2D Materials Focus Topic
Room 103B - Session 2D+MI+SA-MoM

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Matthias Batzill, University of South Florida

8:20am **2D+MI+SA-MoM1 Scanning Tunneling Microscopy and Spectroscopy of Air Exposure Effects on Molecular Beam Epitaxy Grown WSe_2 Monolayers and Bilayers**, *J.H. Park,* Univeristy of California, San Diego; *S. Vishwanath,* Cornell University; *X. Liu,* University of Notre Dame; *H. Zhou,* Cornell University; *S.M. Eichfeld,* Pennsylvania State University; *S.K. Fullerton-Shirey,* University of Pittsburgh; *J.A. Robinson,* Pennsylvania State University; *R. Feenstra,* Carnegie Mellon University; *J. Furdyna,* University of Notre Dame; *D. Jena, H.G. Xing,* Cornell University; ***Andrew Kummel,*** University of California, San Diego

The effect of air exposure on 2H-WSe_2/HOPG was determined *via* scanning tunneling microscopy. WSe_2 was grown by molecular beam epitaxy on highly oriented pyrolytic graphite (HOPG), and afterwards, a Se adlayer was deposited *in-situ* on WSe_2/HOPG to prevent unintentional oxidation during transferring from the growth chamber to the STM chamber. After annealing at 773 K to remove the Se adlayer, STM images show that WSe_2 layers nucleate at both step edges and terraces of the HOPG. The grain boundaries and the step edges of WSe_2 ML have a bias dependence in STM imaging, consistent with difference electronic states with the defect-free terraces. After exposure air for 1 day, although the edge of WSe_2 is partially oxidized, the grain boundaries still maintain a defective electronic structure. Exposure to air for 1 week and 9 weeks caused air-induced adsorbates to be deposited on the WSe_2 surface; however, as shown for localized electronic structure measurement using scanning tunneling spectroscopy (STS), the bandgap of the terraces remained unaffected and nearly identical to those on de-capped WSe_2. The air-induced adsorbates can be removed by annealing at 523 K. In contrast to WSe_2 terraces, air exposure caused the edges of the WSe_2 to oxidize and form protrusions, resulting in a larger STS bandgap compared to the terraces of air exposed WSe_2 monolayers. The preferential oxidation at the WSe_2 edges compared to the terraces is likely the result of dangling bonds at step edges. In the absence of air exposure, the dangling edge bonds have a smaller band gap compared to the terraces and a shift of about 0.73 eV in the Fermi level towards the valence band. However, after air exposure, the band gap of the oxidized WSe_2 edges became larger about 1.08 eV that of the WSe_2 terraces, resulting in the electronic passivation of the WSe_2.

8:40am **2D+MI+SA-MoM2 Tuning the Trion Photoluminescence Polarization in Monolayer WS_2**, ***Aubrey Hanbicki,*** *K.M. McCreary, M. Currie,* Naval Research Laboratory; *G. Kioseoglou,* University of Crete; *C.S. Hellberg, A.L. Friedman, B.T. Jonker,* Naval Research Laboratory

Monolayer transition metal dichalcogenides (TMDs) such as MoS_2 or WS_2 are semiconductors with degenerate, yet inequivalent *k*-points labeled *K* and *K'* that define the direct bandgap. The valence band maximum in each valley has only one spin state in which the spins are opposite for *K* and *K'*. Consequently, one can selectively populate each valley independently with circularly polarized light and determine the valley populations via the polarization of emitted light. Monitoring changes in emitted polarization, therefore provide insights into the fundamental processes of intervalley scattering. We prepare single-layer WS_2 films such that the photoluminescence is from either the neutral exciton or the negatively charged trion [1,2]. In most TMDs, the optical polarization is small at room temperature, and we find that the neutral exciton emission indeed has zero polarization at room temperature. However, we observe a room temperature optical polarization in excess of 40% for the trion. The trion polarization always exceeds that of the exciton and exhibits a pronounced, non-monotonic temperature dependence – the polarization nearly doubles as the temperature increases from 125 K to 175 K. The observed increase in optical polarization directly correlates with a decrease in emission intensity between 125-175 K indicating that this effect is a consequence of the onset of nonradiative processes. Because this dependence involves trion systems, one can use gate voltages to modulate the polarization or intensity emitted from TMD structures. Using an applied gate voltage, we can modulate the electron density and subsequently the polarization of WS_2 trions continuously from 20-40%. Both the polarization and the emission energy monotonically track the gate voltage with the emission energy increasing by 45 meV. We discuss the role electron capture of the trion has on suppressing the intervalley scattering process. 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.

[1] M. Currie, A.T. Hanbicki, G. Kioseoglou, and B.T. Jonker, Appl. Phys. Lett. **106**, 201907 (2015).

[2] A.T. Hanbicki, G. Kioseoglou, M. Currie, C.S. Hellberg, K.M. McCreary, A.L. Friedman, and B.T. Jonker, Sci. Rep. **6**, 18885 (2016).

9:00am **2D+MI+SA-MoM3 Quantum Hall Effect in Graphene Visualized through Scanning Tunneling Microscopy and Spectroscopy**, ***Adina Luican-Mayer,*** University of Ottawa, Canada **INVITED**

The ability to controllably layer atomically thin crystals into custom-made materials holds promise for realizing physical systems with distinct properties, previously inaccessible. The experimental results described in this talk seek to uncover the unique nature of the charge carriers in such few-atoms-thick materials as well as effects that interlayer coupling and disorder have on their properties. To that end we use scanning tunneling microscopy (STM) and spectroscopy (STS) experiments performed on graphene systems at low temperatures and in magnetic field. We study Landau quantization in graphene and by performing spatially resolved STM/STS we demonstrate the true discrete quantum mechanical electronic spectrum within the Landau level band near charged impurities in graphene in the quantum Hall regime.

9:40am **2D+MI+SA-MoM5 Enhancing the Electrical Conductivity of VUV-reduced Graphene Oxide by Multilayered Stacking**, ***Yudi Tu,*** *T. Utsunomiya, T. Ichii, H. Sugimura,* Kyoto University, Japan

Reducing graphene oxide (GO), a highly oxidized graphene derivatives, by utilizing light irradiation has drawn great attention, due to its flexibility to locally fabricating conductive patterns and tuning the electrical property. We have demonstrated the reduction of GO under the 172 nm vacuum-ultraviolet (VUV) irradiation under high vacuum and combined it with mask photolithography to make reduced graphene oxide (rGO) conductive pattern at sub-µm scale.[1,2] The recovery of electrical conductivity at the reduced regions was confirmed by conductive-probe atomic force microscope (CAFM). However, further researches by applying micro Raman spectroscopy (µRS), scanning tunneling microscopy (STM) and CAFM have revealed that the pristine defects induced by the harsh oxidative synthesis of GO is unable to be repaired. On purpose to enhance the electrical conductivity of rGO pattern, generating more conductive paths for the carriers' transportation is of great importance. In this presentation, we will demonstrate the enhanced electrical conductivity in multilayered rGO sheets. The nanoscale conductive sp^2 domains in rGO are connected to construct 3-dimensional conductive paths between the multilayered sheets.

The GO-coated Si substrate was irradiated by the VUV light in the high vacuum ($< 10^{-3}$ Pa) chamber. The CAFM current mapping revealed that GO and the derived rGO were heterogeneous hybrids of both conductive and insulating domains. Interestingly, besides the nanoscale domains distribution revealed by the previous µRS and STM results, the microscale domains distribution was also observed within the sheets, which was attributed to the uncertainly harsh oxidation synthesis. The CAFM current mapping showed obvious enhancement on the electrical conductivity of bi-layered rGO comparing with the single-layered rGO. A triangle approximate model was applied to estimate the lateral electrical conductivity of rGO sheets. It was found that the tip contact area showed no clear influence on the lateral electrical conductivity. By further measuring the current signals from both bi-layered and single-layered rGO sheets, it was found that the enhancement was not due to the parallel-connection of two rGO sheets but originated from the newly constructed 3-dimensional conductive paths between them.

(1) Tu, Y.; Ichii, T.; Utsunomiya, T.; Sugimura, H. *Appl. Phys. Lett.***2015**, *106*, 133105.

(2) Tu, Y.; Ichii, T.; Khatri, O. P.; Sugimura, H. *Appl. Phys. Express***2014**, *7*, 75101.

10:00am **2D+MI+SA-MoM6 Silicene-like Reconstruction via Surface Relaxation of Hexagonal-$MoSi_2$ Crystallites**, ***Cameron Volders,*** *P. Reinke, G. Ramalingam, E. Monzami,* University of Virginia

The exciting properties of 2D materials have intrigued scientists and engineers for over a decade. A new wave of 2D materials are being explored in the scientific community, specifically, Silicene has garnered much attention for its potential in device integration. The current Silicene literature has accepted a synthetic method of depositing monolayer (ML) amounts of Si atoms onto a heated Ag (111) substrate to produce the 2D layer. Alternative substrates such as Ir (111) have been explored to obtain silicene, however, the validity of these results are still being debated.

The current work will address an approach, which is a potential alternative route for growing a silicene layer, based on the observation of a Silicene-like reconstruction (SLR) on the surface of nanometer-scale hexagonal $MoSi_2$ crystallites terminated by the (0001) plane. The bulk (0001) $MoSi_2$ surface is comprised of Si hexagons with a Mo atom in the center. The honeycomb pattern exhibited by the SLR is formed via relaxation of the (0001) plane where the Si atoms decouple from the underlying h-$MoSi_2$ crystallites. Signatures of a 'graphite-like' Si structure have been reported in literature, but have not yet been pursued in 2D materials studies. We will present an extensive study of the SLR based on Scanning Tunneling Microscopy and Spectroscopy data.

Initially, this work will describe a parameter space in which the SLR can be confidently reproduced. Mo atoms are deposited onto a Si (001) surface and annealed to grow the h-$MoSi_2$ crystallites, which is where the SLR resides. Our experimental data supports an optimal growth regime of approximately 750˚C and 3-5 ML's of Mo. The focus will then switch to demonstrating the geometrical parameters of our SLR are strikingly similar with that of the current Silicene literature. Our experimental results indicate the honeycomb pattern of the SLR corresponds to a superstructure. When comparing the lattice constant and Si-Si distance in our structure with that of silicene literature, the results strongly suggest we are observing a low-buckled silicene layer. Also included, will be a statistical treatment contributing to the validity that a surface relaxation process is the pathway by which the layer is grown. Specific features are always observed, including a well-defined 'rim' structure and defect motif, when the SLR is observed.

The final stage of this presentation will focus on addressing the electronic structure of the SLR based on STS data. A few studies have provided STS measurements indicating the observation of a Dirac-point (DP) near 0.5 eV. Our experimental results contain an intriguing feature in the same region, which will be discussed.

10:40am **2D+MI+SA-MoM8 Electron Dynamics in Two-Dimensional Materials*, Philip Hofmann,*** Aarhus University, Denmark **INVITED**

Changing the dimensionality of a material results in significant modifications of its electronic properties. This is even the case if the parent material already has a layered structure with little interaction between the layers, as in the case of graphene, bilayer graphene and single-layer transition metal chalcogenides.

While the static electronic properties of novel two-dimensional materials can be studied by standard angle-resolved photoemission spectroscopy (ARPES), investigations of the ultrafast carrier dynamics require both time- and angular resolution and thus time-resolved (TR)-ARPES. There is, moreover, the technical requirement of high photon energies since the interesting part of the aforementioned materials' electronic structure (i.e. the (gapped) Dirac cone) is placed at the two-dimensional Brillouin zone boundary. Recently, it has become possible to probe states at such high k by TR-ARPES, thanks to the arrival of ultrafast high harmonic laser sources.

Here we characterize the dynamic processes around the Dirac point in epitaxial graphene [1,2], as well as around the band gap of single layer MoS_2 [3,4] using TR-ARPES. In the graphene, we can determine and control the timescales of hot carrier scattering processes. For single layer MoS_2, we can directly measure the size of the direct band gap by pumping electrons into the conduction band minimum. We find that this band gap can be strongly renormalized, both by a static interaction with the substrate and by a dynamic screening due to a high density of excited free carriers.

References

[1] J.C. Johannsen et al., Physical Review Letters 111, 027403 (2013).

[2] S. Ulstrup et al., Physical Review Letters 112, 257401 (2014)

[3] J. Miwa et al., Physical Review Letters 114, 046802 (2015).

[4] A. Grubisic Cabo et al., Nano Letters, 15, 5883 (20150).

11:20am **2D+MI+SA-MoM10 Novel Characterization Techniques for 2D Materials: Visualizing Inherent and External Defects*, Rudresh Ghosh,*** *S.K. Banerjee, D. Akinwande,* University of Texas at Austin

Over the last decade, since the demonstration of exceptional physical, chemical and electrical properties of graphene, there has been a lot of interest in two-dimensional materials. Of these new materials significant effort has been focused on transition metal dichalcogenides (TMDs) due to their various possible applications. Initial work on TMDs, similar to that of graphene, has depended on exfoliated samples. In this work we present controlled large-area synthesis of highly crystalline few to monolayers of various TMDs (MoS2, WS2, WSe2) using both solid and gas precursors. Characterization of the TMDs are done using a combination of conventional techniques such as Raman and Photoluminescence spectroscopy, Atomic force microscopy, scanning and transmission electron microscopy. Shifts in Raman and PL spectra as a function of strain shows obvious differences between exfoliated and CVD grown material. New characterization tools with the capability of localized dielectric mapping (Microwave impedance microscopy) also show us a way to analyze defects that are inherent during CVD growth processes. Elemental identification of individual layers and their interfaces (using Time of Flight SIMS) are demonstrated as extremely useful for studying these 2d heterostructuress. Electrical device characterization and paths of optimization are also presented. Electrical characterization of the devices on various substrates is also presented.

11:40am **2D+MI+SA-MoM11 Anomalous Dynamical Behavior of Freestanding Graphene*, Paul Thibado,*** *M. Ackerman, P. Kumar, S. Singh,* University of Arkansas*; M. Neek-Amal, F. Peeters,* University of Antwerp, Belgium

Local, long-time evolution measurements of the height fluctuations of a 2D membrane allows examination of the fundamental foundations of statistical mechanics in soft condensed matter. However, such measurements have proved elusive, thereby forcing critical theoretical assumptions in our best models. We report sub-nanometer, high-bandwidth height measurements of freestanding graphene using constant-current, point-mode scanning tunneling microscopy, as a follow-up to our previous related works [1-2]. By tracking atoms directly, the ability to measure dynamic events is increased by a factor of 1000 over the present state-of-the-art membrane imaging technology. Surprisingly, the membrane velocities follow the Cauchy-Lorentz distribution consistent with a Lévy process, rather than the expected Maxwell-Boltzmann distribution. We also present molecular dynamics simulations, which illustrate spontaneous mirror buckling events that give rise to the long excursions.

Acknowledgements:

This work was supported in part by Office of Naval Research (USA) under Grant No. N00014-10-1-0181 and National Science Foundation (USA) under Grant No. DMR- 0855358.

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).

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Magnetic Interfaces and Nanostructures
Room 101C - Session MI+2D+AC-MoM

Chiral Magnetism (8:20-10:20 am)/Magnetism and Spin Orbit Effects at Interfaces and Surfaces: Recent Experimental and Theoretical Advances (10:40 am - 12:00 pm)

Moderators: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Hendrik Ohldag, SLAC National Accelerator Laboratory

8:20am **MI+2D+AC-MoM1 Manipulation of Magnetic Skyrmions with STM*, Kirsten von Bergmann,*** University of Hamburg, Germany **INVITED**

Magnetic skyrmions are topologically distinct from their ferromagnetic environment. They may form in an inversion asymmetric environment and are induced by a competition between magnetic exchange, Dzyaloshinsky-Moriya interaction, and typically the Zeeman energy. Scanning tunneling microscopy (STM) is a valuable tool to study the properties of nanometer-scale skyrmions [1]. In addition to measurements with spin-polarized STM tips skyrmions can also be detected with unpolarized electrodes due to spin-mixing effects in the non-collinear spin texture. We employ spatially resolved magnetic field dependent tunneling spectroscopy to identify this effect of non-collinear magnetoresistance and find that it scales with the angle between nearest neighbors [2]. With a non-magnetic STM tip it is also possible to locally switch the topology of a thin magnetic layer via the sign of the electric field between tip and sample [3]. The combination of these two phenomena –electrical detection and electric field switching of topologically distinct states– could lead to a robust non-magnetic read- and write-head for future skyrmion racetracktype devices.

[1] K. von Bergmann et al., *J. Phys.: Cond. Mat.* **26**, 394002 (2014).

[2] C. Hanneken et al., *Nature Nanotechn.* **10**, 1039 (2015).

[3] P.-J. Hsu et al., arXiv:1601.02935.

9:00am **MI+2D+AC-MoM3 Skyrmion Hall Effect**, *W. Jiang,* Argonne National Laboratory*; X. Zhang,* The University of Hong Kong, Hong Kong Special Administrative Region of China*; G. Yu,* University of California Los Angeles*; M.B. Jungfleisch, J.E. Pearson, O. Heinonen,* Argonne National Laboratory*; K.L. Wang,* University of California Los Angeles*; Y. Zhou,* The University of Hong Kong, Hong Kong Special Administrative Region of China*; S.G.E. te Velthuis,* ***Axel Hoffmann,*** Argonne National Laboratory

Magnetic skyrmions are a perfect example for the ensuing complexity of mesoscale magnetism stemming from competitions between interactions crossing many lengthscales [1]. The interplay between applied magnetic fields, magnetic anisotropies, as well as symmetric and antisymmetric exchange interactions, can stabilize topologically distinct spin textures known as magnetic skyrmions. Due to their topology magnetic skyrmions can be stable with quasi-particle like behavior, and can be manipulated with very low electric currents. This makes them interesting for extreme low-power information technologies [2,3], where data is envisioned to be encoded in topological charges, instead of electronic charges as in conventional semiconducting devices. Recently, we demonstrated the ability of generating and stabilizing magnetic skyrmions at room temperature in Ta/CoFeB/TaOx trilayers, where the broken inversion symmetry gives rise to a net chiral exchange interaction [4,5]. Using spin Hall effects [6] from the Ta layer it is possible to efficiently move these skyrmions with electric currents. Theoretically it is expected that the motion of the skyrmions have a significant transverse component, the skyrmion Hall effect, which is directly related to the topological charge resulting in a net gyrotropic force. Here we demonstrate the direct observation of this transverse motion [7] using magneto-optic Kerr effect imaging. We observe that the skyrmion Hall angle varies continuously from zero just above the depinning threshold until 15º for current densities up to 107 A/cm2. This gradual variation of the skyrmion Hall angle indicates the changing competition between pinning and gyrotropic forces as the skyrmion motion transitions from the creep to the flow regime. The maximum observed Hall angle is in good agreement with theoretical expectations.

