Abate, Y.: 2D-ThP2, 33  
Abbott, J.: 2D-TuA8, 11  
Abere, M.J.: SE+2D+NS+SS+TF-WeA8, 28  
Adams, D.P.: SE+2D+NS+SS+TF-WeA11, 28;  
SE+2D+NS+SS+TF-WeA8, **28**  
Afaneh, T.: 2D+EM+SS+TF-WeM6, **16**  
Aghamiri, N.: 2D-ThP2, 33  
Ahsan, A.: 2D+MI-ThM3, 29  
Ajayan, P.: 2D+AS+SA+SP-TuM6, 6  
Alameri, D.: 2D-WeA11, 23  
Aleman, A.: SE+2D+NS+SS+TF-WeA4, 27  
Alim, M.: SU+2D+MS+NS-TuA11, 14;  
SU+2D+MS+NS-TuA12, 14  
Alles, M.L.: MN+2D-WeM3, 18  
Altieri, N.: MI+2D+AC+NS-TuA3, 12  
Aluru, N.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-  
ThP12, 34  
Amino, S.: MI+2D+AC+SA+SS-TuM5, 7  
Amiri, P.K.: MI+2D+AC+NS-TuA3, 12  
Aouadi, S.M.: SE+2D+NS+SS+TF-WeA9, **28**  
Archibald, R.: SP+2D+AS+NS+SS-MoA11, 4  
Argubay, N.: SE+2D+NS+SS+TF-WeA11, **28**  
Arguelles, E.F.: MI+2D+AC+SA+SS-TuM5, **7**  
Arlinghaus, H.F.: AS+2D+NS+SA-WeA1, 24  
Arora, N.: MN+2D-WeM12, 18  
Arslan, I.: AS+2D+NS+SA-WeA7, 24  
Arutt, C.N.: MN+2D-WeM3, 18  
Aspera, S.: MI+2D+AC+SA+SS-TuM5, 7  
Atodiresei, N.: 2D+MI-ThM2, 29  
Atwater, H.A.: 2D+MI+NS+SS+TF-FrM7, 37  
Audoit, G.: AS+2D+NS+SA-WeA3, 24  
Awschalom, D.D.: EM+2D+MI+MN-WeA7, **26**

## — B —

Babuska, T.F.: SE+2D+NS+SS+TF-WeA11, 28  
Baddorf, A.P.: 2D-TuA7, **11**  
Bailey, C.: 2D+MI+NS+SS+TF-FrM10, 38  
Balicas, L.: 2D+MI+NS+SS+TF-FrM4, 37  
Banerjee, K.: 2D+EM+MN+NS-WeA9, **22**  
Banerjee, S.K.: 2D-WeA12, 23  
Banks, C.E.: 2D-ThP13, 34  
Banks, H.: EM+2D+MI+MN-WeA10, 26  
Baraldi, A.: 2D+AS+SS-ThA2, 31  
Barja, S.: 2D+BI+MN+SS-TuA9, **10**  
Barnes, J.-P.: AS+2D+NS+SA-WeA3, **24**  
Barra, A.: MI+2D+AC+SA+SS-TuM13, 8  
Battu, A.K.: SE+2D+NS+SS+TF-WeA7, **27**  
Batzill, M.: 2D+AS+SS-ThA11, 32;  
2D+EM+MI+MN-MoM10, 2; 2D-ThP4, 33;  
2D-ThP5, 33; 2D-ThP7, 33  
Beechem, T.E.: SE+2D+NS+SS+TF-WeA8, 28  
Belianinov, A.: 2D+AS+SS-ThA6, 31  
Bender, H.: 2D-TuA10, 12  
Beniwal, S.: 2D+MI-MoA9, 3  
Berg, M.: 2D+AS+SA+SP-TuM6, 6  
Berry, R.: 2D+BI+MN+SS-TuA12, 10  
Beton, P.H.: 2D+BI+MN+SS-TuA8, 9  
Beyer, A.: 2D+EM+MN+NS-WeA8, 22  
Bianchi, M.: MI+2D+AC+NS-TuA10, 13  
Bignardi, L.: 2D+AS+SS-ThA2, **31**  
Bissell, L.J.: 2D-TuA4, 11  
Bittencourt, C.: 2D+BI+MN+SS-TuA7, 9;  
SA+2D+AC+MI-WeM10, **20**  
Björk, J.: 2D+MI-ThM3, 29  
Blavette, D.: AS+2D+NS+SA-WeA3, 24  
Bleuet, P.: AS+2D+NS+SA-WeA3, 24  
Blomfield, C.J.: 2D-ThP13, 34  
Bonilla, M.: 2D-ThP7, **33**  
Borchers, J.: MI+2D+AC+SA+SS-TuM13, 8  
Borisevich, A.: 2D-TuA2, 10  
Boyce, B.L.: SE+2D+NS+SS+TF-WeA11, 28  
Braun, J.: MI+2D+AC+NS-TuA11, 14

Brown, C.C.: 2D+AS+SS-ThA6, 31  
Brown-Heft, T.: 2D+EM+SS+TF-WeM5, 16  
Browning, J.: MI+2D+AC+NS-TuA9, 13  
Bruemmer, S.M.: AS+2D+NS+SA-WeA7, 24  
Buatier de Mongeot, FrancescoBuatierdeMongeot.:  
2D-WeA3, 22  
Budak, S.: SU+2D+MS+NS-TuA11, 14;  
SU+2D+MS+NS-TuA12, 14  
Buditama, A.: MI+2D+AC+NS-TuA3, 12  
Bullen, H.J.: 2D-TuA3, 11  
Burch, M.J.: 2D+AS+SS-ThA6, 31  
Busse, C.: 2D+MI-ThM2, 29