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).

References

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6. A. Hoffmann, IEEE Trans. Magn. 49, 5172 (2013).
7. W. Jiang, et al., arXiv:1603.07393.

9:20am **MI+2D+AC-MoM4 Microscopic Magnetic Structures in Dy/Y Superlattices Measured by Polarized Neutron Reflectometry with Off-specular Scattering***,* ***Gary Mankey****, J. Yu, P. LeClair,* University of Alabama*; R. Fishman, J.L. Robertson, H. Ambaye, V. Lauter, H. Lauter,* Oak Ridge National Laboratory

Epitaxial Dy/Y superlattices with vertically-oriented c-axes, nanometer-scale layer thicknesses and 8-80 repeats were fabricated by magnetron sputtering on a-sapphire substrates with Nb buffer layers. The samples are designed to study how helical magnetic structures in Dy are modified by coupling through non-magnetic Y layers. X-ray characterization was used to evaluate the crystallographic orientations and interface widths of the superlattices. The macroscopic magnetic properties were characterized by low-temperature magnetometery that shows cooling in a 1 T in-plane field results in significant ferromagnetically-aligned moments below magnetic transition temperatures of approximately 150 K. The microscopic magnetic structures were investigated by polarized neutron reflectometry with off-specular scattering (PNROS) with variable magnetic fields in a temperature range from 300K down to 5K. PNROS confirms the magnetic transition and shows how the microscopic magnetic structures of the multilayered samples change with temperature. The ordering of the helical modulation is sensitive to the interfacial roughness of the multilayers as well as the magnetic and temperature history of the samples. The turn angles of the helical magnetic moment can be extracted from fitting the data. When the samples are cooled from room temperature to 5 K in a 10 mT in-plane applied magnetic field, the helical magnetic structures appear to decompose into lateral domains of opposite chirality, as evidenced by strong off-specular Bragg sheets. The Bragg sheets originate from the magnetic peaks associated with the helical magnetic ordering. The strength of the scattering from these sheets varies from sample to sample, suggesting that some samples may have a preferred chirality, due to differences in the microscopic film structure.

The authors gratefully acknowledge financial support from DOE award DE-FG02-08ER46499. A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

9:40am **MI+2D+AC-MoM5 Chirality Effects in Rare Earth based Thin Films and Multilayers***,* ***Dieter Lott,*** Helmholtz Zentrum Geesthacht, Germany*; K. Chen,* Universität Köln, Germany*; V. Tarnavich,* Petersburg Nuclear Physics Institute, Russian Federation **INVITED**

Films consisting of rare-earth elements became recently in the focus of attention due there rich variety of magnetic effects owed to the complex interplay between their spin and orbital magnetic moments. On the search of novel types of magnetic sensors and other spintronic devices they offer a path for creating complex magnetic spin structures that have the potential for being used in future applications in the field of information technology. In this presentation the focus is on the phenomena of magnetic chirality that was lately found in Rare-Earth multilayers. In the first part the chirality effects will be discussed for Dy/Y and Ho/Y multilayer where the symmetry of left- and right handed helical spirals formed by the RKKY interaction can be broken by the application of a magnetic field leading to a chiral state [1-3]. Here, different theoretical models are applied to explain the observed phenomena and will be discussed here. In the second part it will be shown how chirality in a thin film system consisting of alloys of rare-earth elements and 3d transition metals may be utilized for creating an exchange bias effect that differs fundamental from the one formed by conventional antiferromagnetic/ferromagnetic film systems. Furthermore, an outlook on the highly promising rare-earth elements / 3d transition metals alloys will be given [4]. For the exploration of the chirality effects in the here given examples, the application of polarized neutrons were essential enabling one to identify the magnetic states of the samples and the investigation of the intriguing phenomena of chirality.

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10:40am **MI+2D+AC-MoM8 Is the High Tc Superconductivity in Cuprates an Interface Problem?***,* ***Qi-Kun Xue,*** Tsinghua University, China **INVITED**

We investigate the pairing mechanism of high Tc superconductivity in cuprates by using state-of-the-art molecular beam epitaxy (MBE)-scanning tunneling microscopy (STM) in ultra-high vacuum conditions. By two different approaches in sample preparation, namely Ar^+ ion bombardment and ozone-assisted MBE growth, we are able to study the gap structure of superconducting copper oxide planes in unprecedented way. We show that the Cooper pairing in cuprates is rather conventional and the unique interfacial structure plays a crucial role in the high temperature superconductivity.

11:20am **MI+2D+AC-MoM10 How to do Depth-Dependent Measurements on Magnetic or Magnetoelectric Thin Films***,* ***Mikel Holcomb,*** *R. Trappen, J. Zhou, C-Y. Huang, G. Cabrera,* West Virginia University*; S. Dong,* Southeast University*; Y-H. Chu,* National Chiao Tung University, Taiwan

Analysis of depth-dependent measurements can provide useful information on how material properties change near surfaces or interfaces with other materials. For example, this deviation commonly occurs in magnetic thin films and the variation of these properties can strongly influence how different materials couple with one another. We have recently utilized a combined approach of bulk and surface sensitive x-ray absorption techniques to nondestructively map out depth-dependent atomic valence and magnetization across magnetic $La_{0.7}Sr_{0.3}MnO_3$ and magnetoelectric $La_{0.7}Sr_{0.3}MnO_3/PbZr_{0.2}Ti_{0.8}O_3$ thin films. We have combined measurements on multiple sample thicknesses with theoretical approaches to map out the layer-by-layer atomic valences and how they vary with film thickness. Such efforts may play a critical role in understanding how to build future generations of devices that rely on enhanced surface and interface properties.

11:40am **MI+2D+AC-MoM11 Nano-Pico-Mikro - Dynamic Soft X-ray Microscopy of Magnetic Materials with High Sensitivity*, Hendrik Ohldag,*** SLAC National Accelerator Laboratory

Understanding magnetic properties at ultrafast timescales is crucial for the development of new magnetic devices. Such devices will employ the spin torque or spin Hall effect, whose manifestation at the nanoscale is not yet sufficiently understood, The samples of interest are often thin film magnetic multilayers with thicknesses in the range of a atomic layers. This fact alone presents a sensitivity challenge in STXM microscopy, which is more suited toward studying thicker samples. In addition the relevant time scale is of the order of 10 ps, which is well below the typical x-ray pulse length of 50 – 100 ps. The SSRL STXM is equipped with a single photon counting electronics that effectively allows using a double lock-in detection at 476MHz (the x-ray pulse frequency) and 1.28MHz (the synchrotron revelation frequency). The pulsed or continuous sample excitation source is synchronized with the synchrotron source with a few picosecond drift over 24 hours.

In the first year of operation the excellent spatial resolution, temporal stability and sensitivity of the detection electronics of this microscope has enabled researchers to acquire time resolved images of standing as well as traveling spin waves in a spin torque oscillator in real space as well as detect the real time spin accumulation in a non-metal in contact with a ferromagnet.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+AS+MI-MoM

Advances in High-Resolution Imaging Techniques (8:20-10:20 am)/Pushing the Limits with X-Ray Spectroscopy (10:40 am-12:00 pm)

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

9:00am **SA+AS+MI-MoM3 Applications of Novel Hard X-ray Nanoprobe in Nanoscience*, Gema Martinez-Criado,*** Madrid Materials Science Instititute, CSIC, Spain **INVITED**

Owing to the spatial resolution and sensitivity (i.e., signal to background ratio), nano and micro X-ray beams are emerging tools with a strong impact in nanoscience. Although the optical quality of the X-ray focusing devices has limited the progress of hard X-ray nanoprobes, recent advances in fabrication techniques have pushed the spatial resolution towards the diffraction limit. As a result, the use of nano and micro X-ray beams has begun to extend towards the atomic domain, with concomitant and continuous developments of multiple analytical tools. The study of micro/nanoscale objects, small embedded nanodomains with weak signals and/or heterogeneous structures at the nanometer scales has required the use of intense X-ray pencil beams. Additionally, stimulated by the great brilliance with reduced emittance of current third generation synchrotron sources, and new developments in X-ray detector technology, today intense nano-X-ray beams are available with a variety of focusing devices. Finally, thanks to the multiple interactions of X-rays with matter these X-ray probes can be used for manifold purposes, such as ultra-sensitive elemental/chemical detection using X-ray fluorescence/X-ray absorption, or for identification of minority phases, and/or strain fields by X-ray diffraction with nanometer resolution. In the present talk I describe how hard X-ray nanobeams are produced and exploited today for space-resolved determination of structural and electronic properties, as well as for chemical speciation of nanosized materials. Selected recent examples will range from phase separation in single nanowires to visualization of dislocations and buried interfacial defects, to domain distortions and quantum confinement effects.

10:40am **SA+AS+MI-MoM8 Extreme X-ray Flux to Probe Picosecond Dynamics*, Alfred Baron,*** RIKEN SPring-8, Japan **INVITED**

Inelastic x-ray scattering (IXS), *in principle*, provides a nearly ideal opportunity to probe dynamics on ps and sub-ps time scales via direct measurement of the dynamic structure factor, S(Q,ω). Such measurements are interesting in many areas of science, including fundamental understanding of liquid behavior, investigations of phonons in complex materials such as superconductors and ferroelectrics, and even to help determine the composition of the earth's interior. However, high-resolution non-resonant IXS measurements are *severely flux limited*.

Over the last 18 years, the author has spearheaded a program to increase the world capability for high-resolution IXS measurements through work at SPring-8 in Japan. This began with designing and constructing a beamline based on a standard insertion device [1] then progressed to a second beamline using 3x5m tandem small-gap insertion devices (IDs) [2], while in parallel, upgrading the earlier facility to a optimized small-gap ID. *This has successfully led to world-leading flux at workhorse spectrometers with ~1.25 meV resolution and 30 GHz onto the sample at 21.7 keV*, and up to 30 momentum transfers collected in parallel. Resolution as good as 0.75 meV [3] can be achieved at higher (25.7 keV) energy while medium resolution spectrometer provides in excess of 2 THz onto a sample with 27 meV resolution for measuring electronic dynamics.

The presentation will discuss aspects of the instrumentation for IXS, and recent sample science. On the instrumentation side, on top of "straightforward" issues such as sub-mK temperature control over >50 channels, installation of more that 30 tons of spectrometer, there were unique and new issues related to operating 3x5m tandem small- (6mm-) gap insertion devices [4]. On the sample side, the talk will highlight recent efforts in geoscience, where measurements at record pressures and temperatures have allowed us to constrain to composition of the Earth's core - both the outer liquid core [5] and the inner solid core. This will be complemented by a short discussion of a surprising phonon anomaly in YBa2Cu3O7-d, where phonon line-widths undergo a remarkable increase below the superconducting transition temperature [7] in what is perhaps the largest phonon anomaly observed to date in the absence of a structural phase transition.

[1] Baron, *et. al.*, J. Phys. Chem. Solids **61**, 461 (2000).

[2] Baron, SPring-8 Inf. Newsl. **15**, 14 (2010).

[3] Ishikawa, *et al*., J. Synch. Rad. **22**, (2015).

[4] Baron, *et al*., AIP Conf. Proc. **SRI2015** (Accepted).

[5] Nakajima, *et al*., Nat Commun. **6**, (2015).

[6] Sakamaki, et al., Sci. Adv. **2**, (2016).

[7] Baron*, et al*., in preparation.

11:20am **SA+AS+MI-MoM10 Beating Complexity through Selectivity: Anti-Stokes Resonant Inelastic X-ray Scattering for Excited State Dynamics*, Alexander Föhlisch,*** University of Potsdam, Germany **INVITED**

Ultrafast electronic and structural dynamics of matter govern rate and selectivity of chemical reactions, as well as phase transitions and efficient switching in functional materials. Since X-rays determine electronic and structural properties with elemental, chemical, orbital and magnetic selectivity, short pulse X-ray sources have become central enablers of ultrafast science. Despite of these strengths, ultrafast X-rays have been poor at picking up excited state moieties from the unexcited ones. With time-resolved Anti-Stokes Resonant X-ray Raman Scattering background free excited state selectivity in addition to the elemental, chemical, orbital and magnetic selectivity of X-rays can be achieved. For low symmetry systems energetically off-set signatures dominate, and for inversion symmetric systems a clear separation between ground and excited states occurs. This unparalleled selectivity extracts low concentration excited state species along ultrafast dynamic pathways. These approaches will benefit from recent advances towards non-linear X-ray matter interaction and an outlook is given how future fourier limited X-ray laser pulses will explore ultrafast dynamics.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-MoM

Advances in Scanning Probe Microscopy

Moderators: Saban Hus, Oak Ridge National Laboratory, Chanmin Su, Bruker Nano

8:20am **SP+AS+MI+NS+SS-MoM1 Ultrafast Imaging of Polarization Switching in Ferroelectrics via Complete Information Acquisition in SPM***,* ***Suhas Somnath****, A. Belianinov, S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory

SPM imaging can be represented as an information channel between the dynamic processes at the tip-surface junction and the observer. Current SPM techniques use heterodyne detection methods such as lock-in amplifiers which result in significant loss in vital information such as information from higher eigenmodes, mode-mixing, and other non-linear phenomena in the tip-surface interaction. We present a new technique called General-mode (G-mode) where we capture the complete broad-band response of the cantilever at sampling rates of 1-100 MHz. The availability of the complete cantilever response facilitates the application of various physical models as well as multivariate statistical methods to extract information that has been unavailable from current SPM techniques. Polarization switching in ferroelectric and multiferroic materials underpins the next generation of electronic devices such as tunneling devices, field effect transistors, and race-track memories. The switching mechanisms in these materials are highly sensitive to the local defects and structural imperfections at the micro and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) imaging and spectroscopy techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, measurement area, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, these techniques only capture the narrow-band cantilever response. We report on a fundamentally new approach that combines the full cantilever response from G-mode with intelligent signal filtering techniques to directly measure material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

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.

8:40am **SP+AS+MI+NS+SS-MoM2 Development of Synchrotron X-ray Scanning Tunneling Microscopy***,* ***Nozomi Shirato,*** Center for Nanoscale Materials at Argonne National Laboratory*; H. Chang,* Ohio University*; M. Cummings,* Advanced Photon Source at Argonne National Laboratory*; S.W. Hla,* Center for Nanoscale Materials at Argonne National Laboratory*; V. Rose,* Advanced Photon Source at Argonne National Laboratory

Advancements of scanning probe microscopy have been contributing to broaden fundamental understating of surface physics. By combining high intense X-ray beam as a probe and a functionalized tip as a detector, synchrotron X-ray scanning tunneling microscopy has been developed in Advanced Photon Source at Argonne National Laboratory. The recent studies demonstrated the technique has capabilities to extract chemical information with sensitivity at the atomic limit [1] and localized magnetic contrast by utilizing polarized beams [2]. Furthermore, at Argonne, in order to fully exploit potentials of the microscope, a dedicated beamline is under construction. The soft X-ray beamline has the energy range of 400 to 1600 eV and is equipped with a polarizer and focusing optics. The capabilities of the beamline will benefit the communities to explore chemical, magnetic and electronic properties of materials at atomic resolution.

References

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] A. DiLullo et al., J. Synchrotron Rad. 23, 574 (2016).

9:00am **SP+AS+MI+NS+SS-MoM3 Development and Integration of a Universal SPM head: Design Criteria and Challenges***, B. Guenther,* Sigma Surface Science GmbH, Germany*; J. Hilton,* Mantis Deposition*; A. Feltz,* Sigma Surface Science GmbH*;* ***Andreas Bettac****,* Sigma Surface Science GmbH, Germany

Recently we have developed an SPM microscope head that merges the needs for high resolution STM/QPlus^1-AFM and at the same time satisfies the requirements for integration into different cryogen environments including tip and sample handling.

The new SPM head was integrated into different platforms, e.g. in a UHV Helium Flow Cryostat system for temperatures <10K and in a ^{3}He Magnet Cryostat UHV system for high magnetic fields (±12T) and temperatures <400mK.

This contribution focuses on design aspects and challenges for the new SPM head with respect to spatial restrictions, sample sizes/standards, QPlus and STM signal shielding as well as on first results (STM, STS and QPlus) obtained with the different instrumental setups.

[1] F. J. Giessibl, Applied Physics Letters 73 (1998) 3956

9:20am **SP+AS+MI+NS+SS-MoM4 How Soft Is a Protein? Stress-Strain Curve of Antibody Pentamers with 5 pN and 50 pm Resolutions***,* ***Alma Perrino***[*]*,* Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC,, Spain

Understanding the mechanical functionalities of complex biological systems requires the measurement of the mechanical compliance of their smallest components. Here, we develop a force microscopy method to quantify the softness of a single antibody pentamer by measuring the stress-strain curve with force and deformation resolutions, respectively, of 5 pN and 50 pm [1]. The curve shows three distinctive regions. For ultrasmall compressive forces (5-75 pN), the protein's central region shows that the strain and stress are proportional (elastic regime). This region has an average Young modulus of 2.5 MPa. For forces between 80 and 220 pN, the stress is roughly proportional to the strain with a Young modulus of 9 MPa. Higher forces lead to irreversible deformations (plastic regime). Full elastic recovery could reach deformations amounting 40% of the protein height. The existence of two different elastic regions is explained in terms of the structure of the antibody central region. The stress-strain curve explains the capability of the antibody to sustain multiple collisions without any loss of biological functionality.

[1] Alma P. Perrino and R.Garcia. How soft is a protein? Stress-Strain curve of antibody pentamers with 5 pN and 50 pm resolutions. *Nanoscale,* 10.1039/C5NR07957H (2016)

9:40am **SP+AS+MI+NS+SS-MoM5 AVS Medard W. Welch Award Talk: Action Spectroscopy: Characterizing Molecules at Surfaces and its Dynamics***,* ***Maki Kawai***[†]*,* Institute for Molecular Science, Japan*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; K. Motobayashi,* Nagoya Institute of Technology, Japan*; H. Ueba,* Toyama University, Japan **INVITED**

STM is a useful tool for spectroscopy utilizing its ultimate spatial resolution. Electronic and vibrational information that STS and inelastic electron tunneling spectroscopy (IETS) carries is not only the reflection of the static spectroscopic information but also related to dynamical phenomena as motion or reaction of molecules induced by the excitation of molecular states. Action spectroscopy is the method to related the action of molecules induced and is utilized to identify the quantum states of the molecules. Dynamical information includes as how molecular vibrations can couple with the relevant dynamical processes [1,2]. I will present typical eamples of how the fundamental excitation of vibration modes is coupled with chemical reactions at surfaces.

References:

[1] Y. Kim, K. Motobayashi, T. Frederiksen, H. Ueba and Maki Kawai, Profress in Surface Science 90 (2015) 85-143, and the references within.

[2] K. Motobayashi, Y. Kim, M. Ohara, H. Ueba and Maki Kawai, Surf. Sci. 634 (2016) 18-22.

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[*] **NSTD Student Award Finalist**

[†] **Medard W. Welch Award Winner**

10:40am **SP+AS+MI+NS+SS-MoM8 Near-Field Spectroscopy and Imaging of Single Nanoparticles***, **Yohannes Abate**, D. Seidlitz, A. Fali, S. Gamage, V.E. Babicheva, V.S. Yakovlev, M.I. Stockman,* Georgia State University*; R. Collazo, D. Alden,* North Carolina State University*; N. Deitz,* Georgia State University **INVITED**

We investigate nanoscale phase separation on single InGaN QDs and nanostructures by using high-resolution s-SNIN (scattering type scanning near-field infrared nanoscopy) technique in the mid-IR spectral region. We fabricated patterned nanolayers down to few atomic layers thick that allow determination of the near-field infrared response of InGaN/InN/GaN heterostructures quantitatively. We first calibrate the near-field IR amplitude contrast as a function of composition and thickness of the semiconductor nanolayers and QDs. We then use this quantitative leads to identify phase separation in single QDs. An advanced theoretical model is developed to guide the experimental results. Unlike previous models that consider the probe conical tip as approximate point dipoles or spheroids, our model considers the full geometry of the tip and all the sample and substrate layers.

11:20am **SP+AS+MI+NS+SS-MoM10 Atomically-resolved Three-dimensional Structures of Electrolyte Aqueous Solutions near a Solid Surface***, **Daniel Martin-Jimenez**, E. Chacon,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; P. Tarazona,* IFIMAC Condensed Matter Physics Center, UAM, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

Atomic-resolution three-dimensional images of electrolyte solutions near a mica surface demonstrate the existence of three types of interfacial structures [1-3]. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface [4]. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

[1] E. T. Herruzo, H. Asakawa, T. Fukuma, and R. Garcia, *Nanoscale* **5**, 2678-2685 (2013).

[2] K. Kobayashi *et al.The Journal of Chemical Physics* **138**, 184704 (2013)

[3] T. Fukuma *et al.Physical Review B* **92**, 7 (2015).

[4] M. Ricci, P. Spijker and K. Voitchovsky *Nat. Commun.* **5**, 4400 (2014).

11:40am **SP+AS+MI+NS+SS-MoM11 Super-resolution Optical and Chemical Imaging of Organic Thin Films using Tip-enhanced Near-Field Optical Microscopy***, A.L. Heilman, R. Hermann, **Michael Gordon**,* University of California at Santa Barbara

Sub-diffraction-limited (super-resolution) optical and chemical characterization of organic surfaces using a custom-built tip-enhanced near-field optical microscope with side-on and attenuated total reflectance (ATR) excitation and collection will be discussed. ATR illumination is combined with an Au optical antenna tip to show that (i) the tip can quantitatively transduce the optical near-field (evanescent waves) above the surface by scattering photons into the far-field, (ii) the ATR geometry enables excitation and characterization of surface plasmon polaritons (SPPs), whose associated optical fields can enhance Raman scattering from coumarin-6 (C6) and copper phthalocyanine (CuPc) films, and (iii) SPPs can be used to plasmonically excite the tip for super-resolution chemical imaging of patterned C6 and CuPc via tip-enhanced Raman spectroscopy (TERS). ATR-illumination TERS is quantitatively compared with the more conventional side-on illumination scheme using both experiment and FDTD optical simulations. In both cases, spatial resolution was better than 40 nm and tip on/tip off Raman enhancement factors were >6500. ATR illumination was shown to provide similar Raman signal levels at lower 'effective' pump powers due to additional optical energy delivered by SPPs to the active region in the tip-surface gap. Additional observations, such as the distance scaling of Raman enhancement and inelastic scattering generated by the plasmonic tip, as well as tip-enhanced photoluminescence imaging of patterned phthalocyanine films at spatial resolutions better than 20-30 nm, will be presented.

2D Materials Focus Topic
Room 103B - Session 2D+MI-MoA

Dopants, Defects and Interfaces in 2D Materials

Moderators: Philip Hofmann, Aarhus University, Denmark, Adina Lucian-Mayer, University of Ottawa, Canada

1:40pm **2D+MI-MoA1 High-k Dielectrics on WSe_2 by Ozone-based Atomic Layer Deposition: An In-situ XPS Study**, ***Angelica Azcatl***, *R.M. Wallace,* The University of Texas at Dallas

Two-dimensional tungsten diselenide (WSe_2) is a layered material that have shown a promising performance when implemented in field effect transistors, exhibiting a hole mobility up to 250 cm^2/V·s. [1] Furthermore, WSe_2 possess hole and electron effective masses smaller than those of MoS_2, another widely studied transition metal dichalcogenide, making WSe_2 a promising candidate channel material for tunnel field effect transistor applications (TFETs). For the realization of WSe_2 based TFETs, a high quality ultra-thin high-k dielectric film is a key requirement. However, the integration of high-k dielectrics by a conventional atomic layer deposition (ALD) process results challenging due to the dearth of nucleation sites at the WSe_2 surfaces. Previous studies have shown that the deposition of high-k dielectrics by water-based ALD on WSe_2 leads to non-uniform dielectric films. [2]

In this work, we explore the use of an alternative ALD approach to obtain uniform dielectric films on WSe_2 through the use of ozone as oxidant precursor. The surface chemistry of WSe_2 upon ozone exposure was studied by in-situ X-ray photoelectron spectroscopy to understand the reactivity between ozone and the WSe_2 surface. Then, the ozone-based ALD process was studied for the deposition of Al_2O_3 and HfO_2 on WSe_2. It was found that the interfacial chemistry and the nucleation of the dielectric have a dependence on the deposition temperature. Based on these results, a temperature window was identified at which interfacial oxide formation is avoided while a uniform dielectric film is obtained. Furthermore, the differences in reactivity and growth rate between HfO_2 and Al2O$_3$ will be discussed. This study helps to elucidate the reaction mechanism of the ozone based ALD process on WSe_2 and facilitates the implementation of the ozone based ALD approach to obtain uniform and thin dielectric films on WSe_2 for TFETs applications.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

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[1] H. Fang, et al., Nano Lett. 2012, 12, 3788−3792

[1] A. Azcatl, et al. 2D Materials, 2015, 2, 1, 014004

2:00pm **2D+MI-MoA2 A Two-step Atomic Layer Etching on MoS_2 Realized by Remote O_2 Plasma**, ***Hui Zhu***, *X. Qin, L. Cheng, A. Azcatl, J. Kim, R.M. Wallace,* University of Texas at Dallas

Molybdenum disulfide (MoS_2), a representative layered transition metal dichalcogenide, has obtained considerable research interest in recent years, due to its promising mechanical, electronic, and photonic properties.[1,2] The mechanical exfoliation of MoS_2 has led to an intensive research on thin film field-effect transistors made with MoS_2 flakes.[3,4] However, the scalable layer engineering of MoS_2 flakes is still a challenge for device fabrication. In this work, a novel MoS_2 functionalization and layer thinning process is presented by combining the surface oxidation of MoS_2 with a remote O_2 plasma to form an amorphous MoO_x layer and subsequent annealing to selectively desorb the MoO_x surface layer. Exfoliated MoS_2 is shown to chemically oxidize in a layered manner upon exposure to the remote O_2 plasma. X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and atomic force microscopy (AFM) are employed to characterize the surface chemistry, structure and topography of the oxidation process, and indicates that the oxidation mainly occurs on the topmost layer without altering the chemical composition of underlying layer. After the desorption of MoO_x by the annealing at 500 °C, a clean, flat and chemically undisturbed MoS_2 surface as evidenced from XPS, LEED, AFM and scanning tunneling microscopy (STM) characterization. This work renders promising atomic scale fabrication applications such as surface functionalization, charging engineering and atomic layer etching.

This work was supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

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[4] S. Kim, A. Konar, W.-S. Hwang, J.H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J.-B. Yoo, J.-Y. Choi, Y.W. Jin, S.Y. Lee, D. Jena, W. Choi, and K. Kim, Nat. Commun. **3**, 1011 (2012).

2:20pm **2D+MI-MoA3 Engineering the Atomic Structure of 2D Transition Metal Dichalcogenides using Electron Beam: Experiments and Simulations**, ***Arkady Krasheninnikov***, Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN sheets and transition metal dichalcogenides (TMD) were manufactured. Among them, TMD sheets have received particular attention, as these materials exhibit intriguing electronic and optical properties. Moreover, the properties can further be tuned by introduction of defects and impurities. Specifically, as many in-situ transmission electron microscopy experiments indicate, electron beam irradiation can give rise to phase transitions in 2D TMDs (e.g., from H to T phase), development of line defects and domains with mirror symmetry, and other structural transformations. In my talk, I will present the results [1] of our first-principles theoretical studies of the response of 2D TMDs to electron irradiation, and dwell on the characteristics of irradiation-induced defects, their evolution and agglomeration. I will also touch upon beam-mediated phase transitions in 2D TMDs. The theoretical results to be presented were obtained in close collaboration with several experimental groups, so that a detailed comparison of the theoretical data and experimental results will be given. Finally, I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D TMDs.

[1] Nature Comm. 6 (2015) 6736; ACS Nano 9 (2015) 3274; ACS Nano (2015) ACS Nano 9 (2015) 11249; Phys. Rev. B 91 (2015) 125304; Adv. Mater. 26 (2014) 2857; Phys. Rev. X 4 (2014) 031044; see http://users.aalto.fi/~ark/publist.html for complete list of publications.

3:00pm **2D+MI-MoA5 New Computational Tool for Electron Localization: Application to Low-dimensional Monolayers of h-BN and MoS_2**, ***Chinedu Ekuma***, NRC/NRL Postdoctoral Fellow*; V. Dobrosavljevic,* Florida State University*; D. Gunlycke,* Naval Research Laboratory

Low-dimensional monolayer materials such as graphene, MoS2, and hexagonal BN (h-BN) exhibit electronic degrees of freedom that produce exotic properties, which can be fine-tuned to engineer new functionalities for diverse applications. However, the performance of device applications depends strongly on the defect morphology and the quality of the sample. Herein, we explore the role of vacancy and/or Hubbard-type interactions for a spin-1/2 system in monolayer MoS2 and h-BN. We utilize a first-principles many-body typical medium dynamical cluster formalism, which is an effective medium approach with an intrinsic order parameter for characterizing disordered and/or interacting electron systems even in the regime of insulator-metal quantum transition (IMQT). The focus is mainly on the distribution of the local density of states, which is a key fingerprint of the optoelectronic properties of disordered systems. Within our formalism, we predict an IMQT in both systems and show that IMQT in h-BN is due to a combination of electron interactions and defects. A sulfur vacancy concentration as low as 0.01% in MoS2 is shown to lead to an IMQT in agreement with experiments.

3:20pm **2D+MI-MoA6 Effects of helium-ion beam irradiation on opto-electrical properties of multi-layers WSe2**, ***Anna Hoffman***, *P.R. Pudasaini, M.G. Stanford, P.D. Rack, D.G. Mandrus, N. Cross, J.H. Noh, M. Koehler, G. Duscher,* The University of Tennessee Knoxville*; A. Belianinov, A.J. Rondinone,* Oak Ridge National Laboratory*; I. Ivanov, T.Z. Ward,* Oak Ridge National Lab

Transition metal dichalcogenides (TMD) possess interesting properties that render them attractive for opto-electronic applications. Tuning optical and electrical properties of mono and few layer TMDs, such as tungsten diselenide (WSe_2), by inducing defects is an intriguing opportunity to fabricate the next generation opto-electronic devices. Here we report the effects of helium ion beam irradiation on optical and electrical properties of few layer WSe_2. By controlling the ion dose irradiation**,** we can tune the concentration of point defects present on few layer WSe_2, thereby locally tuning the electrical resistivity of the material. Semiconductor-insulator-metal like transitions have been observed with exposure to increasing helium ion beam dose, resulting in more than a seven order change in electrical resistivity. Furthermore, by selectively exposing the ion beams at the metal-WSe_2 contact area, we demonstrate reduced contact resistance of the described device, thereby reducing the Schottky barrier height. This could be particularly interesting for single layer TMD devices as the Schottky contacts, formed at metal/semiconductor interfaces, have a huge influence on the TMD device's performance.

4:00pm **2D+MI-MoA8 CO_2 Adsorption Kinetics on Nitrogen Doped Graphene and Graphite***, **Takahiro Kondo**, R. Shibuya, D. Guo, J. Nakamura,* University of Tsukuba, Japan

Nitrogen doped carbon materials are known to have CO_2 adsorption property at room temperature under atmospheric pressure. Recently, we have clarified that the CO_2 adsorption property is created by the one of the specific type of nitrogen dopants, pyridinic-N, which has two N-C bonds based on the temperature programmed desorption (TPD) measurements of CO_2 from nitrogen-doped graphene nanosheets (N-GNS) and nitrogen-doped model graphite (N-HOPG) catalysts [1]. According to our scanning tunneling microscopy and spectroscopy (STM/STS) measurements of N-HOPG, the CO_2 adsorption sites are suggested as the carbon atoms next to the pyridinic-N, where the distinct localized states are formed at near the Fermi level in the occupied region as non-bonding p_z orbital of carbon which plays a role of Lewis base site [2]. Furthermore, based on the X-ray photoelectron/absorption spectroscopy, we found that the adsorbed CO_2 is lying flat on the N-HOPG surface [3]. In this work, we reports the kinetics of CO_2 adsorption on both N-GNS and N-HOPG. From the measurements of CO_2-TPD, the desorption temperatures of CO_2 have been found to be 373 K in both N-GNS and N-HOPG, indicating that the same Lewis base sites are formed on N-GNS and N-HOPG. The adsorption energy can be roughly estimated as 100 kJ/mol from the desorption temperature. The relatively small adsorption energy can be attributed to the larger activation barrier and/or small pre-exponential (frequency) factor for CO_2 adsorption. The adsorption probability of CO_2 at 300 K has been estimated to be as 1/100 for N-HOPG. The detail kinetics as well as the selectivity for the CO_2 adsorption among many type of mixture gas will be presented.

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science 351 (2016) 361.

[2] T. Kondo, S. Casolo, J. Nakamura et al., Phys. Rev. B 86 (2012) 035436.

[3] H. Kiuchi, R. Shibuya, T. Kondo, J. Nakamura,et al.,Nano. Res. Lett. 11 (2016) 127.

4:20pm **2D+MI-MoA9 Electronic Structure of Metallic Twin Grain Boundaries in Monolayer $MoSe_2$***, **Matthias Batzill**,* University of South Florida

Monolayers of $MoSe_2$ grown by molecular beam epitaxy on van der Waals substrates (HOPG or MoS_2), may exhibit twin grain boundaries. These Se-deficient line defects have been predicted by DFT to be metallic with dispersing bands. We examine their structural and electronic properties by scanning tunneling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). A dispersing parabolic band is observed that intersects the Fermi-level indicating the metallic property of this defect. Below 235 K the line defect undergoes a Peierls, or charge density wave (CDW), transition. STM indicates a periodicity of 3 lattice constants of the CDW consistent with the Fermi-wavevector determined in ARPES. In addition, we determine that the defect behaves like an ideal one-dimensional metal. More specifically we show evidence of Tomonaga Luttinger liquid suppression of the density of states at the Fermi-level and the splitting of the band in a 'spinon' and 'holon' band, also known as spin-charge separation.

Magnetic Interfaces and Nanostructures
Room 101C - Session MI+2D+AC-MoA

Magnetism and Spin Orbit Effects at Interfaces and Surfaces: Recent Experimental and Theoretical Advances

Moderator: Valeria Lauter, Oak Ridge National Laboratory

1:40pm **MI+2D+AC-MoA1 Bi-$_1$Te$_1$: A New Dual Topological Insulator***, **Lukasz Plucinski**, M. Eschbach, M. Lanius, C. Niu, E. Mlynczak, P. Gospodaric,* FZ Jülich GmbH, Germany*; J. Kellner,* RWTH Aachen University, Germany*; P. Schüffelgen, M. Gehlmann, S. Döring, E. Neumann, M. Luysberg, B. Holländer, G. Mussler,* FZ Jülich GmbH, Germany*; M. Morgenstern,* RWTH Aachen University, Germany*; D. Grützmacher, G. Bihlmayer, S. Blügel, Schneider,* FZ Jülich GmbH, Germany

We present, a combined theoretical and experimental study on the prediction and verification of the dual topological insulating character of the stoichiometric natural superlattice phase $Bi_1Te_1 = [Bi_2]_1[Bi_2Te_3]_2$ [1]. We identify Bi_1Te_1 by density functional theory to exhibit a non-trivial time-reversal symmetry-driven character of $Z_2 = (0; 001)$ and additionally a mirror-symmetry induced mirror Chern number of $v_{M-} = -2$, which indicates that Bi_1Te_1 is both a weak topological insulator (WTI) and a topological crystalline insulator (TCI). The coexistence of the two phenomena preordain distinct crystal planes to host topological surface states that are protected by the respective symmetries. From the analysis of time-reversal invariant momenta (TRIM-points) the surface perpendicular to the stacking direction, for instance, is found as the time-reversal symmetry *dark* surface, while hosting mirror-symmetry protected non-TRIM surface states along the surface-Gamma-M direction. We confirm the stacking sequence of our MBE-grown Bi_1Te_1 thin films by X-ray diffraction and transmission electron microscopy (STEM), and find clear indications of the TCI and WTI character in the surface electronic spin structure by spin- and angle-resolved photoemission spectroscopy.

[1] M. Eschbach et al., arXiv:1604.08886 (2016).

2:00pm **MI+2D+AC-MoA2 Spin-Polarized Scanning Tunneling Microscopy of a Two-Dimensional Ferromagnetic Semiconductor at Room-Temperature***, **Yingqiao Ma**, A.R. Smith,* Ohio University*; A. Barral, V. Ferrari,* Centro At´omico Constituyentes, GIyA, CNEA, Argentina

Ferromagnetic semiconductors are very promising materials for the spintronic applications, as they are good spin-polarized carrier sources and easy to be integrated into semiconductor devices. The search for ferromagnetic semiconductors with Curie temperature above the room-temperature has been a long-standing goal, since the Curie temperature *Tc* of most ferromagnetic semiconductors are at the cryogenic level with little possibility of improvement, which hinders their future practical spintronic applications.