## — C —

Cabrera, G.: MI+2D+AC+SA+SS-TuM12, 8  
Campbell, P.M.: 2D+BI+MN+SS-TuA2, 9  
Campion, R.: SP+2D+AS+NS+SS-MoA3, 4  
Cao, C.H.: 2D-ThP20, 35; 2D-WeA1, **22**  
Cappelluti, E.: 2D-WeA3, 22  
Carman, G.P.: MI+2D+AC+SA+SS-TuM13, 8  
Carr, D.M.: AS+2D+NS+SA-WeA12, 25  
Carter, K.: SU+2D+MS+NS-TuA9, **14**  
Carter, S.G.: EM+2D+MI+MN-WeA10, 26  
Caruso, A.N.: 2D-ThP18, 35  
Caymax, M.: 2D-TuA10, 12  
Centeno, A.: 2D-TuA9, 11  
Chaigneau, M.: 2D-WeA7, 23  
Chan, C.: 2D+AS+SA+SP-TuM6, 6  
Chandross, M.: SE+2D+NS+SS+TF-WeA11, 28  
Chang, A.: SU+2D+MS+NS-TuA9, 14  
Chang, C.-S.: 2D+AS+SA+SP-TuM3, **6**  
Chang, J.P.: MI+2D+AC+NS-TuA3, 12;  
MI+2D+AC+SA+SS-TuM13, 8  
Chang, L.Y.: 2D+AS+SA+SP-TuM11, 7  
Chen, C.-H.: 2D+AS+SA+SP-TuM11, 7  
Chen, G.: MN+2D-WeM4, 18  
Chen, H.: MN+2D-WeM3, **18**  
Chen, J.H.: SU+2D+MS+NS-TuA3, **14**  
Chen, Y.: 2D+MI-MoA5, 3  
Chen, Y.P.: SP+2D+AS+NS+SS-MoA4, 4  
Chen, Z.: 2D+EM+MN+NS-WeA3, 21  
Cheng, L.: 2D+EM+MN+NS-WeA2, 21  
Chen-Wiegart, K.: SA+2D+AC+MI-WeM12, **20**  
Cheon, G.: 2D+MI-MoA5, **3**  
Chirita, V.: SE+2D+NS+SS+TF-WeA12, 28  
Cho, B.: 2D-ThP3, 33  
Cho, H.D.: MN+2D-WeM1, 17  
Cho, Y.: 2D-ThP3, 33  
Choi, S.: 2D-ThP16, 35  
Chong, H.: MN+2D-WeM2, 17  
Chu, X.S.: 2D-WeA8, 23  
Chuang, T.-M.: 2D+MI-ThM12, **30**  
Chung, J.: 2D-ThP1, **33**  
Chyasnovichyus, M.: 2D-TuA2, 10  
Cinquanta, E.: 2D-WeA3, 22  
Ciochoń, P.K.: 2D-TuA1, **10**  
Clark, B.G.: SE+2D+NS+SS+TF-WeA11, 28  
Coelho, P.M.: 2D-ThP5, **33**  
Conner, B.S.: 2D-TuA2, 10  
Conrad, E.H.: 2D-WeA2, 22  
Conroy, M.A.: AS+2D+NS+SA-WeA7, 24  
Costa, P.S.: 2D+MI-MoA9, 3  
Coultas, S.J.: 2D-ThP13, 34  
Counsell, J.D.P.: 2D-ThP13, 34  
Coy Diaz, H.: 2D+AS+SS-ThA11, **32**; 2D-ThP7,  
33  
Crommie, M.F.: 2D+BI+MN+SS-TuA9, 10  
Cui, T.: 2D-ThP20, **35**  
Culbertson, J.C.: 2D+BI+MN+SS-TuA2, 9  
Cullen, D.A.: 2D-TuA2, 10  
Cullen, W.G.: 2D+MI-ThM4, 29  
Currie, M.: 2D+MI+NS+SS+TF-FrM3, 37;  
2D+MI-ThM11, 30  
Curry, J.F.: SE+2D+NS+SS+TF-WeA11, 28

Cyganik, P.: AS+2D+NS+SA-WeA10, 25

## — D —

da Silva, E.R.: AS+2D+NS+SA-WeA12, 28  
Dadap, J.: 2D+AS+SA+SP-TuM1, 6  
Dalmiglio, M.: 2D+AS+SS-ThA2, 31  
Daly, M.: 2D-WeA1, 22  
Daniels, K.M.: 2D+EM+SS+TF-WeM5, 16;  
EM+2D+MI+MN-WeA10, 26  
Datzler, C.: MI+2D+AC+NS-TuA11, 14  
Davaji, B.: MN+2D-WeM1, 17  
Davis, R.F.: 2D-TuA8, 11; MN+2D-WeM4, 18  
de Andrade, R.R.: AS+2D+NS+SA-WeA12, 25  
Debnath, A.: 2D-WeA8, 23  
DeJarlid, M.T.: EM+2D+MI+MN-WeA10, 26  
Delabie, A.: 2D-TuA10, 12  
Dendzik, M.: MI+2D+AC+NS-TuA10, 13  
Dhesi, S.: SP+2D+AS+NS+SS-MoA3, 4  
Di Santo, G.: 2D+BI+MN+SS-TuA7, 9  
Diercks, D.R.: AS+2D+NS+SA-WeA11, 25  
Dino, W.A.: MI+2D+AC+SA+SS-TuM5, 7  
Dodson, B.: MN+2D-WeM4, **18**  
Donath, M.: MI+2D+AC+NS-TuA10, 13;  
MI+2D+AC+NS-TuA11, **14**  
Dong, R.: 2D-WeA11, 23  
Doucette, R.: 2D-ThP18, 35  
Duerloo, K.-A.N.: 2D+MI-MoA5, 3  
Dugger, M.T.: SE+2D+NS+SS+TF-WeA11, 28  
Duguay, S.: AS+2D+NS+SA-WeA3, 24  
Duncan, S.E.: SU+2D+MS+NS-TuA1, **14**  
Duscher, G.: 2D+AS+SS-ThA9, 32  
Dyck, O.: 2D-ThP22, 35  
Dzara, M.J.: AS+2D+NS+SA-WeA11, 25

## — E —

Ebert, H.: MI+2D+AC+NS-TuA11, 14  
Ebnonnasir, A.: SE+2D+NS+SS+TF-WeA4, 27  
Eda, G.: 2D+MI+NS+SS+TF-FrM1, **37**  
Eddy, Jr., C.R.: 2D+EM+SS+TF-WeM5, 16  
Edmonds, K.: SP+2D+AS+NS+SS-MoA3, 4  
Edström, D.: SE+2D+NS+SS+TF-WeA12, **28**  
Edwards, D.J.: AS+2D+NS+SA-WeA7, 24  
Eickholt, P.: MI+2D+AC+NS-TuA10, **13**  
Ekuma, C.: 2D+AS+SS-ThA8, **31**  
Ellsworth, A.A.: AS+2D+NS+SA-WeA12, **25**  
Enders, A.: 2D+MI-MoA9, **3**  
Engstrom, J.R.: 2D-TuA3, **11**  
Estivill, R.: AS+2D+NS+SA-WeA3, 24

## — F —

Fairley, N.: AS+2D+NS+SA-WeA9, 25  
Fali, A.: 2D-ThP2, **33**  
Fankhauser, J.: SE+2D+NS+SS+TF-WeA4, 27  
Fatayer, S.: 2D+MI-ThM3, 29  
Fathipour, S.: 2D+EM+MN+NS-WeA3, 21  
Fedynshyn, T.H.: EM+2D+MI+MN-WeA9, 26  
Feigelson, B.N.: 2D-ThP15, 35  
Feng, P.X.-L.: MN+2D-WeM10, 18; MN+2D-  
WeM13, 19; MN+2D-WeM3, 18  
Ferrah, D.: AS+2D+NS+SA-WeA9, 25  
Filleter, T.: 2D-ThP20, 35; 2D-WeA1, 22  
Fisher, B.: 2D+MI-ThM10, 30  
Fisher, G.L.: AS+2D+NS+SA-WeA12, 25  
Fitzell, K.: MI+2D+AC+NS-TuA3, **12**  
Förster, T.: MI+2D+AC+NS-TuA11, 14  
Frégnaux, M.: AS+2D+NS+SA-WeA9, 25  
Friedman, A.L.: 2D+BI+MN+SS-TuA2, 9;  
2D+MI-ThM11, 30  
Furnish, T.A.: SE+2D+NS+SS+TF-WeA11, 28  
Füser, M.: 2D+EM+SS+TF-WeM10, 17