Here, we observed the ferromagnetic domain structure at room-temperature on a GaN-based two-dimensional MnGaN semiconducting surface alloy, using spin-polarized scanning tunneling microscopy/spectroscopy which is sensitive to the surface magnetic nanostructures and can completely rule out the extrinsic origin of the ferromagnetism such as magnetic elements segregation by its ultimate spatial resolution. In contrast to the randomly doped dilute magnetic semiconductors, the two-dimensional surface structure has a unique and well-ordered hexagonal-like Mn √3 x √3 - R30° symmetry. The total density of states of the Mn √3 x √3 - R30° structure calculated by the density functional theory agree well with our normalized differential tunneling *dI/dV* spectroscopy, which clearly reveal the spin-polarized and spin-split Mn surface density of states peaks and prove the semiconducting nature of the surface as the normalized *dI/dV* goes to zero at the Fermi level. By applying a small magnetic field to the sample, the magnetic hysteresis is mapped out, which further proves its ferromagnetic nature. In conclusion, we demonstrated the room-temperature ferromagnetic nature of the two-dimensional Mn √3 x √3 - R30° structure, which makes it a promising material for future realistic magnetic storage, field-controlled, and quantum computing nano spintronic devices.

2:20pm **MI+2D+AC-MoA3 Spin-Orbit Induced Surface States of Rashba Systems and Topological Insulators***, **Peter Krüger**, T. Förster, M. Rohlfing, P. Eickholt, A.B. Schmidt, M. Donath,* Westfälische Wilhelms-Universität Münster, Germany **INVITED**

The generation of spin-polarized electrons on the basis of spin-orbit coupling at the surfaces of nonmagnetic solids has attracted considerable interest in recent years. Adlayers of heavy atoms, in particular, give rise to an interesting physics of spin-split surface states going far beyond the simple Rashba model. However, only very few studies have been reported that address unoccupied states of these systems, despite their relevance for potential applications. In the first part of this contribution, we present results from ab-initio calculations as well as spin- and angle-resolved inverse photoemission (IPE) for systems showing empty bands with a giant spin splitting and a unique structure of the spin polarization. For Tl/Si(111) and Tl/Ge(111), we identify spin-split states whose polarization vector rotates from the Rashba direction to an out-of-plane polarization when going from Gamma to K. Surprisingly, the spin splitting of the bands on Tl/Ge(111) is much smaller than on Tl/Si(111) despite the stronger surface localization and the heavier substrate. Our detailed analysis of the electronic structure shows that a remarkable interplay between spin-orbit coupling and hybridization is responsible for this unexpected result. Furthermore, we notice a distinct spin asymmetry in the intensity of the measured spectra at M, a time-invariant k-point. Our simulations of the IPE process unravel this puzzling behavior.

In the case of topological insulators, spin-orbit coupling gives rise to topologically protected surface states. We identify problems of the widely used density-functional theory (DFT) with a proper description of these states and demonstrate that they can be overcome by employing the GW self-energy operator within ab initio many-body perturbation theory. In particular we have investigated thin films of Bi2Se3, Bi2Te3, and Sb2Te3 with thicknesses from one to six quintuple layers. The quasiparticle band structures show highly improved agreement with experiments compared to DFT. In addition to a correction of the band gaps, the energetic positions and dispersions of the surface states change significantly around the Dirac point. As the wave functions are updated in our approach, the two-dimensional topological phases (quantum spin Hall or trivial) in GW can be different from the DFT result. We find the nontrivial quantum spin Hall phase, together with a sizable band gap 0.13 eV for a Bi2Te3 slab of 2 QL thickness.

[1] P. Eickholt et al., Phys. Rev. B 93, 085412 (2016)

[2] T. Förster et al., Phy. Rev. B 92, 291404 (R) (2015)

3:00pm **MI+2D+AC-MoA5 Spin-Resolved Momentum Microscopy of Strongly Correlated Electron Systems and Topological Insulators*, Christian Tusche,*** Forschungszentrum Jülich, Germany **INVITED**

One of the fundamental concepts in solid state physics is the description of the degrees of freedom of the electrons in the solid by the relation of the energy E vs. the crystal momentum k in a band structure of quasi particles. Of particular importance is the spin of the electron that leads to phenomena like ferromagnetism, spin-polarized surface- and interface-states, and recently, the discovery of new material classes like topological insulators. The latter attracted wide interest by the unusual relations of electron-spin and -momentum. In addition, strong spin-orbit coupling also leads to a rich band-structure of highly polarized states beyond the well known "Dirac cone" surface state. A direct conclusion on the ground state polarization in these systems is rather complicated by the peculiar interplay between spin- and light-polarization, as directly observed in spin-resolved photoemission maps over the full surface Brillouin zone .

On the experimental side, the novel concept of momentum microscopy evolved to provide an intuitive and comprehensive insight to these band structures. A momentum microscope captures the complete 2π solid angle of emitted photoelectrons into a high resolution image of electronic states in reciprocal space [1]. With the introduction of imaging spin analyzers, the efficiency of spin-resolved measurements experienced a tremendous boost [2]. Together with modern synchrotron radiation sources, delivering photon energies from UV to soft X-rays as well as a flexible timing structure, the electron spin now becomes routinely accessible in photoemission experiments. In particular, new developments like time-of-flight momentum microscopy now provide comprehensive three-dimensional data sets of the complete valence band region within a single measurement [3]. Here, we discuss examples and prospects of spin resolved momentum microscopy, ranging from tomographic imaging of the spin-resolved Fermi surface of ferromagnets to the rapid band-structure mapping of novel materials.

[1] C. Tusche, A. Krasyuk, J. Kirschner: Ultramicroscopy 159, p. 520 (2015),

[2] C. Tusche, M. Ellguth, A. A. Ünal, C.-T. Chiang, A. Winkelmann, A. Krasyuk, M. Hahn, G. Schönhense, J. Kirschner: Appl. Phys. Lett. 99, 032505 (2011)

[3] C. Tusche, P. Goslawski, D. Kutnyakhov, M. Ellguth, K. Medjanik, H. J. Elmers, S. Chernov, R. Wallauer, D. Engel, A. Jankowiak, G. Schönhense: Appl. Phys. Lett., in press (2016)

4:00pm **MI+2D+AC-MoA8 Spin-orbit-Induced Effects in the Electronic Structure of W(110) and Ta(110): Similarities and Differences*, Markus Donath,*** *K. Miyamoto, H. Wortelen, B. Engelkamp,* Muenster University, Germany; *H. Mirhosseini,* Max Planck Institute for Microstructure Physics, Germany; *T. Okuda,* Hiroshima Synchrotron Radiation Center, Japan; *A. Kimura,* Hiroshima University, Japan; *A.B. Schmidt,* Muenster University, Germany; *J. Henk,* Martin Luther University Halle-Wittenberg, Germany

Tungsten and tantalum are direct neighbors in the periodic table and exhibit, at first glance, a very similar electronic structure. Only the bands of tantalum are less occupied due to the lack of one electron. For W(110), an exceptional surface state was discovered [1]: Resembling a topological surface state (TSS), it exhibits a linear dispersion with a helical spin texture in reciprocal space, often called Dirac-cone-like behavior. Interestingly and again reminiscent of the TSS behavior, photoemission calculations predict a spin reversal upon changing the light polarization used for excitation from *p* to *s* [2]. We verified this orbital-symmetry-selective spin texture by spin-resolved photoemission [3]. This result unveils, in which way spin-orbit interaction entangles spin and orbital degrees of freedom. “Spin control” is not restricted to topological insulators but a much more general phenomenon.

A surface state, similar to the Dirac-cone-like state on W(110), may be expected for Ta(110), yet above the Fermi level. Surprisingly, our spin-resolved inverse-photoemission results do not show this state. Instead, spin-polarized unoccupied surface bands [4] and an occupied d_{z^2}surface state with Rashba-like spin texture [5] were identified, which have no equivalents on W(110). These findings are explained by subtle differences in the energetic positions of the surface states relative to the bulk states for W(110) and Ta(110), which critically depend on the values for the lattice constant and the surface relaxation.

[1] K. Miyamoto *et al.*, Phys. Rev. Lett. **108**, 066808 (2012); Phys. Rev. B **86**, 161411(R) (2012); J. Electron Spectrosc. Relat. Phenom. **201**, 53 (2015).

[2] H. Mirhosseini *et al.*, New J. Phys. **15**, 033019 (2013).

[3] K. Miyamoto *et al.*, Phys. Rev. B **93**, 161403(R) (2016).

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[5] H. Wortelen *et al.*, Phys. Rev. B **92**, 161408(R) (2015).

4:20pm **MI+2D+AC-MoA9 Formation of a 2D Interface by Low Energy Proton Implantation in ZnO Microwires*, Israel Lorite*,** *Y. Kumar,* Universität Leipzig, Germany; *B. Straube, S. Perez,* Universidad Nacional de Tucumán, Argentina; *C. Rodriguez,* Universidad Nacional de La Plata, Argentina; *P. Esquinazi,* Universität Leipzig, Germany

Recently we showed the possibility of obtaining room temperature magnetic order by implanting protons (H+) at low energies (300 V) into Li-doped ZnO microwires [1]. The low energy implantation is enough to produce Zn vacancies (V_{Zn}) within 10 nm from the surface, without creating too much disorder in the ZnO lattice. The formation of a stable density of defects in the 10 nm depth region is possible since Li doping reduces the energy of stabilization of V_{Zn}. Thus, the concentration of V_{Zn} will be approximately the one of the Li doping. Along with the observation of magnetic order at room temperature, the ZnO microwires present an anomalous temperature dependence of the negative magnetoresistance. Such a behavior can be related to the formation of an interface at the boundary between the magnetic and non-magnetic structure produced by the implantation. In this contribution we show the observation of a photo-galvanic effect related to the Rashba effect. This effect is due to the formation of a 2D electron gas at the interface of the magnetic/non-magnetic structure. In addition, an increase of this effect is observed by the application of a small external magnetic field, related to the existence of a 10 nm magnetic region produced during the proton irradiation.

[1] I.Lorite, et al; Advances in methods to obtain and characterize room temperature magnetic, Appl. Phys. Lett. 106, 082406 (2015)

4:40pm **MI+2D+AC-MoA10 Density Functional Studies of Magnetic and Spintronic Materials, *Ruqian Wu,*** University of California Irvine **INVITED**

Magnetism, one of the oldest branches of physics, is having its renaissance in recent years due to the interest in developing various nanomagnets, molecular magnets and magnetic nanojunctions for the development of innovative devices. Magnetization of surfaces and nanostructures is sensitive to the change of environment and hence the availability of ultrahigh vacuum is crucial for the exploration of various magnetic systems. Equally important is the rapid advance of density functional theory (DFT) approaches, which now can reliably predict large amount physical properties of real materials in either their ground states or excited states. In this talk, I will discuss several our recent theoretical progresses in spin-related physics, including 1) the search for giant magnetic anisotropy energy in nanostructures; 2) the design to imprint large spin orbit coupling into graphene and other two-dimensional materials for the realization of quantum spin Hall effect and quantum anomalous Hall effect; 3) the photo-spin-voltaic effect; and 4) the generation of spin-polarized two-dimensional electron gas at oxide interfaces. Most of our DFT studies are performed in close collaboration with experimental groups so some experimental results will also be discussed.

Work at UCI was supported by DOE-BES (Grant No. DE-FG02-05ER46237) and NERSC.

2D Materials Focus Topic
Room 103B - Session 2D+MI-TuM

Novel 2D Materials

Moderators: Daniel Gunlycke, Naval Research Laboratory, Yuanbo Zhang, Fudan University, China

8:00am **2D+MI-TuM1 Computational Design of 2D Materials and Layered Heterostructures for Opto-electronics**, ***Kristian Thygesen***, Technical University of Denmark **INVITED**

The class of 2D materials is rapidly expanding and now includes semiconductors, insulators, metals, and superconductors. Many of these novel materials exhibit unique properties that are easily tuneable due to their atomically thin nature making them potential candidates for applications in a large range of technological areas. In this talk I will give a general introduction to the electronic structure of 2D materials including the characteristic features of screening and collective excitations. Concrete illustrations will be given from the Computational 2D Materials Repository (1+2) which contains high-accuracy first-principles calculations for a large number of 2D materials. The 2D materials form the basis of a much larger class of materials consisting of vertically stacked 2D layers held together by weak van der Waals forces. I will describe challenges and opportunities for the first-principles modelling of van der Waals heterostructures including our multi-scale Quantum Classical Heterostructure (QEH) model (3) that enables accurate modelling of plasmons, excitons and band structures of general incommensurable heterostructures containing hundreds of layers. Examples of computational designed heterostructures will be given.

(1) Computational Materials Repository, https://cmr.fysik.dtu.dk/

(2) Computational 2D Materials Database: Electronic structure of transition metal dichalcogenides and oxides, F. A. Rasmussen and K. S. Thygesen, J. Phys. Chem. C 119, 13169 (2015)

(3) The Dielectric Genome of van der Waals Heterostructures, K. Andersen, S. Latini, and K. S. Thygesen, Nano Letters 15, 4616 (2015)

8:40am **2D+MI-TuM3 Mo_2Ga_2C: Structural Determination of a New Nanolaminated Carbide and its 2D Modification by Selective Etching**, ***Chung-Chuan Lai***, *R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund,* Linköping University, Sweden; *O. Rivin, E.N. Caspi,* Nuclear Research Center-Negev, Israel; *O. Ozeri,* Nuclear Research Center-Soreq, Israel; *L. Hultman, P. Eklund,* Linköping University, Sweden; *M.W. Barsoum,* Drexel University; *J. Rosen,* Linköping University, Sweden

Studies of molybdenum carbides are motivated by, for example, the electric and the catalysis properties, including the recently predicted high Seebeck coefficient of 2D Mo_2C [1]. It has been reported that 2D transition metal carbides (also known as MXenes) can be made by selective etching of corresponding nanolaminated ternary carbides [2], e.g., $M_{n+1}AC_n$ phases where M is typically from group 4 – 6, A is from group 13 – 14, and n is 1 – 4 [3]. However, no suitable precursor has been available to make 2D Mo_2C until most recently, through the discovery of Mo_2Ga_2C [4]. Here, we determined the structure of Mo_2Ga_2C phase from X-ray and neutron diffraction, scanning transmission electron microscopy and X-ray photoelectron spectroscopy, and further validated the structure by ab initio calculations [5]. The structure of Mo_2Ga_2C can be described as Mo_2C layers interleaved by two Ga layers, standing head-to-head along the *c*-axis of the hexagonal lattice. The Mo_2Ga_2C phase is closely related to another known nanolaminated carbide, Mo_2GaC, in its crystal structures, evident from chemical bonding analysis. However, selective etching of Ga using hydrofluoric acid (HF) is easily attained for the new Mo_2Ga_2C phase, while being more challenging for Mo_2GaC. A reduction in Ga signal with subsequent exfoliation of Mo_2C layers upon etching is here presented for Mo_2Ga_2C, making Mo_2Ga_2C the first precursor for MXene synthesis based on A = Ga, and for MXene synthesis of 2D Mo_2C [6].

References:

[1] M. Khazaei, M. Arai, T. Sasaki, M. Estili, and Y. Sakka, Phys. *Chem. Chem. Phys.* 16 (2014) 7841-7849.

[2] M. Naguib, G. W. Bentzel, J. Shah, J. Halim, E. N. Caspi, J. Lu, L. Hultman, and M. W. Barsoum, *Mater. Res. Lett.* 2 (2014) 233-240.

[3] P. Eklund, M. Beckers, U. Jansson, H. Högberg, and L. Hultman, *Thin Solid Films* 518 (2010) 1851-1878.

[4] C. Hu, C.-C. Lai, Q. Tao, J. Lu, J. Halim, L. Sun, J. Zhang, J. Yang, B. Anasori, J. Wang, Y. Sakka, L. Hultman, P. Eklund, J. Rosen, and M. W. Barsoum, *Chem. Commun.* 51 (2015) 6560.

[5] C.-C. Lai, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund, O. Rivin, E. N. Caspi, O. Ozeri, L. Hultman, P. Eklund, M. W. Barsoum, and J. Rosen, *Acta Mater.* 99 (2015) 157-164.

[6] R. Meshkian, L.-Å. Näslund, J. Halim, J. Lu, M. W. Barsoum, and J. Rosen, *Scripta Mater.* 108 (2015) 147-150.

9:00am **2D+MI-TuM4 Synthesis of Borophenes: Anisotropic, Two-Dimensional Boron Polymorphs**, ***Andrew Mannix***[*, †], *B. Kiraly,* Northwestern University/Argonne National Lab.; *J.D. Wood, M.C. Hersam,* Northwestern University; *N.P. Guisinger,* Argonne National Laboratory

As the lightest metalloid element, bulk boron exhibits great physical and chemical complexity. In contrast, atomic clusters of boron form simple planar and cage-like structures that resemble those of carbon. Theoretical studies suggest that nanostructured boron allotropes (e.g., nanotubes and sheets) should exhibit structures similar to atomic boron clusters. To date, however, boron nanostructures have been scarcely explored experimentally, partly due to difficulties in synthesis and the need for atomically pristine experimental conditions. Recently, we have reported the synthesis of two-dimensional boron sheets (i.e., borophenes) on a silver surface under ultra-high vacuum conditions [*Science* **350,** 1513–1516 (2015)]. Atomic-scale scanning tunneling microscopy shows the growth of two distinct phases, both of which exhibit anisotropic, chain-like structures. We confirm that these sheets are planar, chemically distinct, and atomically thin through extensive ex situ characterization supported by first principles calculations. Furthermore, in situ scanning tunneling spectroscopy of the borophene sheets shows metallic characteristics consistent with theoretical predictions, in contrast to semiconducting bulk boron.

9:20am **2D+MI-TuM5 Atomic and Electronic Structures of Graphitic Carbon Nitride (g-C3N4) Monolayers on HOPG**, ***Sangwoo Park***, *HM. Kang,* Sungkyunkwan University, Republic of Korea; *J.H. Yang, J.H. Choy,* Ewha Womans University, Republic of Korea; *YJ. Song,* Sungkyunkwan University, Republic of Korea

In this work, we report atomic and electronic studies of graphitic carbon nitride (g-C3N4) monolayers on a highly-ordered pyrolytic graphite (HOPG) by using atomic force microscope (AFM), kelvin probe force microscope (KPFM) and low temperature scanning tunneling microscope (LT-STM). The g-C3N4 is the most stable allotrope of carbon-nitrides and a very promising candidate for metal-free coordination chemistry and heterogeneous catalyst. Also it is applicable photocatalytic hydrogen production and fuel cell. After successful spin-coating of the g-C3N4 monolayers on HOPG, we found the inter-molecular interactions between the flakes or the atomic registries of adsorption on the substrate. This coating mechanism and atomic/electronic properties of g-C3N4 on HOPG will be discussed in detail.

9:40am **2D+MI-TuM6 Periodic Array of Graphene Quantum Dots Embedded in a Carbon-Boron-Nitrogen Alloy**, ***Jakob Jørgensen***, Aarhus University, Denmark; *L. Camilli, A. Stoot,* Technical University of Denmark; *A. Cassidy, R. Balog,* Aarhus University, Denmark; *J. Sadowski,* Brookhaven National Laboratory; *P. Bøggild,* Technical University of Denmark; *L. Hornekær,* Aarhus University, Denmark

Two-dimensional (2D) materials have received enormous attention in the field of materials science and condensed matter physics in the last decade, with the ultimate goal being developing a new technology based on these materials [1]. A huge variety of promising 2D materials have been identified and the ability to combine these into complex structures is essential. For this reason the synthesis of 2D hetero-structures – i.e., structures resulting from the combination of two or more 2D materials – have been subject to an intense research effort over the last few years [2]. Here we report the first observation of spontaneous formation and self-assembly of graphene quantum dot superlattices embedded in a two-dimensional boron-carbon-nitrogen alloy.

By exposing a hot Ir(111) surface to carbon and boron-nitrogen precursor molecules it is found, using scanning tunnelling microscopy (STM), that the otherwise bulk-immiscible graphene and hexagonal boron nitride (hBN) materials can form a stress induced BCN alloy. Furthermore, pure-phase dislocations are found to co-exist with the alloy resulting in the bright triangular pattern of carbon enriched nanoribbons with a width of approximately 1 nm. Above a critical carbon concentration, an array of quantum dots (QD) of highly regular size and periodicity appears. Based on

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[*] **Morton S. Traum Award Finalist**

[†] **National Student Award Finalist**

STM in combination with synchrotron x-ray photoemission spectroscopy (XPS) these QDs are determined consist of pure phase carbon, i.e. they are graphene QDs. These findings are consistent with well-established theories on elastic relaxations in ultrathin strained systems [3]. Thus our findings show a pathway to grow a highly periodic array of graphene quantum dots imbedded in a semiconducting BCN alloy.

In addition, using low energy electron microscopy (LEEM), the growth of the alloy structure is followed *in-situ* and diffraction experiments confirm the presence of the ordered quantum dot pattern even on a macroscopic level.

[1] A.C. Ferrari et al. Nanoscale 7, (2015) 4598

[2] H. Lim et al., Chemistry of Materials 26 (2014) 4891

[3] V. Ozolins et al. Phys. Rev. Lett. 88 (2002) 096101

11:00am **2D+MI-TuM10 Electric Field Control of 2D Materials with Electron Correlation***, **Yoshi Iwasa**,* University of Tokyo, Japan **INVITED**

Scaling down materials to an atomic-layer level produces rich physical and chemical properties as exemplified in various two-dimensional (2D) crystals extending from graphene, transition metal dichalcogenidesto black phosphorous. These include Dirac physics, quantum Hall physics, and valleytronic functions, which are caused by the dramatic modification of electronic band structures, simply by thinning. In the case of transition metal dichalcogenides (TMDs), the band gap becomes direct in monolayers, and the broken inversion symmetry and the strong spin-orbit interaction causes peculiar valley-dependent spin polarization in zero-magnetic field [1], as well as peculiar opto-valleytronics [2, 3].

In reduced dimensions, on the other hand, the electron correlation effects and their consequence, electronic phase transitions, are also significantly changed from bulk systems, and thus result in new properties and functions. Here we address unique physical properties of correlated 2D electron system 1T-TaS_2, which was achieved simply by thinning. The ordering kinetics of the charge density wave transition was revealed to become extremely slow with reduction of thickness [4], resulting in an emergence of metastable states [5]. Furthermore, we realized the unprecedented memristive switching to multi-step non-volatile states by applying in-plane electric field.

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[2] Y. J. Zhang et al., *Nano Lett.* 12, 1136 (2012), *ibid.* 13, 3023 (2013).

[3] Y. J. Zhang et al., *Science* 344, 725 (2014).

[4] M. Yoshida et al., *Sci. Rep*. 4, 7302 (2014).

[5] M. Yoshida et al., *Sci. Adv.* 1, e1500606 (2015).

11:40am **2D+MI-TuM12 Graphene-based Hybrid Materials by Designer Interfaces for High-Performance Hybrid Supercapacitors***, **Sanju Gupta**,* Western Kentucky University

Intense research in renewable energy is stimulated by global demand of electric energy. E lectrochemical energy storage and conversion systems namely, supercapacitors and batteries,represent the most efficient and environmentally benign technologies. Moreover, controlled nanoscaled architectures and surface chemistry of electrochemical electrode materials is enabling emergent next-generation devices approaching theoretical limit of energy and power densities and deliver electrical energy rapidly and efficiently. This talk will present our recent activities to advance design, development and deployment of composition, morphology and microstructure controlled graphene-base hybrid multilayer architectures with carbon nanotubes, conducting polymers, transition metal oxides and mesoproprous silicon wrapped with grapheme sheets as engineered electrochemical electrodes for supercapacitor cathodes and battery anodes. Experimental studies showed significant enhancement towards integrating graphene with other nanomaterials in terms of gravimetric specific capacitance, interfacial capacitance, charging-discharging rate and cyclability. We also present fundamental physical-chemical interfacial processes that govern the underlying mechanisms (surface ion adsorption versus redox reactions) in these electrodes revealed using scanning electrochemical microscopy. The findings are discussed from viewpoint of reinforcing the role played by heterogeneous 'hybrid' electrode surfaces composed of nanoscale graphene sheets (conducting) and other nanomaterials (semiconducting) via higher/lower probe current distribution maps. It allows us to determine ion transfer kinetics and diffusion constant, imaging electrochemical reactions and topography in a microscale at electrode/electrolyte interface.

12:00pm **2D+MI-TuM13 Realization of TaS_2 in the Single-Layer Limit***, **Charlotte Sanders**, M. Dendzik,* Aarhus University, Denmark*; A.S. Ngankeu,* Aarhus University*; A. Eich,* Radboud University, Netherlands*; A. Bruix, J.A. Miwa, B. Hammer,* Aarhus University, Denmark*; A.A. Khajetoorians,* Radboud University, Netherlands*; P. Hofmann,* Aarhus University, Denmark

The electronic properties of bulk TaS_2 have long been a topic of significant interest, due to the fact that the material exhibits unusual charge density wave phases alongside Mott physics and superconductivity. However, little has been known about single-layer (SL) TaS_2. How the electronic properties of this material may change in the SL limit is of great interest, raising questions about the effects of quantum confinement and substrate interactions on exotic electronic states already seen in the bulk. Work on related materials that have been successfully fabricated as SLs points to complex consequences for the CDW and superconducting states. [1] In order to address this topic, one needs to be able to controllably fabricate high-quality, uniform samples with low defect densities for probing *in situ*. We have now succeeded in epitaxially growing high-quality SL TaS_2. We have characterized the SL with angle-resolved photoemission spectroscopy (ARPES), low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S), and low-energy electron diffraction (LEED). Using the Au(111) substrate as a starting point, we find that the TaS_2 SL on Au(111) assumes a well-defined orientation with respect to the substrate, and a moiré superstructure; simultaneously, and counterintuitively, it adopts a "carpet flow" growth mode over substrate steps, suggesting weak interaction with the substrate. Comparing our measurements to calculations from density functional theory (DFT), we have determined that the SL assumes the trigonal prismatic ("1H") phase. While the bulk parent material is characterized by a CDW transition temperature T_{CDW} = 75K [2], we do not observe either CDWs or superconductivity at temperatures down to 4.7K on Au(111) using STM/STS. We do, however, observe slight doping of the TaS_2 epilayer. While the absence of superconductivity at this temperature is not surprising, considering that the superconducting transition temperature T_C in the bulk is only 600mK [3], the absence of CDWs is of interest. This is particularly so in light of recent research on the closely related system SL-$NbSe_2$ on bilayer graphene: despite having a lower bulk CDW onset at T_{CDW} = 33K, $NbSe_2$ in the SL exhibits complete transition to the CDW state by T_{CDW} = 5K. [1]

[1] M. M. Ugeda *et al.*, *Nat. Phys.***12**, 92 (2016). http://dx.doi.org/10.1038/nphys3527

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Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderator: Tae-Hwan Kim, Pohang University of Science and Technology

8:00am **SP+AS+MI+NS+SS-TuM1 *In Situ* Probing of Oxygen Vacancy Diffusion Across Multilayer Oxide Heterostructures***, J. Zhu,* University of Massachusetts - Amherst*; J.-W. Lee, H. Lee,* University of Wisconsin - Madison*; R. DeSouza,* RWTH Aachen University, Germany*; C.-B. Eom,* University of Wisconsin - Madison*; **Stephen Nonnenmann**,* University of Massachusetts - Amherst

Complex oxide heterostructures display an extraordinary array of exotic collective and correlated physical phenomena that result from exploiting the strong interplay between structural and electronic degrees of freedom. Oxygen vacancies often facilitate or govern the interfacial phenomenon observed at or across well-defined discrete interfaces, ranging from domain wall pinning within ferroic systems to electron donors in conducting systems. Realization of multifunctionality within oxide heterostructures therefore necessitates a direct, proper understanding of the interrelationship exhibited by concomitant, defect-mediated transport mechanisms with adequate spatial resolution. Here we utilize a modified, *in situ* scanning probe technique to measure the surface potential across a multi-layered yttria-stabilized zirconia / strontium titanate (YSZ/STO) heterostructured film at 500 °C. Subsequent application of a classic semiconductor dopant formalism to the work function profile derived from the surface potential enables mapping of the oxygen vacancy distribution within STO with a resolution < 100 nm. The results presented herein demonstrate the promise of *in situ* scanning surface potential microscopy

(SSPM) to investigate complex oxide interfacial systems multilayers that exhibit vacancy-dominated properties, under extreme environmental perturbation, on a highly localized scale.

8:20am **SP+AS+MI+NS+SS-TuM2 Study of Surface Chemistry on Various Noble Metal Surfaces by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy***, **Naihao Chiang,*** Northwestern University*; D. Chulhai,* Pennsylvania State University*; G. Goubert, L. Madison, X. Chen, E. Pozzi, M.C. Hersam, T. Seideman,* Northwestern University*; N. Jiang,* University of Illinois at Chicago*; L. Jensen,* Pennsylvania State University*; G. Schatz, R.P. Van Duyne,* Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of nanoscale vibrational spectroscopy. Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning tunneling microscopy (STM) to resolve atomic scale surface features with the single molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). The goal is to understand and manipulate chemistry on the nanometer length scale using the properties of the collective electronic excitations in noble metal nanostructures, known as localized surface plasmon resonance (LSPR).

Two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this nanoscale vibrational spectroscopy will be presented. First, our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved in the UHV-TERS of the N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (Ag(111), Ag(100), Cu(111), and Au(111)) which probed by a Ag tip will be discussed. This study demonstrates that TERS is a substrate general technique. Additionally, the LSPR of the Ag tip-Ag sample junction is as broad as a Ag nanoparticle dimer system. Therefore, TERS on Ag tip-Ag sample systems is also excitation general.

Second, new insights into the nature of a conformational dynamics involved at room temperature will be described. We have interrogated the conformational change of *meso*-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on a Cu(111) surface between two stable conformations. At room temperature, the barrier between the porphyrin ring buckling up/down conformations of the H_2TBPP-Cu(111) system is easily overcome, and our group has achieved unprecedented sub-nm resolution by simultaneous UHV-TERS and STM analysis. This topic illuminates that TERS can unambiguously distinguish the conformational differences between neighboring molecules with single molecule resolution. Furthermore, the sub-nm resolution led to the direct observation of single molecule transitions between states from one scan to the next.

8:40am **SP+AS+MI+NS+SS-TuM3 Exploring Surface-assisted Reactions Toward Functional Carbon Nanostructures***, **Xiaohui Qiu,*** National Center for Nanoscience and Technology, China **INVITED**

Understanding the dehydrogenation and dehalogenation reactions of molecular entities on surface is essential for the controlled synthesis of carbon-based nanostructures. Delicately designed precursor molecules exploit the potential of selective activation of functional groups and templating effect of substrates and promise the fabrication of nanoscale building blocks with desired geometries. Here we employed a combination of scanning tunneling microscopy, atomic force microscopy, and theoretical calculation to elucidate self-assembling of halogen-containing molecules on metal surfaces. Metallo-supramolecular assemblies are constructed via coordination bonding between metal atoms and halogen ligands. The spontaneously formed molecular scaffolds are further explored to program the structure and chemical composition of hybrid carbon architecture. We reveal the hierarchic reaction pathway of a few aromatic derivatives in an effort toward realizing carbon-based nanostructures with controllable electronic, optical and magnetic properties.

9:20am **SP+AS+MI+NS+SS-TuM5 Landscapes in Conversion of Quasi-Free-Standing Polymer Chains to Graphene Nanoribbons***, **Chuanxu Ma,*** Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; L. Liang,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; K. Hong, B.G. Sumpter, A.-P. Li,* Oak Ridge National Laboratory

Although the cyclodehydrogenation is well known as a key step in the bottom-up preparation of graphene nanoribbons (GNRs), the mechanism is still unclear. To understand and control the cyclodehydrogenation can help to create novel intraribbon heterojunctions of GNR-based structures. Here, we demonstrate the conversion of quasi-free-standing polymer chains to GNRs induced by thermal annealing and manipulations with a scanning tunneling microscope tip. Combined with the density functional theory calculations, a domino-like fashion and the hole-involved cyclodehydrogenation are proposed for the thermal annealing and tip-induced conversion of polymer chains to GNRs, respectively. Our results provide the first direct experimental evidence that the catalytic effect of the Au substrate is critical to the thermal-induced cyclodehydrogenation in forming bottom-up GNRs. Strongly localized density of states in the short GNR segment of the polymer–GNR herterojunction is observed. The significant confinement of the charge carriers is attributed to the big bandgap difference between the two segments of the heterojunction. Our findings might pave new ways to form GNR-based intraribbon heterojunctions by controlling the cyclodehydrogenation during bottom-up preparation, and shed light to the potential applications of the polymer–GNR herterojunctions.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and partially supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

11:00am **SP+AS+MI+NS+SS-TuM10 Imaging Single Molecule Chemistry***, **Wilson Ho,*** University of California Irvine **INVITED**

Single molecule chemistry can now be probed at unprecedented spatial resolution with a low temperature scanning tunneling microscope (STM) in ultrahigh vacuum. Advances in this field have provided new measurements and insights into the structure and function of molecules through real space imaging and high resolution vibrational spectroscopy. The combination of the STM with optical spectroscopy and femtosecond lasers has added a new dimension of time to space and enabled the probing of single molecule dynamics in light-matter interaction with better than 0.1 nm resolution. The ability to visualize single molecule chemistry has reinvigorated the study of molecules and their transformations on solid surfaces. Much of the scientific advancement and understanding in surface chemistry have derived from the well-defined conditions that have long been championed by surface science in providing unambiguous results that are appealing to the theoretical and experimental communities. Imaging single molecule chemistry has a broader impact on general chemistry due principally to direct visualization of molecules and their inner machinery at the limit of space and time.

11:40am **SP+AS+MI+NS+SS-TuM12 Atomic Force Microscopy: A Tool for Chemical Analysis of Surfaces and Molecules on Atomic Scale***, **Pavel Jelinek,*** Institute of Physics of the AS CR, Czech Republic **INVITED**

Atomic resolution and manipulation is routinely achieved by both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) nowadays. Despite of large activities in development of the scanning probe technique, still some challenges remain, namely the chemical analysis on atomic and molecular level.

First, we will present a novel method extending further the chemical analysis [1,2] by means of AFM. Namely we will discuss a new methodology to measure Pauling's electronegativity of individual atoms on surfaces using AFM. Electronegativity has been an important concept in chemistry, originally defined by Pauling as "*the power of an atom in a molecule to attract electrons to itself*". However, its experimental determination on individual surface atoms was not possible so far.

Second, we will discuss the origin of sub molecular AFM/STM resolution acquired with functionalized tips. We will show that the electrostatic force can substantially affect the sub molecular contrast. We will show, that the electrostatic potential on a single molecule can be mapped out with sub molecular resolution.

[1] Y. Sugimoto et al Nature 446, 64 (2007)

[2] M. Setvin et al ACS Nano 6, 6969 (2012)

[3] P. Hapala et al, Phys. Rev. Lett. 113, 226101 (2014)

[4] J. vad der Lit et al, Phys. Rev. Lett. 096102 (2016)

[5] P. Hapala et al. Nature comm. (accepted 2016)

Thin Film
Room 102B - Session TF+SA+MI-TuM

Thin Films for Synchrotron and Magnetism Applications

Moderators: Joshua Ballard, Zyvex Labs, Divine Kumah, North Carolina State University

8:00am **TF+SA+MI-TuM1 Achieving High-Temperature Ferromagnetic Topological Insulator by Proximity Coupling***, **Valeria Lauter**,* Oak Ridge National Laboratory

Topological insulators (TIs) are insulating materials that poses conducting surface states protected by time-reversal symmetry, wherein electron spins are locked to their momentum. This exclusive property offers novel prospects for creating next-generation electronic and spintronic devices, including TI-based quantum computation. Introducing ferromagnetic order into a TI system without compromising its distinctive quantum coherent properties could lead to a realization of a number of innovative physical phenomena. In particular, achieving robust long-range magnetic order at the TI surface at specific locations without introducing spin scattering centers could open up new potentials for devices. Here, we demonstrate topologically enhanced interface magnetism by coupling a ferromagnetic insulator (FMI) to a TI (Bi_2Se_3); this interfacial ferromagnetism persists up to room temperature, even though the FMI (EuS) is known to order ferromagnetically only at low temperatures (< 17 K). The induced magnetism at the interface resulting from the large spin-orbit interaction and spin-momentum locking property of the TI surface is found to greatly enhance the magnetic ordering (Curie) temperature of the TI/FMI bilayer system. Due to the short range nature of the ferromagnetic exchange interaction, the time-reversal symmetry is broken only near the surface of a TI, while leaving its bulk states unaffected [1]. The topological magneto-electric response originating in such an engineered TI could allow for an efficient manipulation of the magnetization dynamics by an electric field, providing an energy efficient topological control mechanism for future spin-based technologies. Work supported by U.S. DOE, Office of Science, BES.