## — G —

Gade, L.H.: 2D+MI-ThM3, 29  
Gai, Z.: SP+2D+AS+NS+SS-MoA10, 4  
Gali, A.: EM+2D+MI+MN-WeA11, 27

Gamage, S.: 2D-ThP2, 33  
 Ganesh, P.: 2D-TuA2, 10  
 Gao, H.J.: 2D+EM+MI+MN-MoM2, 1  
 Garg, S.: 2D+EM+MN+NS-WeA4, 21  
 Garley, A.: 2D+BI+MN+SS-TuA12, 10  
 Gaskill, D.K.: 2D+EM+SS+TF-WeM5, 16;  
 EM+2D+MI+MN-WeA10, 26  
 Gay, M.: AS+2D+NS+SA-WeA9, 25  
 Geis, M.W.: EM+2D+MI+MN-WeA9, 26  
 Geohegan, D.B.: 2D+AS+SS-ThA9, 32; 2D+MI-  
 MoA8, 3  
 Ghafari, A.: 2D+AS+SS-ThA2, 31  
 Ghahari, F.: 2D+MI-ThM4, 29;  
 MI+2D+AC+SA+SS-TuM2, 7  
 Ghiringhelli, G.: SA+2D+AC+MI-WeM3, 19  
 Glad, X.: 2D+AS+SS-ThA7, 31  
 Glaser, E.R.: EM+2D+MI+MN-WeA10, 26  
 Glavin, N.R.: 2D-TuA4, 11  
 Götzhäuser, A.: 2D+EM+MN+NS-WeA8, 22;  
 2D+EM+SS+TF-WeM10, 17  
 Gona, R.S.: 2D+BI+MN+SS-TuA11, 10  
 Gonzales, J.M.: 2D+EM+MI+MN-MoM9, 2  
 Goorsky, M.S.: SE+2D+NS+SS+TF-WeA4, 27  
 Goret, G.: AS+2D+NS+SA-WeA3, 24  
 Gougousi, T.: 2D-ThP8, 33  
 Grant, J.T.: SE+2D+NS+SS+TF-WeA3, 27  
 Green, A.A.: 2D-WeA8, 23  
 Greene, J.: SE+2D+NS+SS+TF-WeA12, 28  
 Grenier, A.: AS+2D+NS+SA-WeA3, 24  
 Grezes, C.: MI+2D+AC+NS-TuA3, 12  
 Groven, B.: 2D-TuA10, 12  
 Grutter, A.J.: MI+2D+AC+SA+SS-TuM13, 8  
 Gu, G.: 2D-TuA7, 11  
 Guimarães, P.S.S.: AS+2D+NS+SA-WeA12, 25  
 Gunlycke, D.: 2D+AS+SS-ThA8, 31  
 Guo, H.X.: 2D-WeA10, 23  
 Guo, J.-H.: 2D+AS+SA+SP-TuM5, 6  
 Gupta, G.: 2D+AS+SA+SP-TuM6, 6  
 Gutierrez, C.: 2D+MI-ThM4, 29;  
 MI+2D+AC+SA+SS-TuM2, 7  
 Gutierrez, H.R.: 2D+EM+SS+TF-WeM6, 16;  
 2D+MI+NS+SS+TF-FrM4, 37

— H —  
 Hagen, J.: AS+2D+NS+SA-WeA11, 25  
 Hall, J.: 2D+MI-ThM2, 29  
 Hanbicki, A.T.: 2D+BI+MN+SS-TuA2, 9;  
 2D+MI+NS+SS+TF-FrM3, 37; 2D+MI-  
 ThM11, 30  
 Harthcock, C.: 2D-WeA9, 23  
 Hasegawa, Y.: SP+2D+AS+NS+SS-MoA8, 4  
 Haubrichs, R.: 2D+BI+MN+SS-TuA8, 9  
 He, Q.: 2D-TuA2, 10  
 Hedlund, J.K.: 2D+EM+SS+TF-WeM1, 16  
 Heeger, M.: AS+2D+NS+SA-WeA1, 24  
 Heinz, H.: 2D+BI+MN+SS-TuA12, 10  
 Heinz, T.: EM+2D+MI+MN-WeA1, 26  
 Herath, N.: MI+2D+AC+NS-TuA9, 13  
 Heyns, M.: 2D-TuA10, 12  
 Hinze, P.: 2D+EM+MN+NS-WeA8, 22  
 Hite, J.K.: 2D-ThP15, 35  
 Hla, S.W.: 2D+MI-ThM10, 30  
 Hoffman, A.N.: 2D+MI+NS+SS+TF-FrM8, 38  
 Hoffmann, A.: MI+2D+AC+NS-TuA4, 13  
 Hofmann, P.: MI+2D+AC+NS-TuA10, 13;  
 MI+2D+AC+NS-TuA11, 14  
 Holcomb, M.B.: MI+2D+AC+SA+SS-TuM12, 8  
 Hollis, M.A.: EM+2D+MI+MN-WeA9, 26  
 Holtmann, M.: MI+2D+AC+NS-TuA10, 13  
 Hong, K.: MI+2D+AC+NS-TuA9, 13  
 Hooper, J.: 2D+MI-MoA9, 3  
 Howard, M.: SU+2D+MS+NS-TuA11, 14;  
 SU+2D+MS+NS-TuA12, 14  
 Huang, C.-Y.: MI+2D+AC+SA+SS-TuM12, 8  
 Huang, J.: MI+2D+AC+NS-TuA9, 13  
 Hultman, L.: SE+2D+NS+SS+TF-WeA12, 28  
 Hus, S.M.: SP+2D+AS+NS+SS-MoA4, 4  
 Hutton, S.J.: 2D-ThP13, 34  
 Hwang, C.: 2D-ThP11, 34

Hybertsen, M.S.: 2D+AS+SA+SP-TuM1, 6;  
 2D+EM+MI+MN-MoM5, 1  
 Hyun, M.S.: 2D-ThP11, 34

— I —  
 Idrobe, J.: 2D+AS+SS-ThA9, 32  
 Ievlev, A.V.: 2D+AS+SS-ThA6, 31  
 Islam, A.I.: MN+2D-WeM13, 19  
 Ivanov, I.N.: MI+2D+AC+NS-TuA9, 13  
 Ivas, T.: 2D+MI-ThM3, 29  
 Iversen, B.: MI+2D+AC+NS-TuA11, 14

— J —  
 Jahanbekam, A.: 2D-WeA9, 23  
 Jakowski, J.: 2D+AS+SS-ThA6, 31;  
 MI+2D+AC+NS-TuA9, 13  
 Jamer, M.E.: MI+2D+AC+SA+SS-TuM13, 8  
 Jariwala, D.J.: 2D+MI+NS+SS+TF-FrM7, 37  
 Jauho, A.-P.: 2D+MI-ThM5, 29  
 Jernigan, G.G.: 2D+BI+MN+SS-TuA2, 9  
 Jesse, S.: 2D+AS+SS-ThA6, 31; 2D-ThP22, 35;  
 SP+2D+AS+NS+SS-MoA11, 4  
 Ji, S.: 2D-ThP16, 35  
 Jia, H.: MN+2D-WeM3, 18  
 Jiao, L.: 2D+AS+SA+SP-TuM10, 6  
 Jin, W.: 2D+AS+SA+SP-TuM1, 6  
 Johnson, A.T.: 2D+BI+MN+SS-TuA11, 10  
 Jolie, W.: 2D+MI-ThM2, 29  
 Jonker, B.T.: 2D+EM+MI+MN-MoM3, 1;  
 2D+MI+NS+SS+TF-FrM3, 37; 2D+MI-  
 ThM11, 30  
 Ju, J.Y.: 2D-ThP16, 35  
 Juhel, M.: AS+2D+NS+SA-WeA3, 24  
 Jung, T.A.: 2D+MI-ThM3, 29  
 Jungfleisch, M.B.: MI+2D+AC+NS-TuA4, 13  
 Jungwirth, T.: SP+2D+AS+NS+SS-MoA3, 4

— K —  
 Kaiser, D.: 2D+EM+SS+TF-WeM10, 17; 2D-  
 TuA9, 11  
 Kaiser, U.: 2D+EM+SS+TF-WeM10, 17  
 Kalanyan, B.: 2D+EM+SS+TF-WeM2, 16  
 Kalinin, S.V.: 2D-ThP22, 35; SP+2D+AS+NS+SS-  
 MoA11, 4  
 Kang, I.S.: 2D-ThP11, 34  
 Kang, T.W.: MN+2D-WeM1, 17  
 Kanjolia, R.: 2D+EM+SS+TF-WeM2, 16  
 Karaba, C.T.: MI+2D+AC+NS-TuA3, 12  
 Kasai, H.: MI+2D+AC+SA+SS-TuM5, 7  
 Kawai, S.: 2D+MI-ThM3, 29  
 Keum, J.: MI+2D+AC+NS-TuA9, 13  
 Keyshar, K.: 2D+AS+SA+SP-TuM6, 6  
 Kidwell, D.: 2D+BI+MN+SS-TuA1, 9  
 Kim, B.: 2D+AS+SA+SP-TuM2, 6  
 Kim, D.-H.: 2D-ThP3, 33  
 Kim, D.S.: 2D-ThP14, 35  
 Kim, D.-W.: 2D-ThP3, 33  
 Kim, E.: 2D-ThP3, 33  
 Kim, G.: 2D-ThP11, 34  
 Kim, H.: AS+2D+NS+SA-WeA9, 25  
 Kim, H.-S.: 2D+EM+MN+NS-WeA2, 21  
 Kim, J.: 2D+EM+MN+NS-WeA2, 21  
 Kim, J.K.: 2D-ThP16, 35  
 Kim, K.S.: 2D-ThP14, 35  
 Kim, P.: 2D+MI-MoA3, 3  
 Kim, R.: 2D-TuA4, 11  
 Kim, S.: 2D+AS+SS-ThA6, 31; 2D+EM+MN+NS-  
 WeA4, 21; 2D-ThP22, 35  
 Kim, S.J.: 2D+EM+MN+NS-WeA2, 21  
 Kim, S.-K.: 2D-ThP16, 35  
 Kim, U.J.: 2D-ThP1, 33  
 Kim, Y.: 2D-ThP3, 33  
 Kim, Y.S.: 2D-ThP1, 33  
 Kim, Y.-S.: 2D-TuA7, 11  
 Kimes, W.A.: 2D+EM+SS+TF-WeM2, 16  
 King, P.D.C.: MI+2D+AC+NS-TuA7, 13  
 Kioseoglou, G.: 2D+MI-ThM11, 30  
 Kioissis, N.: MI+2D+AC+NS-TuA3, 12  
 Kirby, B.J.: MI+2D+AC+SA+SS-TuM13, 8  
 Kis, A.: AS+2D+NS+SA-WeA9, 25  
 Kittell, D.E.: SE+2D+NS+SS+TF-WeA8, 28

Klein, P.B.: EM+2D+MI+MN-WeA10, 26  
 Ko, W.: SP+2D+AS+NS+SS-MoA4, 4  
 Kobashi, M.: SE+2D+NS+SS+TF-WeA4, 27  
 Kolekar, S.: 2D-ThP4, 33; 2D-ThP7, 33  
 Kolmakov, A.: 2D-WeA10, 23  
 Kołodziej, J.J.: 2D-TuA1, 10  
 Korolkov, V.V.: 2D+BI+MN+SS-TuA8, 9  
 Kralj, M.: 2D+MI-ThM2, 29  
 Krasheninnikov, A.V.: 2D+AS+SS-ThA1, 31  
 Krayev, A.: 2D+MI+NS+SS+TF-FrM10, 38;  
 2D+MI+NS+SS+TF-FrM7, 37; 2D-WeA7, 23  
 Kropp, J.A.: 2D-ThP8, 33  
 Krüger, P.: MI+2D+AC+NS-TuA11, 14  
 Kruska, K.: AS+2D+NS+SA-WeA7, 24  
 Krzykawska, A.: AS+2D+NS+SA-WeA10, 25  
 Ku, Y.-H.: 2D+AS+SA+SP-TuM11, 7  
 Kuljanishvili, I.: 2D-WeA11, 23  
 Kumar, P.: 2D+EM+MI+MN-MoM1, 1  
 Kumari, S.: MI+2D+AC+SA+SS-TuM12, 8  
 Kummel, A.C.: 2D+EM+MN+NS-WeA3, 21; 2D-  
 WeA12, 23  
 Kung, P.: 2D+EM+MN+NS-WeA4, 21  
 Kuo, Y.-C.: 2D+AS+SA+SP-TuM11, 7  
 Kuroda, K.: MI+2D+AC+NS-TuA1, 12  
 Kurtz, R.J.: AS+2D+NS+SA-WeA7, 24  
 Kustas, A.B.: SE+2D+NS+SS+TF-WeA11, 28  
 Kwak, I.J.: 2D+EM+MN+NS-WeA3, 21; 2D-  
 WeA12, 23  
 Kwon, S.: 2D-ThP3, 33