[1]F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi^5, D. Heiman, P. Jarillo-Herrero, J. Moodera, "Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling", *Nature 2016*

8:20am **TF+SA+MI-TuM2 Soft X-ray Induced Spin Crossover Transition at Room Temperature***, **Paulo Costa**, X. Zhang, S. Beniwal,* University of Nebraska-Lincoln*; A.T. N'Diaye,* Lawrence Berkeley National Laboratory*; J-F. Létard,* Université de Bordeaux*; P.A. Dowben, A. Enders,* University of Nebraska-Lincoln

The spin crossover Fe(II) complex (SCO) of the type $[Fe(H_2B(pz)_2)_2(bipy)]$ has been previously shown to exhibit spin state transitions between its low spin (LS) and high spin (HS) states as a response to external stimulus such as electric fields, temperature changes, and light. It is well established that this SCO complex exhibits a crossover from its LS state to the HS state if the temperature is increased above approximately 150 K. It is demonstrated here that this spin crossover can be suppressed by mixing the SCO with strongly dipolar *p*-benzoquinonemonoimine zwitterion (PZI) molecules, so that unlike before, the LS state still prevails even at room temperature (RT). With the metastable LS state now locked in at RT, a spin state transition to the HS state can now be triggered optically by soft X-rays over a relatively short time of several minutes. This process is fully reversible, as cooling the mixture to 78 K has been shown to de-excite it back to its original LS state. Experiments were performed using X-ray absorption spectroscopy measurements (XAS) with synchrotron radiation tuned to the Fe L_3 absorption edge as well as accompanying magnetic moment measurements taken by a superconducting quantum interference device (SQUID). The effects of temperature, photon flux, and the stoichiometric ratio between SCO and PZI in the mixture were systematically studied, and the results will be presented here. This study provides a demonstration that the spin crossover transition temperature can be tailored to create a material that exists in a meta-stable LS state at RT wherein spin states can then be switched optically.

8:40am **TF+SA+MI-TuM3 Probing Thermochromic Phase Transitions in ALD VO_2 using Synchrotron Radiation***, **Alexander Kozen**,* U.S. Naval Research Laboratory*; H. Joress,* Cornell University*; V.D. Wheeler, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 is a thermochromic material, one class of "smart materials" that are receiving considerable interest due to a sharp semiconductor to metal (S-M) phase transition that occurs at a specific, material dependent temperature (T_c = 68˚C for VO_2). The S-M transition occurs as a result of a phase transition between a semiconducting monoclinic phase below T_c and a metallic tetragonal phase above T_c. While VO_2 has been widely utilized as a microbolometer material for IR detectors, current deposition processes used to fabricate thin film VO_2 (PLD, MBE, sputtering) are not adequate to realize complex device architectures. Use of ALD to deposit VO_2 thin films allows for uniform, low temperature coating of large area 3D substrates that could open the door to new applications.

Temperature dependent *in-situ* grazing incidence synchrotron XRD was utilized to probe lattice strain and structural reordering in both as-deposited (amorphous) and annealed (polycrystalline) ALD VO_2 thin films during the S-M transition. GIXRD allows us to selectively sample the bulk or the film-substrate interface of thin ALD films with excellent depth resolution, while the high flux provided by the synchrotron (10^{12} photons/s) enables fast data collection. Initial results show that as-deposited ALD VO_2 films are polycrystalline at the VO_2-sapphire interface, while the bulk of the as-deposited VO_2 is amorphous. Annealing VO_2 on sapphire in an oxygen-rich environment forms a fiber-textured polycrystalline VO_2 film with a more pronounced S-M transition. We will discuss how substrate selection, ALD growth and processing conditions, and film thickness influence VO_2 morphology and/or structure and relate these materials properties to device data.

The authors wish to acknowledge Cornell University's CHESS synchrotron facilities for GIXRD work and The Office of Naval Research for support. Dr. Kozen acknowledges support by the ASEE-NRL postdoctoral fellows program.

9:00am **TF+SA+MI-TuM4 Standing-wave Synchrotron Photoemission Studies of Electronic Structure in $SrTiO_3$-$LaCrO_3$ Superlattices***, **Ryan Comes**,* Auburn University*; S.C. Lin,* University of California, Davis*; C.T. Kuo,* Lawrence Berkeley National Laboratory (LBNL)*; L. Plucinski,* FZ Juelich*; S. Spurgeon,* Pacific Northwest National Laboratory*; D. Kepaptsoglou, Q. Ramasse,* SuperSTEM*; J.E. Rault,* Synchrotron SOLEIL*; S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; C. Fadley,* Lawrence Berkeley National Laboratory (LBNL)*; P.V. Sushko, S.A. Chambers,* Pacific Northwest National Laboratory

The polar discontinuity at the interface between $SrTiO_3$ (STO) and $LaCrO_3$ (LCO) has been shown to produce a varying band alignment between the two materials with a built-in potential gradient.[1] We have recently shown that this built-in potential gradient can be harnessed to induce a polarization in STO-LCO superlattices through interface engineering.[2] This work demonstrated that by controlling interfacial termination between layers we can induce a built-in polarization in STO, with Ti cations displaced off-center in surrounding oxygen octahedra. To further study this system, we have synthesized a series of STO-LCO superlattices with varying interfacial and surface terminations for synchrotron standing-wave x-ray photoemission measurements.[3] These measurements make use of Bragg diffraction from the superlattice to induce an x-ray standing wave that can be scanned across a single period of the superlattice. Through careful material design, we have achieved the strongest standing-wave effects to date, enabling angle-resolved photoemission measurements of electronic dispersion in both the STO and LCO layers of the material. Density functional theory models of the electronic structure of the superlattices are used to corroborate our experimental results with the expected behavior. Monochromated, aberration-corrected scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) measurements also enable further studies into changes in electronic behavior at interfaces.

[1] S.A. Chambers, L. Qiao, T.C. Droubay, T.C. Kaspar, B.W. Arey, and P.V. Sushko, Phys. Rev. Lett. **107**, 206802 (2011).

[2] R.B. Comes, S.R. Spurgeon, S.M. Heald, D.M. Kepaptsoglou, L. Jones, P.V. Ong, M.E. Bowden, Q.M. Ramasse, P.V. Sushko, and S.A. Chambers, Adv. Mater. Interfaces, (2016). DOI: 10.1002/admi.201500779

[3] A.X. Gray, C. Papp, B. Balke, S.-H. Yang, M. Huijben, E. Rotenberg, A. Bostwick, S. Ueda, Y. Yamashita, K. Kobayashi, E.M. Gullikson, J.B. Kortright, F.M.F. de Groot, G. Rijnders, D.H.A. Blank, R. Ramesh, and C.S. Fadley, Phys. Rev. B **82**, 205116 (2010).

9:20am **TF+SA+MI-TuM5 *In Situ* Synchrotron X-ray Studies of Complex Oxide Thin Film Growth***, **Dillon Fong**,* Argonne National Laboratory**INVITED**

Functional materials based on complex oxides in thin film form offer new and exciting strategies for meeting many of our outstanding energy challenges through systematic control of layer sequencing, strain, etc. However, the synthesis of such oxide films can be a major challenge even when utilizing reactive molecular-beam epitaxy (MBE), a powerful deposition technique that allows the construction of materials atomic plane by atomic plane. To understand the fundamental physics of oxide growth by reactive MBE, we present *in situ* surface x-ray diffraction results on the growth of $SrTiO_3$ and SrO-$SrTiO_3$ thin films on (001)-oriented $SrTiO_3$ substrates. For homoepitaxy, we compare sequential deposition (alternating Sr and Ti monolayer doses) with that of co-deposition of Sr and Ti, both in a background of oxygen pressure, and observe drastically different growth pathways due to the presence of a TiO_2 double layer. For heteroepitaxial growth of Ruddlesden-Popper SrO-$SrTiO_3$ films, we find that layers rearrange dynamically, resulting in layer sequences distinct from the shutter sequence. In general, the starting surface structure and composition, in combination with local thermodynamic considerations, strongly influence our ability to atomically construct new complex oxides.

Work at Argonne, including the Advanced Photon, is supported by the U.S. Department of Energy.

11:00am **TF+SA+MI-TuM10 Probing CVD Growth Mechanisms of SiC with *In Operando* Synchrotron-based X-ray Diagnostics***, **Philip DePond**, A.A. Martin, J.H. Yoo, M. Bagge-Hansen, J. Lee, S. Elhadj, M. Matthews, T. van Buuren,* Lawrence Livermore National Laboratory

Laser chemical vapor deposition (LCVD) of ultra-hard coatings, such as SiC, offers sub-mm spatial control over composition and phase, while addressing multiple growth processes under the same conditions for comparison. Normally, optimization requires extensive and costly "cook and look" experiments. Using an in situ approach instead, we develop fundamental insights into the growth mechanisms to unravel the complex roles of deposition parameters. We have conducted a series of in operando synchrotron-based X-ray absorption experiments that interrogate the LCVD growth region during growth. SiC was grown in a compact, portable CVD system from tetramethylsilane using a CW 532nm YAG to achieve laser-based pyrolytic precursor decomposition. We will present the results of Si K-edge (1.8keV) X-ray absorption near-edge structure (XANES) measurements conducted concurrently for the film during LCVD growth with an emphasis on the effects of variation of temperature, flow, substrates, and pressure conditions.

11:20am **TF+SA+MI-TuM11 Unusual Effects in Organic Thin Film Growth as Revealed by the Use of *In Situ* Real Time Synchrotron X-ray Techniques***, R.K. Nahm, H.J. Bullen, T. Suh, **James Engstrom**,* Cornell University

The effects of molecular scale events on the growth of crystalline thin films has been long been an active area of research as the resulting thin film properties depend sensitively on the microstructure. The growth of high quality, smooth thin films in the vast majority of these systems is favored at low rates of growth and high substrate temperatures. Here we report on the growth of thin films of tetracene, an organic semiconductor that possesses one less aromatic ring as compared to the much more studied pentacene. We examine the growth on SiO_2 using *in situ* real time X-ray synchrotron radiation and *ex situ* atomic force microscopy (AFM). First, using *in situ* X-ray reflectivity, we observe a transition from 3D island growth to 2D layer-by-layer growth as the growth rate of tetracene is *increased* on SiO_2 at room temperature, T_s ~ 30 °C. This unusual phenomenon, 2D growth favored at higher rates, has not been observed in previous work with pentacene, despite the similarities between these two molecules. Results from AFM indicate that tetracene may tend to quickly traverse "upwards" on thin film features such as the edges of islands, making these thin films susceptible to reorganization during and/or after growth. Thus, at sufficiently high rates of growth the rate of admolecule attachment at the tetracene island/SiO_2 substrate edges effectively outcompetes the rate of upward step-edge transport, and 2D growth results. We find additional evidence for this mechanism by examining the effect of substrate temperature. In particular we find that the transition to 2D growth occurs at a lower rate of growth at a substrate temperature of T_s ~ 0 °C, consistent with suppression in the rate of upward transport at lower values of T_s. Finally, we have also examined the evolution of the thin film crystal structure in real time using *in situ* grazing incidence X-ray diffraction. Many thin film organic semiconductors are known to crystallize in different structures, and tetracene is no exception. At room temperature we find that first a thin film phase grows, then, after a delay, a bulk phase begins to grow, while the growth of the thin film phase saturates. We also find that the film thickness at which X-ray scattering from the bulk phase becomes apparent is found to vary with deposition rate. These phenomena are also dependent on substrate temperature. For example, for the range of thin films thicknesses examined, we found no evidence for growth of the bulk phase at the lower substrate temperature, T_s ~ 0 °C. These results highlight the potential complexity of crystalline thin film growth in what appears to be a very simple system, tetracene on SiO_2.

11:40am **TF+SA+MI-TuM12 Understanding the Effect of Nitrogen Plasma on Plasma Assisted Atomic Layer Epitaxy of InN Monitored by Real Time GISAXS***, **Neeraj Nepal**, V. Anderson, S.D. Johnson, D.J. Meyer, B.P. Downey, A.C. Kozen,* US Naval Research Laboratory*; Z.R. Robinson,* SUNY College at Brockport*; D.R. Boris, S.C. Hernández, S.G. Walton,* US Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* US Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, Plasma assisted atomic layer epitaxy (PA-ALE) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [1]. Since growth using this technique is far from thermodynamic equilibrium, understanding how nitrogen plasma affects nucleation and growth kinetics is essential for development.

Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the Cornell High Energy Synchrotron Source were used to study the effect of variation in nitrogen plasma pulse conditions on PA-ALE of InN at 250 °C. Current results show the evolution of GISAXS characteristics such as the correlated peak (CP) length scale in the Yoneda Wing (YW) directly relates to the surface roughness, impurities, and electrical properties of the material. During the initial cycles of InN growth, the diffuse specular reflection broadens and CPs start to evolve along the YW with different correlated length scales. For the nitrogen plasma pulse time (t_p) of 15 seconds, the CPs have two different correlated length scales of 33.36 and 8.38 nm. With increasing t_p to ≥ 20s (the empirically optimal pulse length), a YW with only one CP evolves and the longest correlated length scale of 11.22 nm is for T_p = 25s. The correlated length scale of this single CP decreases to 10.75 nm for t_p = 30s. Additionally at t_p = 25s, the growth rate is largest (0.035nm/cycle – consistent with previously reported self-limited growth [1]) with root mean square surface roughness and carbon impurity at or below AFM and XPS sensitivity limits, respectively. The nature of GISAXS CP correlated length scale directly relates to the material quality. GISAXS also shows that the N_2/Ar flow ratio significantly affect the nucleation and growth of InN. Based on various *ex situ* characterization methods, the quality of the PA-ALE grown films is similar or better than the material grown by conventional growth methods, for example, molecular beam epitaxy at higher temperature (>400 °C).

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

12:00pm **TF+SA+MI-TuM13 Spintronics Based on the Chiral Induced Spin Selectivity (CISS) Effect***, **Yossi Paltiel**,* The Hebrew University, Israel*; R. Naaman,* The Weizmann Institute of Science, Israel

The high level of energy dissipation associated with the present semiconductor-based integrated-circuit technology limits the operating frequency of the devices. Therefore there is interest in new concepts that may solve this problem. One such concept that attracts considerable attention nowadays combines spins with electronics (spintronics). In principle, the application of spintronics should result in reducing power consumption of electronic devices and efficiency should be closer to the thermodynamic limit.

Two major issues complicate the use of spintronics; material problems and the inefficiency in producing spin-polarized current. Spintronics devices usually require the use of complicated structures of magnetic material layers and the need for permanent magnetic layers puts constrains on the miniaturization of these devices. In addition, high currents are required to produce highly polarized spin current which results in induced heating.

We present a new concept in which spin current is produced by using the spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS). The CISS effect allows realization of simple local and power efficient spintronics devices. Studying the CISS effect, we found that chiral molecules, especially helical ones, can serve as very efficient spin filters at room temperature, with no need for a permanent magnetic layer. Recently, by utilizing this effect we demonstrated a simple magnetless spin based magnetic memory. Moreover, we show that when chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, without the application of current or external magnetic field.

The CISS-based spintronics technology has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements.

Electronic Materials and Photonics
Room 102A - Session EM+MI+MN-TuA

New Materials and Devices for Emerging Memory Technologies

Moderators: Andy Antonelli, Nanometrics, Sean King, Intel Corporation

2:20pm **EM+MI+MN-TuA1 Emerging Processing Challenges for Advanced Memory Technologies*, Bart Van Schravendijk,*** Lam Research **INVITED**

The rapid scaling of semiconductor memory is radically changing the memory industry. Flash memory has switched from lateral scaling to vertical scaling while other new memory technologies are aggressively vying for new opportunities in the memory market. Their targets range from niche applications to replacing any one of the three big memory technologies : SRAM, DRAM or Flash.

For vertical NAND flash largely conventional materials are used in its fabrication at present. However, the unabated drive for higher density is driving agressive vertical scaling, which poses new problems for stack design and processing. This drives improvements and maybe even changes in the materials.

Newer memory technologies, such as STT-RAM, ReRAM and PCRAM, bring with them different challenges to the processing arena. These new memories come with materials whose full scope of interactions with semiconductor processing are still poorly understood. These materials provide new challenges for the processing tools when scaling these memory technologies to dimensions that are economically attractive.

In this talk we will review some of the more challenging problems for advanced memories and some potential solutions.

4:20pm **EM+MI+MN-TuA7 Resistance Change Memory and its Perspective toward 3D Integration*, Yoshio Nishi,*** *B. Magyari-Kope,* Stanford University **INVITED**

As we face a situation in the next decade where further scaling of traditional CMOS based devices would not be cost effective from manufacturing issues such as superfine lithography/etching and device physics barriers. Thus non-traditional new materials and devices research have been instigated, which resulted in new principle based non-volatile memories. A short list of such newly emerging memory consists of resistance change memory ReRAM, phase change memory, PCRAM, spin based MRAM/STT RAM, depending upon desirable characteristics to implement.

Though resistance change phenomena in metal oxides have been recognized since early days, it is in the past few years when aggressive research for application as nonvolatile memory has taken off. Basic switching mechanism is formation and annihilation of conductive vacancy chain in the metal oxide sandwiched by two electrodes. Both atomistic and macroscopic models have been investigated. Role of electrode materials and switching oxide interfaces during memory operation have attracted strong attention, as it would imply not only memory characteristics but also device endurance and scalability. Further, development of this type of resistance change memory is toward vertical integration with multi-memory layers which could replace ultra-high density flash memory.

This talk will review progresses made for resistance change memories, covering fundamental physical mechanism, implementation of memory cells including scaling limit studies, and 3 dimensional integration of such devices.

5:00pm **EM+MI+MN-TuA9 Atomic Disorder As an Intrinsic Source of Variability in Filamentary Rram Devices – Ab Initio Investigations*, Sergiu Clima,*** IMEC, Belgium*; L. Goux, B. Govoreanu, M. Jurczak, G. Pourtois, A. Fantini,* IMEC **INVITED**

Resistive Random Access Memory concept is probably close to production in a new generation of non-volatile memories, but there are still some reliability issues to be fully understood. Resistive RAM devices can be scaled down below 10 nm [1], meaning that the discrete nature of atomic structure of the materials may already be observed in device operation properties. Material-wise, the transition metal oxides attracted the scientific interest due to their CMOS compatibility and their ability to operate on intrinsic defects (oxygen vacancies). For RRAM working with extrinsic defects like metallic inclusions called Conductive Bridge RAM (CBRAM), a larger spectrum of solid electrolytes can be used. Using Density Functional Theory simulations of RRAM materials, we evaluated the kinetics of the defects migration of the conducting species to show that atomic disorder of amorphous state can exhibit large variability in terms of defect stability and kinetic barriers.[2] These have a great impact on filament resistance evolution in time, which can be observed during forming step of the resistive filament, but not only. In the short time immediately after filament formation, the atomic configuration can relax to a metastable state, therefore changing the resistivity of the filament. In a long time retention of the filament resistance we can still measure resistance change. All these observations can be explained with the computed statistical distributions of the defect stability and kinetic barriers in the RRAM materials.