— L —  
 Lacovig, P.: 2D+AS+SS-ThA2, 31  
 Lamperti, A.: 2D-WeA3, 22  
 Larciprete, R.: 2D+AS+SS-ThA2, 31  
 Larsen, K.: 2D-TuA8, 11  
 Latt, K.Z.: 2D+MI-ThM10, 30  
 Lauter, V.: MI+2D+AC+NS-TuA9, 13  
 Law, K.: SP+2D+AS+NS+SS-MoA11, 4  
 Lee, C.H.: MN+2D-WeM1, 17  
 Lee, D.Y.: 2D-WeA9, 23  
 Lee, J.B.: 2D+EM+MN+NS-WeA2, 21  
 Lee, J.-K.: MN+2D-WeM1, 17  
 Lee, K.: 2D+AS+SA+SP-TuM2, 6  
 Lee, S.: 2D-ThP11, 34  
 Lee, S.S.: 2D-ThP16, 35  
 Lee, W.-K.: 2D+BI+MN+SS-TuA1, 9  
 Lee, W.O.: 2D-ThP14, 35  
 Lee, Y.H.: 2D+AS+SA+SP-TuM3, 6  
 Legendre, S.: AS+2D+NS+SA-WeA3, 24  
 Lehnardt, S.: 2D-TuA8, 11  
 Lennon, D.M.: EM+2D+MI+MN-WeA9, 26  
 Levesque, P.: 2D+AS+SS-ThA7, 31  
 Levitov, L.S.: 2D+MI-ThM4, 29;  
 MI+2D+AC+SA+SS-TuM2, 7  
 Li, A.-P.: 2D-TuA7, 11; SP+2D+AS+NS+SS-  
 MoA3, 4; SP+2D+AS+NS+SS-MoA4, 4  
 Li, C.: SE+2D+NS+SS+TF-WeA4, 27  
 Li, C.H.: 2D+EM+MI+MN-MoM3, 1  
 Li, D.O.: 2D-WeA8, 23  
 Li, L.: SP+2D+AS+NS+SS-MoA10, 4  
 Li, X.: 2D+AS+SS-ThA9, 32; MI+2D+AC+NS-  
 TuA3, 12  
 Li, Y.: 2D+AS+SA+SP-TuM1, 6; 2D+MI-ThM10,  
 30; SU+2D+MS+NS-TuA9, 14  
 Lian, R.: 2D+EM+MN+NS-WeA1, 21  
 Liang, L.: 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3  
 Liao, W.: MN+2D-WeM3, 18  
 Lii-Rosales, A.: 2D-TuA11, 12  
 Lin, M.-W.: 2D+AS+SS-ThA9, 32  
 Lin, Y.: 2D+AS+SA+SP-TuM1, 6  
 Liu, L.: 2D-TuA7, 11  
 Liu, S.Y.: 2D+MI-MoA9, 3  
 Liu, X.: 2D+MI+NS+SS+TF-FrM9, 38  
 Liu, Z.-F.: 2D+BI+MN+SS-TuA9, 10  
 Lizzit, S.: 2D+AS+SS-ThA2, 31  
 Lobo-Checa, J.: 2D+MI-ThM3, 29  
 Lu, P.: SE+2D+NS+SS+TF-WeA11, 28  
 Lu, Y.: 2D+MI-MoA2, 3  
 Lu, Z.: 2D+AS+SA+SP-TuM10, 6



Lucero, A.T.: 2D+EM+MN+NS-WeA2, 21  
Lyding, J.W.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-ThP12, 34

## — M —

M. Ugeda, M.: 2D+BI+MN+SS-TuA9, 10  
Ma, C.: 2D-TuA7, 11  
Ma, D.: 2D-WeA8, 23  
Ma, Y.: 2D-ThP7, 33  
Maccherozzi, F.: SP+2D+AS+NS+SS-MoA3, 4  
Machado, A.B.M.: AS+2D+NS+SA-WeA12, 25  
Mahjouri-Samani, M.: 2D+AS+SS-ThA9, 32  
Maksymovych, P.: 2D-TuA2, 10  
Manandhar, S.: SE+2D+NS+SS+TF-WeA7, 27  
Marchant, M.F.: EM+2D+MI+MN-WeA9, 26  
Marschewski, E.: 2D+EM+MN+NS-WeA8, 22  
Martel, R.: 2D+AS+SS-ThA7, 31  
Martella, C.: 2D-WeA3, 22  
Martin, K.L.: SU+2D+MS+NS-TuA9, 14  
Maruyama, B.: 2D-TuA4, 11  
Maslar, J.E.: 2D+EM+SS+TF-WeM2, 16  
Matena, M.: 2D+MI-ThM3, 29  
Mazel, Y.: AS+2D+NS+SA-WeA3, 24  
McAllister, K.D.: 2D-WeA2, 22  
McConney, M.E.: 2D-TuA4, 11  
McCreary, K.M.: 2D+EM+MI+MN-MoM3, 1; 2D+MI+NS+SS+TF-FrM3, 37  
McCurdy, M.W.: MN+2D-WeM3, 18  
McFadden, A.P.: 2D+EM+SS+TF-WeM5, 16  
McGuire, M.A.: 2D-TuA2, 10  
McMurray, J.W.: 2D-TuA2, 10  
Memaran, S.: 2D+MI+NS+SS+TF-FrM4, 37  
Mennucci, C.: 2D-WeA3, 22  
Meyer, E.: 2D+MI-ThM3, 29  
Mi, J.: MI+2D+AC+NS-TuA11, 14  
Michely, T.: 2D+MI-ThM2, 29  
Miller, DP.: 2D+MI-MoA9, 3  
Minár, J.: MI+2D+AC+NS-TuA11, 14  
Mo, S.-K.: 2D+BI+MN+SS-TuA9, 10; 2D+EM+SS+TF-WeM3, 16  
Mohite, A.: 2D+AS+SA+SP-TuM6, 6  
Mohn, M.: 2D+EM+SS+TF-WeM10, 17  
Mollah, A.: 2D+EM+MN+NS-WeA4, 21  
Molle, A.: 2D-WeA3, 22  
Monazami, E.: 2D-ThP10, 34  
Moon, E.J.: 2D-ThP18, 35  
More, S.: MN+2D-WeM11, 18  
Mottaghi, N.: MI+2D+AC+SA+SS-TuM12, 8  
Mousavi, S.F.: 2D+MI-ThM3, 29  
Mouton, I.: AS+2D+NS+SA-WeA3, 24  
Mowll, T.R.: 2D+EM+SS+TF-WeM11, 17  
Mun, M.K.: 2D-ThP14, 35  
Muratore, C.: 2D-TuA4, 11; SE+2D+NS+SS+TF-WeA9, 28  
Murphy, N.R.: SE+2D+NS+SS+TF-WeA3, 27  
Murray, C.: 2D+MI-ThM2, 29  
Myers-Ward, R.L.: 2D+EM+SS+TF-WeM5, 16; EM+2D+MI+MN-WeA10, 26

## — N —

Nahm, R.K.: 2D-TuA3, 11  
Naik, A.K.: MN+2D-WeM12, 18  
Nakanishi, H.: MI+2D+AC+SA+SS-TuM5, 7  
Nalin Mehta, A.: 2D-TuA10, 12  
Nam, S.: 2D+EM+MI+MN-MoM4, 1  
Nation, B.L.: SE+2D+NS+SS+TF-WeA11, 28  
Natterer, F.D.: 2D+MI-ThM4, 29  
Naylor, C.H.: 2D+BI+MN+SS-TuA11, 10  
Neaton, J.B.: 2D+BI+MN+SS-TuA9, 10  
Neumann, C.: 2D+EM+SS+TF-WeM10, 17; 2D-TuA9, 11  
Ngo, A.: 2D+MI-ThM10, 30  
Ngo, C.: AS+2D+NS+SA-WeA11, 25  
Nguyen, G.: SP+2D+AS+NS+SS-MoA3, 4  
Ni, B.: 2D+EM+MI+MN-MoM2, 1  
Nijjs, T.: 2D+MI-ThM3, 29  
Nilsson, A.N.: SA+2D+AC+MI-WeM1, 19  
Nolot, E.: AS+2D+NS+SA-WeA3, 24  
Nowakowska, S.: 2D+MI-ThM3, 29  
Nowakowski, J.: 2D+MI-ThM3, 29

Nyakiti, L.O.: 2D-ThP15, 35

## — O —

O'Brien, C.J.: SE+2D+NS+SS+TF-WeA11, 28  
Ocola, L.E.: 2D-WeA11, 23  
Ogletree, D.F.: 2D+BI+MN+SS-TuA9, 10  
Ohta, T.: 2D+AS+SA+SP-TuM6, 6  
Oleynik, I.I.: 2D+EM+MI+MN-MoM9, 2  
Olszta, M.J.: AS+2D+NS+SA-WeA7, 24  
Orlando, F.: 2D+AS+SS-ThA2, 31  
Ortega, J.E.: 2D+MI-ThM3, 29  
Osgood, R.: 2D+AS+SA+SP-TuM1, 6  
Ossowski, J.: AS+2D+NS+SA-WeA10, 25  
Ouyang, W.: AS+2D+NS+SA-WeA2, 24  
Ovchinnikova, O.S.: 2D+AS+SS-ThA6, 31  
Oyedele, A.: 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3

## — P —

Pacholski, M.L.: AS+2D+NS+SA-WeA2, 24  
Palmström, C.J.: 2D+EM+SS+TF-WeM5, 16  
Pang, C.S.: 2D+EM+MN+NS-WeA3, 21  
Parambath Mundayodan, S.: 2D-ThP20, 35  
Park, J.: 2D+EM+SS+TF-WeM12, 17; 2D-TuA7, 11  
Park, J.H.: 2D+EM+MN+NS-WeA3, 21; 2D-WeA12, 23  
Park, J.W.: 2D-ThP14, 35  
Park, K.: 2D+AS+SA+SP-TuM10, 6  
Park, Y.C.: 2D-ThP11, 34  
Parker, D.S.: SP+2D+AS+NS+SS-MoA10, 4  
Parsons, K.: 2D-ThP12, 34  
Pascual, G.: 2D+AS+SA+SP-TuM2, 6  
Pashaei, V.: MN+2D-WeM3, 18  
Pavunny, S.P.: EM+2D+MI+MN-WeA10, 26  
Pearson, J.E.: MI+2D+AC+NS-TuA4, 13  
Pellouchoud, L.A.: 2D-WeA4, 22  
Pelster, A.: AS+2D+NS+SA-WeA1, 24  
Pennachio, D.J.: 2D+EM+SS+TF-WeM5, 16  
Penner, P.: 2D+EM+MN+NS-WeA8, 22  
Perkins, F.K.: 2D+BI+MN+SS-TuA2, 9  
Perriot, R.: 2D+EM+MI+MN-MoM9, 2  
Petaccia, L.: 2D+AS+SS-ThA2, 31; 2D+BI+MN+SS-TuA7, 9  
Petrov, I.: SE+2D+NS+SS+TF-WeA12, 28  
Pielic, B.: 2D+MI-ThM2, 29  
Piquero-Zulaica, I.: 2D+MI-ThM3, 29  
Pop, E.: 2D+MI+NS+SS+TF-FrM10, 38  
Popova, O.: 2D+MI-ThM3, 29  
Porter, C.: 2D+MI-MoA5, 3  
Portner, F.: 2D+MI-ThM2, 29  
Pour, M.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-ThP12, 34  
Prasad, P.: MN+2D-WeM12, 18  
Priebe, A.: AS+2D+NS+SA-WeA3, 24  
Pudasaini, P.R.: 2D+MI+NS+SS+TF-FrM8, 38  
Pulkin, A.: 2D+BI+MN+SS-TuA9, 10  
Puretzy, A.A.: 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3  
Pylypenko, S.: AS+2D+NS+SA-WeA11, 25

## — Q —

Qian, X.: 2D+MI+NS+SS+TF-FrM5, 37  
Qiu, D.: 2D+BI+MN+SS-TuA9, 10  
Qu, Z.: AS+2D+NS+SA-WeA2, 24

## — R —

Rack, P.D.: 2D+MI+NS+SS+TF-FrM8, 38  
Radenovic, A.: 2D+BI+MN+SS-TuA3, 9  
Radocea, A.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-ThP12, 34  
Radu, I.: 2D-TuA10, 12  
Rai, A.: 2D-WeA12, 23  
Rai, R.H.: 2D-TuA4, 11  
Ramalingam, G.: 2D-ThP10, 34  
Ramana, C.V.: SE+2D+NS+SS+TF-WeA7, 27  
Rao, R.S.: 2D-TuA4, 11  
Reed, E.J.: 2D+MI-MoA5, 3; 2D-WeA4, 22  
Reed, R.A.: MN+2D-WeM3, 18  
Refaely-Abramson, S.: 2D+BI+MN+SS-TuA9, 10  
Reinke, P.: 2D-ThP10, 34