[1] B. Govoreanu et al., Ext.Abstr. SSDM Conf.,Nagoya, Japan, 1005 (2011)

[2] S. Clima et al., Electron Device Lett , 769 (2015)

5:40pm **EM+MI+MN-TuA11 Reduction of Radiation Damage to HfOx-Based Resistive Random Access Memory using a Thin ALD HfOx Film*, Kai-wen Hsu,*** *T. Chang,* University of Wisconsin-Madison*; L. Zhao, Z. Wang,* Stanford University*; R. Agasie, T. Betthauser, J. Nickles, Z. Ma, J. Chang,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

Resistive Random Access Memory (RRAM) [1], is considered to be a very promising memory technology for the next generation of computer memory, It has undergone intense research in both industry and academia in the last ten years. As RRAM technology matures and electronic devices using RRAM are likely to be built soon, a RRAM cell which is resistant to radiation will become an important topic in industry to prevent the malfunction of these devices. In this work, neutron and proton-induced effects on two types of RRAM cells are investigated. Type 1 HfOx RRAM cell is different from the Type 2 RRAM cell in two aspects, (1) the thickness of the HfOx film (Type 1 is thicker than Type 2) and (2) the fabrication process for depositing the HfOx within the RRAM cell. (Type 1 uses spin-on technology and Type 2 uses ALD technology)

Many Type 1 RRAM cells can be formed under neutron irradiation and end up in the LRS. On the other hand, unformed neutron-irradiated Type 1 RRAM cells only require a lower voltage to form. In addition, the resistance of the HRS increased on the Type 1 RRAM cell. The shift in values of the set voltage can be seen on the I-V characteristic of the neutron-irradiated Type 1 RRAM cell. A similar increase in the resistance of HRS is also observed in proton-irradiated Type 1 RRAM cells. The shift in values of the set voltage can be seen on the I-V characteristic of the proton-irradiated Type 1 RRAM cell.

There are no obvious changes to Type 2 RRAM cells after either neutron or proton irradiation. It is very likely that both the changes in thickness and fabrication are very important since these two modifications can cut down on the number of defects which affect the switching mechanism of the RRAM cell.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359, by the National Science Foundation under Grant No. CBET-1066231.

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6:00pm **EM+MI+MN-TuA12 Potential Dependent Resistance of Doped TiO_2 Film Fabricated by Solgel Process: Perspective for Resistive Memory*,*** *R.R. Pandey,* ***Jyotirmay Sharma****, C. Kant, K. Saini,* CSIR-National Physical Laboratory, India

Fastest growth has been registered in the field of electronics. It is the only field which has transformed every corner of the society and every age of the civic society, from youngest child to elderly persons. The growth was outcome of the miniaturization of the basic active device in electronics. The journey started from few millimeter size around 1965 and now reached to few tense of nanometers. At the beginning of this journey, the new smaller size devices not only performed better to its predecessor but were cost effective also. As we reached below ~300nm, the production was no longer economic. At around few tense of nanometer size the device performance also affected and at this junction the need was felt to explore alternate working principles for the device to maintain growth of the field and continue to benefit the society. New devices such as SET, RTD, resistive memory, magnetic memory, spintronic etc. were studied. Working device size of less than ten nanometers is expected from this new class of devices. Here we report fabrication of titanium oxide based resistive memory device by solgel technique. Thin films of high quality doped and undoped titanium oxide were applied on cleaned FTO or Pt-FTO glass substrates by solgel dip process. We doped titanium oxide with aliovalent cations by suitable choice of doped cation salt. Sequence of undoped and doped layers of titanium oxide was altered in different devices. Final structure was completed by thermal evaporation of metal electrode for electrical connection.

A resistance change of 2-3 orders of magnitude was observed up to the maximum applied potential of ±3.0 volts. The resistance change has complex dependence on nature of the dopant, dopant concentration, electrode material and sequence of the doped and undoped layers. We tried to explore the resistance change behavior and remembrance of resistance on the basis of basic studies viz; XRD, XPS, SEM, etc. cyclic voltameteric studies were also carried out to understand the contact between electrode and TiO_2 layer.

Magnetic Interfaces and Nanostructures
Room 102B - Session MI-TuA

Magnetic Phenomena in Organic Systems

Moderators: Gary Mankey, University of Alabama, Mikel Holcomb, West Virginia University

2:20pm **MI-TuA1 Promises and Challenges of Organic Spintronics***, **Christoph Boehme**,* University of Utah **INVITED**

While the term “Spintronics" was originally introduced as label for technologies that represent information through spin states rather than charge states, it is nowadays oftentimes used solely in the context of spin-polarization, spin-injection, and spin-transport effects, for all of which spin-orbit interaction plays an important role. Many organic semiconductors display only weak spin-orbit coupling and charge transport via hopping through localized electronic states which are exposed to hydrogen induced strong local and random hyperfine fields. These materials therefore appear at first glance to be entirely unsuitable for spintronics. However, they also exhibit pronounced spin-related effects not seen in materials with strong spin-orbit coupling[1-3] which can be used for alternative, different approaches to spintronics based, for instance, on spin-permutation symmetry states of charge carrier pairs which, in contrast to spin-polarization states, are not directly dependent on temperature and magnetic field strength[4]. Weak spin-orbit coupling can also promote long spin-coherence times and thus, allow for electrically readable spin memory of electron-[5] or nuclear-spins[6]. The successful implementation of organic spintronics will require a fundamental understanding of the microscopic electronic processes that are to be utilized for such technologies. In this presentation, some of the progress as well as challenges[7] for the exploration of these spin-dependent processes will be reviewed. Measurements of spin-coupling types and strengths of charge carriers will be discussed[2] as well as examples for unusual physical behaviors of these materials, such as an electrically detectable spin-Dicke effect caused by charge carrier spin collectivity[8].or the presence of an inverse spin-Hall effect[9].

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3:00pm **MI-TuA3 Spin-Polarized STM Observation of Hybridization at the Interface between Different 8-hydroxyquinolates and the Cr(001) Surface***, **Daniel Dougherty**, J. Wang, A. Deloach,* North Carolina State University

The field of organic spintronics has focused dominant attention on organic emitters such as tris-(8-hydroxyquinolate) aluminum (Alq3). This particular molecule has been reported to show large magnetoresistive effects including a 300% effect nanoscale tunnel barriers [1] that is tied to molecular orbital mixing at the magnetic electrode interface. Here we report on a direct study of this orbital mixing using spin polarized scanning tunneling microscopy and local spectroscopy measurements. We focus on the well-known Alq3 molecule adsorbed on a Cr(001) surface and report evidence for spin polarized interface states near the Fermi level. When the adsorbate is replaced with the paramagnetic variant Crq3, the interface remains polarized but the magnetic states are significantly farther from the Fermi level. These results will be discussed in the broad context of molecular orbital control if interfacial polarization in tunneling devices.

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3:20pm **MI-TuA4 Charge Transport in Thin Films of a Molecular Spin-Crossover Compound***, **Greg Szulczewski**, E. Ellingsworth,* The Univeristy of Alabama

Spin-crossover in molecular complexes containing divalent Fe ions (six d-electrons) is a phenomena associated with a reversible change in the magnetic state (diamagnetic to paramagnetic and vice versa) as a function of temperature, pressure or optical excitation. In this study we demonstrate the growth of bis(1,10-phenanthroline)dithiocyanato iron (II) or $Fe(phen)_2(NCS)_2$ thin films, a well-known spin crossover material. A detailed SQUID magnetometry and spectroscopic analysis using Raman, IR, UV-Vis, and XPS, indicates that the as-deposited films are largely a diamagnetic compound that can be best described as $Fe(phen)_3(NSC)_2$. Upon annealing the films under high vacuum, the diamagnetic compound can be converted into a paramagnetic compound, which is consistent with the formation of $Fe(phen)_2(NCS)_2$. The annealed films are polycrystalline as revealed by x-ray diffraction and exhibit a spin-crossover transition near 180 K. The DC electrical conductivity of these films was measured from 100-300 K. A small (but repeatable) change in the electrical conductivity was observed. An unequivocal interpretation of this observation is difficult because of competing factors. For example, the unit cell expands across the spin-crossover transition, the geometric structure of the molecule changes, and the frontier molecular orbital energies also change. The relative contribution of these factors will be discussed in detail.

4:20pm **MI-TuA7 Single Organic Radicals on Metal Surfaces: A Model System for Spin-1/2 Kondo Physics***, **Peter Wahl**,* University of St Andrews, UK **INVITED**

The Kondo effect is one of the most intensely investigated many-particle problems in solid-state physics. While it was discovered originally in dilute magnetic alloys, the same physics emerges in seemingly unrelated contexts, such as the zero-bias anomalies observed in quantum dots or the dynamical behavior close to a Mott transition. The simplicity of the underlying hamiltonian – a single spin coupled by an exchange interaction J to a bath of conduction electrons – contrasts the complex physics emerging from it as well as the challenges met in theoretical calculations. Apart from being a drosophila for electronic correlation effects, the single impurity Kondo effect is an elementary building block for model lattice systems relevant for strongly correlated electron materials such as high temperature superconductors.

Studies of transition metal atoms on metal surfaces by low temperature scanning tunneling microscopy and spectroscopy have renewed interest in the Kondo problem by providing access to local properties; however a quantitative comparison with theoretical predictions remained challenging.

Here I present a study of an organic radical with a single spin ½ on Au(111) [1]. Tunneling spectra reveal a zero bias anomaly as would be expected for a Kondo system, yet comparison of the temperature and magnetic field dependence of the zero bias anomaly with predictions of the Kondo effect in the strong coupling regime are in apparent disagreement. Detailed comparison with theoretical models reveals quantitative agreement with the original Kondo model in the weak coupling regime.

1. Y. Zhang et al., Nat. Commun. 4, 2110 (2013).

5:00pm **MI-TuA9 Tunneling in III-N Heterostructures for Low Power Electronics***, **Patrick Fay**, W. Li, L. Cao, K. Pourang,* University of Notre Dame*; S. Islam,* Cornell University*; C. Lund,* University of California at Santa Barbara*; H. Ilatikhameneh, R. Rahman, T. Amin,* Purdue University*; D. Jena,* Cornell University*; S. Keller,* University of California at Santa Barbara*; G. Klimeck,* Purdue University **INVITED**

Continuing increases in circuit complexity and capability for logic and computation applications as well as for emerging low-power systems require fundamental advances in device technology and scaling. Due to power constraints, devices capable of achieving switching slopes (SS) steeper than 60 mV/decade are essential if conventional computational architectures are to continue scaling. Similarly, low power systems such as mobile devices and distributed sensing applications also benefit from devices capable of delivering high performance in low-voltage operation. Tunneling field effect transistors (TFETs) are one promising alternative to achieve these objectives. A great deal of work has been devoted to realizing TFETs in Si, Ge, and narrow-gap III-V materials, but the use of III-N heterostructures and the exploitation of polarization engineering in particular offers unique opportunities. From physics-based simulations, GaN/InGaN/GaN heterostructure TFETs offer the potential for achieving switching slopes approaching 20 mV/decade with on-current densities exceeding 100 µA/µm in nanowire configurations. In this talk, the operational principles of III-N-based TFETs will be described, and device design and performance considerations will be discussed. In addition, experimental efforts demonstrating heterostructure backward diodes in III-N heterostructures as well as progress towards nanostructure-based III-N FETs and TFETs will be reviewed.

5:40pm **MI-TuA11 A Spins-Inside Quantum Processor***, T. Fujita,* Delft University of Technology, The Netherlands*; L.M.K. Vandersypen,* Delft University of Technology, The Netherlands*; **T. Hensgens,*** Delft University of Technology, The Netherlands **INVITED**

A quantum computer holds the promise of solving some problems that are beyond the reach of the most powerful supercomputers. Due to theoretical and experimental breakthroughs in the last few years, we are now at a point where the feeling grows that a large-scale quantum computer can actually be built. Increasingly, this requires bridging the disciplines, from physics to engineering, materials science and computer science. In this talk, I will present the start-of-the-art in quantum computing and outline the challenges ahead, with a focus on electron spin qubits in semiconductors.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+AS+BI+MI-TuA

Synchrotron and XFEL Advances for Biological Systems (2:20-3:40 pm)/Synchrotron Radiation at the Frontiers of Device Technology (4:20-6:20 pm)

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm **SA+AS+BI+MI-TuA1 Crystal Growth Mechanisms of Biominerals Revealed by Polarization-dependent Imaging Contrast (PIC) Mapping***, **Pupa Gilbert,*** University of Wisconsin - Madison **INVITED**

X-ray linear dichroism was first shown in natural biominerals by Metzler et al. [1]. Based on this effect, we developed Polarization-dependent Imaging Contrast (PIC)-mapping, which displayed non-quantitative crystal orientation at the nanoscale as gray levels in ratios of images acquired at different linear polarizations [2]. A later development provided grayscale, semi-quantitative PIC-maps by acquiring stacks of 19 images as the linear polarization was rotated in 5° intervals from 0° to 90° [3-7]. The latest development uses the same stacks of images to fully, quantitatively display crystal orientations in colors, including hue and brightness, which represent in-plane and off-plane crystallographic c-axis orientation angles [8-10].

Using PIC-mapping in these 3 subsequent modes, we discovered several biomineral formation mechanisms in nacre [11,7], sea urchin teeth [12-14], ascidian spicules [10], corals, eggshells, modern and fossil sea shell ultrastructure [15].

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15. PUPA Gilbert et al., in preparation, (2016).

3:00pm **SA+AS+BI+MI-TuA3 New Dimensions in Synchrotron IR Spectroscopy***, **Michael Martin,*** Lawrence Berkeley National Laboratory **INVITED**

Synchrotron infrared beamlines use the diffraction-limited beam properties to enable a variety of cutting edge science - how can we go further?

By combining scattering-scanning near-field optical microscopy (s-SNOM) with mid-infrared synchrotron radiation, synchrotron infrared nano-spectroscopy (SINS) enables molecular and phonon vibrational spectroscopic imaging, with rapid spectral acquisition, spanning the full mid-infrared (500-5000 cm^{-1}) region with nanoscale spatial resolution. This highly powerful combination provides access to a qualitatively new form of nano-chemometric analysis with the investigation of nanoscale, mesoscale, and surface phenomena that were previously impossible to study with IR techniques. We have installed a SINS end-station at Beamline 5.4 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, making the s-SNOM technique widely available to non-experts, such that it can be broadly applied to biological, surface chemistry, materials, or environmental science problems. We demonstrate the performance of synchrotron infrared nano-spectroscopy (SINS) on semiconductor, biomineral and protein nanostructures, providing vibrational chemical imaging with sub-zeptomole sensitivity.

The spatial field localization at the tip apex can also result in a large near-field momentum sufficient to optically excite phonon polaritons (PhPs), which are quasiparticles resulting from the strong coupling of photons with optical phonons. Here, we use SINS to image the PhP spectral response in thin hexagonal boron nitride (hBN) crystals. The large spectral bandwidth of the synchrotron source enables the simultaneous measurement of both the out-of-plane (780 cm-1) and in-plane (1370 cm-1) hBN phonon modes. In contrast to the strong and dispersive in-plane mode, the out-of-plane mode PhP response is weak. Measurements of the PhP wavelength reveal a proportional dependence on sample thickness for thin hBN flakes [2].

This talk will present the novel SINS instrumentation and a variety of scientific examples. Future directions, both technical and scientific, will be discussed.

*With Hans A Bechtel, Markus B. Raschke, Z. Shi, F. Wang, R.W. Johns, D.J. Miliron, E.A. Muller, R.L. Olmon

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4:20pm **SA+AS+BI+MI-TuA7 Sample Delivery Methods for X-ray Free Electron Lasers***, **Uwe Weierstall,*** Arizona State University **INVITED**

Serial crystallography at XFEL's has shown great promise in recent years for solving crystal structures of proteins, which produce only micron sized crystals. Liquid jets have been very successful for delivery of microcrystals to the X-ray beam. The commonly used liquid injection system will be discussed. High sample consumption has motivated the development of an injector, which uses high viscosity media like Lipidic Cubic Phase (LCP). G-protein coupled receptors are an important group of membrane proteins which are often crystallized in LCP. The injector generations a microscopic stream of LCP with adjustable speed for sample delivery to the X-ray beam[1]. Some important GPCR structures could be solved with this device at the LCLS[2]. In addition, new media with similar viscosity to LCP have been developed which enable delivery of soluble or membrane proteins into the X-ray beam with low sample consumption[3]. The high viscosity injection method has also been shown to facilitate serial diffraction experiments with microcrystals at synchrotron microfocus beamlines. This talk will highlight these developments and discuss the possibilities.

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5:00pm **SA+AS+BI+MI-TuA9 Synchrotron-based Spectroscopy Investigation for Electronic Phase Transition at Highly-Charged Electric-Double-Layer Interfaces***, **Hongtao Yuan**,* SLAC National Accelerator Laboratory **INVITED**

Electric-field control of charge carrier density has attracted much attention since it is remarkably simple for modulating physical properties of condensed matters and for exploring new functionalities with a transistor configuration. Owing to the limitation of dielectric breakdown in most solid dielectrics, the maximum carrier density accumulated in conventional field-effect transistors (FETs) is quite low (<< 10^{13} cm^{-2}) and thus seriously limits the tunability of electronic states of solids, for example, not sufficient enough to induce insulator-to-superconductor transition. While the electric-double-layer transistor (EDLT) with ionic liquids (ILs, or ionic gel) as gate dielectrics have been proved to be able to effectively attain a high carrier density up to levels of around 10^{15} cm^{-2} and to realize a large local electric field up to 50 MV/cm at liquid/solid interfaces. For example, electric-double-layer transistors have been demonstrated for an electric-field control of emergent interfacial quantum phenomena and the electronics phase transitions in condense matters, such as insulator-superconductivity and paramagnetism-ferromagnetism transitions. However, the mechanistic/spectropic understanding of the local electronic structures at such highly charged IL/oxide EDL interfaces and also further modification under gate-bias remain elucidated and challenging.