Rementer, C.R.: MI+2D+AC+SA+SS-TuM13, 8  
Ren, Y.: 2D-TuA2, 10  
Renault, O.J.: AS+2D+NS+SA-WeA9, 25  
Robert-Bigras, G.: 2D+AS+SS-ThA7, 31  
Roberts, A.J.: 2D-ThP13, 34  
Robinson, A.E.: 2D-WeA7, 23  
Robinson, E.: 2D+MI+NS+SS+TF-FrM7, 37  
Robinson, J.T.: 2D+BI+MN+SS-TuA1, 9  
Robinson, Z.R.: 2D+EM+SS+TF-WeM11, 17  
Rodgers, B.: SU+2D+MS+NS-TuA11, 14; SU+2D+MS+NS-TuA12, 14  
Rodriguez-Nieva, J.R.: MI+2D+AC+SA+SS-TuM2, 7  
Rodrigues, W.N.: AS+2D+NS+SA-WeA12, 25  
Rodriguez, M.A.: SE+2D+NS+SS+TF-WeA11, 28  
Rodriguez-Nieva, J.F.: 2D+MI-ThM4, 29  
Rogalev, A.: MI+2D+AC+SA+SS-TuM6, 7  
Rohlfing, M.: MI+2D+AC+NS-TuA11, 14  
Rosch, A.: 2D+MI-ThM2, 29  
Rosen, J.: SE+2D+NS+SS+TF-WeA1, 27  
Rouleau, C.M.: 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3; MI+2D+AC+NS-TuA9, 13  
Rowley, J.T.: 2D-TuA8, 11  
Rowley-Neale, S.J.: 2D-ThP13, 34  
Ryu, H.: 2D+BI+MN+SS-TuA9, 10

## — S —

Sadowski, J.: 2D+AS+SA+SP-TuM1, 6  
Sahoo, P.K.: 2D+EM+SS+TF-WeM6, 16; 2D+MI+NS+SS+TF-FrM4, 37  
Saikia, N.: 2D+BI+MN+SS-TuA12, 10  
Salmeron, M.B.: 2D+BI+MN+SS-TuA9, 10  
Saltonstall, C.B.: SE+2D+NS+SS+TF-WeA8, 28  
Sanders, C.E.: MI+2D+AC+NS-TuA10, 13  
Sangiovanni, D.: SE+2D+NS+SS+TF-WeA12, 28  
Santos, E.J.G.: 2D-WeA8, 23  
Sato, M.: SE+2D+NS+SS+TF-WeA4, 27  
Scardamaglia, M.: 2D+BI+MN+SS-TuA7, 9  
Schmidt, A.B.: MI+2D+AC+NS-TuA11, 14  
Schmitt, T.: SA+2D+AC+MI-WeM5, 20  
Schram, T.: 2D-TuA10, 12  
Schreiber, D.K.: AS+2D+NS+SA-WeA7, 24  
Schrimpf, R.D.: MN+2D-WeM3, 18  
Schröder, M.: 2D+BI+MN+SS-TuA8, 9  
Schuler, B.: 2D+BI+MN+SS-TuA9, 10  
Seabaugh, A.: 2D+EM+MN+NS-WeA3, 21  
Sefat, A.: SP+2D+AS+NS+SS-MoA10, 4  
Sendek, A.D.: 2D+MI-MoA5, 3  
Shara, K.: MN+2D-WeM2, 17  
Sharma, A.P.: 2D-WeA2, 22  
Sheehan, P.E.: 2D+BI+MN+SS-TuA1, 9  
Shen, Z.-X.: 2D+BI+MN+SS-TuA9, 10  
Shepperd, K.: 2D-WeA2, 22  
Sherrott, M.C.: 2D+MI+NS+SS+TF-FrM7, 37  
Shih, K.: SP+2D+AS+NS+SS-MoA1, 3  
Shin, D.: 2D-TuA2, 10  
Shin, J.: 2D-ThP1, 33  
Shiu, H.-W.: 2D+AS+SA+SP-TuM11, 7  
Singh, C.V.: 2D-WeA1, 22  
Singh, S.: 2D+EM+MI+MN-MoM1, 1  
Simitskii, A.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-ThP12, 34  
Sinnott, S.: 2D+MI-MoA2, 3  
Smets, Q.: 2D-TuA10, 12  
Smithe, K.: 2D+MI+NS+SS+TF-FrM10, 38  
Snyders, R.: 2D+BI+MN+SS-TuA7, 9  
Sobczak, C.: SE+2D+NS+SS+TF-WeA8, 28  
Somnath, S.: SP+2D+AS+NS+SS-MoA11, 4  
Sperling, B.A.: 2D+EM+SS+TF-WeM2, 16  
Sridhara, K.: 2D-ThP15, 35  
Stafford, L.: 2D+AS+SS-ThA7, 31  
Stanford, M.G.: 2D+MI+NS+SS+TF-FrM8, 38  
Steffen, A.C.: MI+2D+AC+NS-TuA9, 13  
Stine, R.: 2D+BI+MN+SS-TuA1, 9  
Stöhr, M.: 2D+MI-ThM3, 29  
Strand, M.B.: AS+2D+NS+SA-WeA11, 25  
Strasser, A.: 2D+MI-MoA8, 3  
Strelcov, E.: 2D-WeA10, 23  
Strocio, J.A.: 2D+MI-ThM4, 29; MI+2D+AC+SA+SS-TuM2, 7

Struzzi, C.: 2D+BI+MN+SS-TuA7, 9  
 Sui, Y.: MN+2D-WeM2, 17  
 Sumpter, B.G.: 2D+AS+SS-ThA6, 31;  
 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3  
 Sun, L.: SE+2D+NS+SS+TF-WeA3, 27  
 Sun, T.: 2D+MI+NS+SS+TF-FrM9, 38; 2D-  
 ThP12, 34  
 Sun, X.: 2D+AS+SA+SP-TuM5, 6  
 Sun, Y.: 2D-ThP20, 35; 2D-WeA1, 22  
 Susi, T.: 2D+BI+MN+SS-TuA7, 9  
 Susner, M.A.: 2D-TuA2, 10  
 Sykes, E.C.H.: 2D+MI-MoA9, 3

— T —

Tamanaha, C.: 2D+BI+MN+SS-TuA1, 9  
 Tanaguchi, T.: 2D+MI-ThM4, 29  
 Tanaka, K.: SE+2D+NS+SS+TF-WeA4, 27  
 Tang, A.A.: 2D-WeA8, 23  
 Taniguchi, T.: MI+2D+AC+SA+SS-TuM2, 7  
 Tao, C.: 2D+AS+SA+SP-TuM10, 6  
 Tegenkamp, C.: SP+2D+AS+NS+SS-MoA5, 4  
 Tempez, A.L.: AS+2D+NS+SA-WeA3, 24  
 Terfort, A.: 2D+EM+SS+TF-WeM10, 17  
 Terrones, M.: 2D+MI+NS+SS+TF-FrM7, 37  
 Thibado, P.: 2D+EM+MI+MN-MoM1, 1  
 Thiel, P.A.: 2D-TuA11, 12  
 Tian, M.: 2D+AS+SS-ThA9, 32  
 Timokhin, I.G.: 2D+BI+MN+SS-TuA8, 9  
 Tolbert, S.H.: MI+2D+AC+NS-TuA3, 12  
 Trappen, R.: MI+2D+AC+SA+SS-TuM12, 8  
 Turchanin, A.: 2D+EM+SS+TF-WeM10, 17; 2D-  
 TuA9, 11  
 Tyler, B.J.: AS+2D+NS+SA-WeA1, 24

— U —

Ural, A.: 2D+EM+MN+NS-WeA1, 21

— V —

Valeriano, W.W.: AS+2D+NS+SA-WeA12, 25  
 Vandervorst, W.: 2D-TuA10, 12  
 Vanfleet, R.R.: 2D-TuA8, 11; MN+2D-WeM4, 18  
 Varghese, J.O.: EM+2D+MI+MN-WeA9, 26  
 Vasco, J.P.: AS+2D+NS+SA-WeA12, 25  
 Vasudevan, R.: SP+2D+AS+NS+SS-MoA11, 4  
 Ventrice, Jr., C.A.: 2D+EM+SS+TF-WeM11, 17  
 Vila, R.A.: 2D-TuA4, 11  
 Vishwanath, S.: 2D-TuA3, 11

Vitale, S.A.: EM+2D+MI+MN-WeA9, 26  
 Vlasiouk, I.: 2D+AS+SS-ThA6, 31  
 Vlasiouk, I.: 2D-WeA10, 23  
 Voevodin, A.A.: SE+2D+NS+SS+TF-WeA9, 28  
 Volders, C.: 2D-ThP10, 34  
 Voronine, D.: 2D+MI-ThM1, 29  
 Vurpillot, F.: AS+2D+NS+SA-WeA3, 24

— W —

Wäckerlin, A.: 2D+MI-ThM3, 29  
 Wäckerlin, C.: 2D+MI-ThM3, 29  
 Wade, T.: EM+2D+MI+MN-WeA9, 26  
 Wadley, P.: SP+2D+AS+NS+SS-MoA3, 4  
 Walker, A.V.: 2D+EM+SS+TF-WeM1, 16  
 Walkup, D.: 2D+MI-ThM4, 29;  
 MI+2D+AC+SA+SS-TuM2, 7  
 Wang, C.: AS+2D+NS+SA-WeA7, 24  
 Wang, K.L.: MI+2D+AC+NS-TuA3, 12  
 Wang, Q.H.: 2D-WeA8, 23  
 Wang, Y.-X.: 2D+AS+SA+SP-TuM11, 7  
 Wang, Z.: MN+2D-WeM10, 18  
 Warner, J.H.: 2D+AS+SS-ThA3, 31  
 Watanabe, K.: 2D+MI-ThM4, 29  
 Watanabe, K.G.: MI+2D+AC+SA+SS-TuM2, 7  
 Waters, J.: 2D+EM+MN+NS-WeA4, 21  
 Weber-Bargioni, A.: 2D+BI+MN+SS-TuA9, 10  
 Weimann, T.: 2D+EM+MN+NS-WeA8, 22; 2D-  
 TuA9, 11  
 Wen, H.: MI+2D+AC+NS-TuA4, 13  
 Whitener, K.E.: 2D+BI+MN+SS-TuA1, 9  
 Wickenburg, S.: 2D+BI+MN+SS-TuA9, 10  
 Wilhelm, F.: MI+2D+AC+SA+SS-TuM6, 7  
 Williams, M.D.: 2D-WeA2, 22  
 Willman, J.T.: 2D+EM+MI+MN-MoM9, 2  
 Wilson, N.S.: 2D+EM+SS+TF-WeM5, 16  
 Winter, A.: 2D-TuA9, 11  
 Wong, K.: MI+2D+AC+NS-TuA3, 12  
 Wu, D.: MI+2D+AC+NS-TuA3, 12  
 Wu, Y.-S.: EM+2D+MI+MN-WeA3, 26  
 Wyrick, J.: 2D+MI-ThM4, 29

— X —

Xiao, K.: 2D+AS+SS-ThA9, 32; 2D+MI-MoA8, 3  
 Xiao, Z.: SU+2D+MS+NS-TuA11, 14;  
 SU+2D+MS+NS-TuA12, 14  
 Xin, Y.: 2D+MI+NS+SS+TF-FrM4, 37  
 Xing, G.: 2D-TuA3, 11

— Y —

Yang, H.: MI+2D+AC+SA+SS-TuM3, 7  
 Yang, L.: 2D-ThP2, 33  
 Yang, S.: 2D+BI+MN+SS-TuA8, 9; 2D+MI-  
 MoA8, 3  
 Yarrington, C.D.: SE+2D+NS+SS+TF-WeA8, 28  
 Yazyev, O.V.: 2D+BI+MN+SS-TuA9, 10  
 Ye, P.D.: 2D-ThP2, 33  
 Yeom, G.Y.: 2D-ThP14, 35  
 Yoo, K.J.: 2D-ThP11, 34  
 Yoon, M.: 2D+AS+SS-ThA9, 32; 2D-TuA7, 11  
 Young, S.M.: 2D-ThP18, 35  
 Yousaf, A.: 2D-WeA8, 23  
 Yousefi Sarraf, S.: MI+2D+AC+SA+SS-TuM12, 8  
 Yu, D.: SE+2D+NS+SS+TF-WeA4, 27  
 Yu, G.: MI+2D+AC+NS-TuA3, 12  
 Yulaev, A.: 2D-WeA10, 23  
 Yun, D.: 2D-ThP1, 33

— Z —

Žaba, T.: AS+2D+NS+SA-WeA10, 25  
 Zhai, Z.: AS+2D+NS+SA-WeA7, 24  
 Zhang, F.: 2D+AS+SA+SP-TuM10, 6  
 Zhang, H.: 2D+AS+SA+SP-TuM5, 6;  
 MI+2D+AC+NS-TuA9, 13  
 Zhang, Q.: MI+2D+AC+NS-TuA4, 13  
 Zhang, W.: MI+2D+AC+NS-TuA4, 13  
 Zhang, X.: 2D+EM+MN+NS-WeA8, 22  
 Zhang, Y.: 2D+BI+MN+SS-TuA9, 10; 2D-WeA9,  
 23  
 Zhang, Z.: MI+2D+AC+NS-TuA3, 12  
 Zhao, Y.: 2D+MI-ThM4, 29  
 Zheng, H.: 2D+AS+SA+SP-TuM10, 6  
 Zhitenev, N.B.: 2D+MI-ThM4, 29;  
 MI+2D+AC+SA+SS-TuM2, 7  
 Zhizhimontov, V.: 2D-WeA7, 23  
 Zhou, B.B.: EM+2D+MI+MN-WeA7, 26  
 Zhou, Y.: 2D-WeA4, 22  
 Zorman, C.A.: MN+2D-WeM2, 17; MN+2D-  
 WeM3, 18  
 Zou, Q.: SP+2D+AS+NS+SS-MoA10, 4  
 Zumbülte, A.: MI+2D+AC+NS-TuA11, 14  
 Zurek, E.: 2D+MI-MoA9, 3  
 Zurutuza, A.: 2D-TuA9, 11