In this talk, we conducted synchrotron radiation based X-ray absorption spectroscopy (XAS) and Auger electron spectroscopy (AES) combined with in situ electrical measurements to directly characterize the evolution of the electronic structure at a representative IL/$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin film interface. We find a significant valence reduction localized to the topmost LSMO layer after interface formation, and that the gate-bias predominantly modulates this surface reduced Mn species effectively converting these top layers into an insulator. We expect the synchrotron radiation based photon science probing techniques will directly shed light on the understanding of interfacial electronic phase control under the electric field.

(This work was done in collaboration with Bongju Kim, Jun-Sik Lee, Yasuyuki Hikita adn Harold Y. Hwang. This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515.)

5:40pm **SA+AS+BI+MI-TuA11 Correlation of the Conductivity/Magnetic Properties and the Electronic, Crystalline and Compositional Structure of Strongly Correlated Complex-oxide Interfaces and Thin Films***, **Juan Rubio-Zuazo**,* SpLine CRG Beamline at the ESRF The European Synchrotron, France*; G.R. Castro,* SpLIne CRG Beamline at the ESRF The European Synchrotron, France

We study the structural and electronic properties of strongly correlated complex-oxide thin films and interfaces using Hard X-ray Photoelectron Spectroscopy (HAXPES), Electron Energy Loss Spectroscopy (EELS) and Grazing Incidence X-ray diffraction (GIXRD) at the BM25-SpLine beamline (Branch B) at the ESRF. Strongly correlated complex-oxide exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. Usually, the interface drives the magnetic and electric response of the heterostructure. The chemical, mechanical, electric and magnetic properties of such devices are often intimately related to the structure, composition profile and morphology of their surface and internal interfaces. Several mechanisms are present at these interfaces as crystallographic space group modification, presence of oxygen vacancies, dislocations due to lattice strain, deviation from stoichiometry, phase segregation. In general all these phenomena modify the intrinsic properties of the materials used at the heterostructure, offering a unique way to produce artificial correlated materials with tailored properties. The growth of these materials in thin film form opens possibilities for magneto-electronic and spintronic devices applications. The results shown here are focused on the study of the influence of buried interfaces on the electric and magnetic properties of CMR and multiferroics systems. We will show the experimental methodologies at SpLine based on synchrotron radiation techniques to gain quantitative knowledge on the crystallographic and electronic properties at the interface between different complex oxides. There are few techniques able to provide an accurate insight of what is happening at these buried interfaces which in general are buried by several tens of nanometres in the material. The simultaneous combination of hard and soft X-ray photoelectron spectroscopy, electron energy loss spectroscopy with surface/interface X-ray diffraction gives unique capabilities in this respect. Here we will present a series of example to show how the interface properties can change the magnetic-conductivity properties.

6:00pm **SA+AS+BI+MI-TuA12 Interface Passivation of III-V/High-k Materials by High Energy X-ray Photoelectron Spectroscopy: A Quantitative Evaluation***, **Thierry Conard**, V. Spampinato, L. Nyns, S. Sioncke,* IMEC, Belgium*; J.M. Ablett,* Synchrotron SOLEIL- Ligne GALAXIES, France*; W. Vandervorst,* IMEC, KU Leuven, Belgium

The use of InGaAs as a high carrier mobility CMOS-channel material requires a proper electrical passivation of its interface with the gate dielectric. One of the passivation schemes investigated involves the use of Sulphur. In this work, high-k stacks on Sulphur passivated InGaAs substrates involving both Al2O3 and HfO2 are investigated. A major question related to the use of Sulphur relates to the chemical states at the interfaces. XPS is traditionally an important technique for interface analysis but faces several challenges in its application to the above mentioned stacks. First, due to the large number of elements involved, numerous peak interferences are present limiting the choice of useful photoemission peaks. Second, relevant stacks have total thicknesses of the order of 4 nm, which lead to very low intensities , certainly for minority elements like Sulfur. In this work, we discuss the impact of the H_2S passivation temperature as well as the use of TMA pre-pulses in the growth of Al_2O_3. We show that the Sulphur bind to In but that no As-S or Ga-S bonds could be detected. The use of a TMA pre-pulse after surface passivation leads to a reduction of the amount of Sulphur present at the interface and likely increases the amount of In-O bonds. Higher temperature H_2S passivation leads to a reduction of the amount of Sulphur at the surface.

We also observe that the presence/absence of S at the interface, as well as the presence of the Al_2O_3 buffer, which has a major impact on the relative peak position in the spectra between the substrate and the overlayer. This will be compared with the electrical characteristics of the stacks.

Finally, we show that using the Sessa software, full quantification of the stack can be obtained under the condition that all instrumental parameters are correctly taken into account.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuA

Probing Spin-Dependent Phenomena

Moderators: Phillip First, Georgia Institute of Technology, Shivani Rajput, Oak Ridge National Laboratory

2:20pm **SP+AS+MI+NS+SS-TuA1 Spin Sensing and Magnetic Design at the Single Atom Level***, **Alexander Khajetoorians**,* Radboud University, The Netherlands **INVITED**

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) [1] and inelastic STS (ISTS) [2-3], can address single spins at the atomic scale with unprecedented precession. While SP-STS reads out the projection of the impurity magnetization, ISTS detects the excitations of this magnetization as a function of an external magnetic field. They are thus the analogs of magnetometry and spin resonance measurements pushed to the single atom limit. We have recently demonstrated that it is possible to reliably combine single atom magnetometry with an atom-by-atom bottom-up fabrication to realize complex atomic-scale magnets with tailored properties [4-6] on metallic surfaces [1,7]. I will discuss the current state of the art of this growing field as it pertains to single spin information storage, and how the functionality of coupled magnetic adatoms can be tailored on surfaces by substrate mediated interactions. I will discuss our recent efforts toward realizing tailored chiral magnets [8] and present an outlook on future perspectives toward probing quantum matter at ultra-low temperatures.

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3:00pm **SP+AS+MI+NS+SS-TuA3 Electron Spin Resonance of Single Atom and Engineered Spin Structures***, **Taeyoung Choi**, W. Paul, C.P. Lutz, A.J. Heinrich,* IBM Almaden Research Center **INVITED**

The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Inelastic spin excitation and spin-polarized tunneling have been employed to study spin physics of individual atoms and engineered structures, demonstrating nanoscale memory bits [1] and logic gates [2]. However, the energy resolution of the STM is mainly limited by a temperature of a system surrounding the atomic spins (>100 µeV).

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [3]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10µeV) while the ESR linewidth is in the range of only a few MHz (~10neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024\pm0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [4].

Coherent quantum control of individual atoms on surfaces combined with atom manipulation may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

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4:40pm **SP+AS+MI+NS+SS-TuA8 Controlling Kondo Effect of Magnetic Molecules on Au(111) by Small Molecule Binding***, **MinHui Chang**, S.J. Kahng,* Korea University, Republic of Korea*; Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H.W. Kim, S.H. Lee,* Korea University, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin interactions of Co-porphyrin on Au(111) can be controlled by adsorption and desorption of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo effect in STS, whereas Co-porphyrin adsorbed small molecules showed modified zero-bias peaks, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in $d_{z}2$ Orbitals. Our study opens up ways to tune molecular spin interactions by means of chemical binding.

5:00pm **SP+AS+MI+NS+SS-TuA9 Spin-polarized Scanning Tunneling Microscopy on Surfaces Prepared by Molecular Beam Epitaxy***, **Arthur Smith**,* Ohio University Nanoscale and Quantum Phenomena Institute **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful *in-situ* technique for obtaining detailed information about spin structures at surfaces down to atomic scale.[1] It has been applied extensively to investigate pristine ferromagnetic and antiferromagnetic (aFM) transition metal surfaces, with many great results in the case of model systems such as nano-sized magnetic islands and single magnetic monolayers.[2] This has led to fascinating discoveries of nanoscale magnetic domains, domain walls, spin spirals, spin skyrmions, and much more.[3,4] Although not simple in practice, SP-STM can in principle also yield unprecedented spin characterization on a broad spectrum of material surfaces, including practical, real world systems. For example, it could be applied to investigate surfaces of intermetallic compounds, superconductors, complex magnetic oxides, and magnetic semiconductors.

We are applying SP-STM to study various magnetic systems grown *in-situ* by molecular beam epitaxy, including transition metal nitrides,[5] magnetic-doped nitride semiconductors, and several bi-metallic magnetic systems. I will present our recent work using STM and SP-STM, beginning with a discussion of manganese nitrides, including our work on aFM θ-phase MnN and ferrimagnetic ε-phase Mn_4N. The θ-phase films are very complex due to the expectation of canted spins within each atomic layer with four unique canting angles, while the ε-phase films contain two types of spins (Mn^I and Mn^{II}) with equally complex spin arrangements.

A second material we are working on is the chromium nitride system in which we investigate its electronic and spin properties in a low-temperature SP-STM system. Spectroscopy results to date suggest a *d*-wave resonance on the surface and a Kondo signature for nanoscale iron islands grown on atomically-smooth CrN surfaces.

I will also present results for Mn δ-doped semiconducting gallium nitride surfaces in which we find atomic layer ferromagnetism within a unique and stable √3 x √3 - R30° MnGaN surface reconstruction. Spectroscopy clearly reveals spin-polarized and spin-split Mn states, as predicted by first principles theory calculations. SP-STM measurements map out ferromagnetic domains at *room temperature*, and the additional presence of magnetic rim states seen at the edges of ferromagnetic islands, as well as magnetic hysteresis, give further interest to this intriguing system.

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5:40pm **SP+AS+MI+NS+SS-TuA11 The Use of Scanning Probe Techniques to Study the Behaviour of Second Phase Particles in Beryllium and Their Role in Localised Corrosion***, **Christopher Mallinson**, J.F. Watts,* University of Surrey, UK

Scanning Kelvin probe force microscopy (SKPFM) has been employed to examine the galvanic activity of a wide range of second phase particles in S-65 beryllium that are believed to have a role in the localised corrosion of the metal. SKPFM and AFM analysis has been combined with additional surface and bulk analysis techniques of scanning electron microscopy, energy dispersive x-ray spectroscopy and Auger electron spectroscopy to provide a detailed overview of the link between the bulk and surface composition of particles and their Volta potential or surface contact potential.

Initial results appear to show that all second phase particles are more noble than the beryllium matrix with the greatest potential difference observed for $AlFeBe_4$ and alumina or carbide like particles. The more negative Volta potential indicates that the particles should act as local cathodes when the metal is exposed to an aqueous environment.

The initial investigation, which is being performed in-air, will be expanded to determine the effect of increasingly higher humidity environments on the behaviour of the particles. It is hoped that this will provide a greater understanding about the onset of pitting corrosion in beryllium.

6:00pm **SP+AS+MI+NS+SS-TuA12 Many-body Interaction induced Spin-split States of Single Vacancy in Graphite**, ***Wonhee Ko**,* Samsung Advanced Institute of Technology, Republic of Korea*; H.W. Kim, Y. Cho,* Samsung Advanced Institute of Technology*; Y. Kuk,* Seoul National University, Korea, Republic of Korea*; S.W. Hwang,* Samsung Advanced Institute of Technology

Although carbon atoms have no magnetic states, it has been known that defects in graphene or graphite can have magnetic states induced by many-body interaction. By utilizing ultra-low-temperature scanning tunneling microscopy, we observed the spin-split states of single vacancy in graphite, which is a hallmark of magnetic states. Evolution of the spin splitting in the magnetic field did not follow the Zeeman effect of single electron states, and can be explained only when we consider electron-electron interaction. Quantitative analysis showed that the strength of the electron-electron interaction is in the range of 1~3 meV. Our observation implies that the simplest defect in graphite like single vacancy can behave as magnetic, which would be an important ingredient for development of carbon-based spintronic devices.

Magnetic Interfaces and Nanostructures
Room Hall D - Session MI-TuP

MIND Poster Session

MI-TuP1 Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Heterostructures for Multiferroic Applications, *C.R. Rementer, Q. Xu, P. Nordeen, G.P. Carman, Y. Wang,* ***Jane P. Chang,*** University of California Los Angeles

Iron-gallium (FeGa) is one of the most promising magnetic materials for use in composite multiferroics due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in MHz range or below.[1] In order to make it suitable for high frequency (GHz) applications, metalloid dopants have been used to soften magnetic materials and enhance their frequency dependent properties, but at the cost of the saturation magnetization as well as magnetoelastic properties.[2] A viable approach to circumvent this trade-off problem is to integrate a magnetic material with complementary properties into magnetic heterostructures. In this work, multilayer laminates were fabricated with FeGa and NiFe, a material with excellent properties in high frequency regimes.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets with compositions $Fe_{85}Ga_{15}$ and $Ni_{81}Fe_{19}$ (at%) into multilayers with layer thicknesses ranging from 3-50 nm, with FeGa being used as the first and last layer in the stack. XPS confirmed the composition and showed there was no intermixing of the layers. Static magnetic properties were evaluated via SQUID magnetometry, and it was found that the incorporation of NiFe layers reduced the coercivity by up to 85%, from 30 Oe to 4 Oe. FMR studies showed a reduction of the linewidth of up to 50%, from 70 Oe to 38 Oe. It is believed that this effect is largely due to the decrease of magnetic anisotropy dispersion in the multilayers.[3] The multilayer films maintained a high magnetostriction of up to 190 ppm, on the same order of magnitude as giant magnetostrictive materials such as thin film Terfenol-D.[4] FeGa/NiFe heterostructures have been shown to be an excellent candidate for strain-coupled microwave multiferroics.

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MI-TuP2 The Microstructure and Isotope Effects on Spin Response in Organic Spintronic Devices, ***Nuradhika Herath****, J. Keum, H. Zhang, K. Hong, J. Jakowski, J. Huang, J. Browning, S. Bennett, C. Rouleau, I. Ivanov, V. Lauter,* Oak Ridge National Laboratory

There is currently a strong drive to realize magnetoelectronic heterostructures with controls of magnetic ordering and electron-spin transport for use in the next generation spintronic devices. One proposed method to gain such controls is the use organic spintronics (OS). The general configuration of OS device consists of two ferromagnetic (FM) electrodes separated by an organic layer to form a sandwich structure. While basic concepts of OS device have been demonstrated, there is very little understanding about the detailed effects of the organic layer and the interface interactions within the multilayers on the physical properties of the system. Amongst the difficulties limiting high performances OS are the subtle structural variations, including i.e., interdiffusion of FM electrode into the soft organic layer during the fabrication. Using the depth sensitive method of polarized neutron reflectometry we have been able to probe the fine details of the structural and magnetic properties of prototype spintronic devices (STO\\LSMO\polymer\Co\Ag). We fabricated heterostructures using two electron conducting polymers (P3HT and PFO) and their deuterated substitutions to study the isotope effect of polymer layer in the spintronic devices. While our main goal is on understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus 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.

Acknowledgements: This work was sponsored by Oak Ridge National Laboratory Directed Research and Development (LDRD 7938) and conducted at the Center for Nanophase Materials Sciences (CNMS) and Spallation Neutron Source (SNS), which are sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

Actinides and Rare Earths Focus Topic
Room 103C - Session AC+MI-WeM

Magnetism, Complexity, and Superconductivity in the Actinides and Rare Earths (8:00-11:00 am)/Actinide and Rare Earth Theory (11:00 am-12:20 pm)

Moderators: Tomasz Durakiewicz, Los Alamos National Laboratory, Ladislav Havela, Charles University, Prague, Czech Republic, Alexander Lichtenstein, University of Hamburg

8:00am **AC+MI-WeM1 Local Magnetic Properties of Uranium Compounds Probed with XMCD*, Fabrice Wilhelm*,** *A. Rogalev,* ESRF, France **INVITED**

In these last years actinides and actinide compounds, mainly Uranium based compounds, have been the subject of increasing interest due to their very different magnetic behaviors, such as Pauli paramagnetism, localized and itinerant magnetism, and heavy fermions. The element specific X-ray Magnetic Circular Dichroism (XMCD) spectroscopy technique has been proven over two decades to be the best suitable technique to probe the orbital and spin magnetism and to isolate those different contributions separately using the magneto-optical sum-rule under given assumption regarding the magnetic dipole contribution. XMCD experiments have been reported for a great number of uranium compounds and have permitted to understand which is the ground state. It has also revealed differences between localized and itinerant systems that are not yet fully understood. This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of uranium based compounds.

8:40am **AC+MI-WeM3 Neutron and X-ray Scattering as a Probe of Complex Order in Actinides*, Helen Walker,*** STFC, UK **INVITED**

Neutron and X-ray scattering are powerful probes of complex ordering in the actinides, giving access to the spatial and temporal fluctuations of structural and electronic degrees of freedom. To demonstrate the vast array of different types of information obtainable using different scattering techniques, I will focus on the question of the elusive hidden order parameter in URu_2Si_2.

Innumerable different theories have been proposed for the nature of the hidden order [1], with a preponderance directed towards multipolar order. With this in mind I will discuss how X-ray Resonant Elastic Scattering has shown that no quadrupolar ordering is present [2], and future opportunities for probing higher order multipoles. I will also discuss the valence state, which is of vital significance for any multipolar model, and how this might be investigated by probing the f-states at the M-edges using Resonant X-ray Emission Spectroscopy.

More recently, there is a growing consensus pointing towards some electronic nematic state, resulting in an orthorhombic distortion [3,4,5]. Inelastic neutron and X-ray scattering experiments, which have searched for a change in the band structure associated with such a distortion, will be discussed.

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9:20am **AC+MI-WeM5 Hydrogen Contributing to 5*f*-localization in UTX Compounds*, Silvie Maskova,*** Charles University in Prague, Czech Republic*; K. Miliyanchuk,* Ivan Franko National University of Lviv, Ukraine*; S. Danis, B. Vondrackova,* Charles University in Prague, Czech Republic*; O. Stelmakhovych,* Ivan Franko National University of Lviv, Ukraine*; L. Havela,* Charles University in Prague, Czech Republic

U-based ternary compounds, which were studied in large isostructural series, allow large variations of the 5*f* localization due to variable 5*f*-5*f* overlap and the 5*f* hybridization with the *d*- and *p*-states. An additional tuning parameter is the H absorption, working primarily as a negative pressure. At 5*f*-band systems it leads to enhancement of magnetic properties in most of cases [1]. However, this tool is restricted to cases in which substantial H absorption can be achieved. In the system of UTX compounds (T = later transition metal, X = p-metal) with the ZrNiAl structure type, a high absorption was registered only for UNiAl, leading to $UNiAlH_{2.3}$, in which the Neel temperature is enhanced from 19 K to 95 K. Recently we discovered a new UTX compound, UNiZn [2], which is itself non-magnetic, as the 5*f*-*p* hybridization is stronger in the case of smaller Zn than for larger Al. This material forms an equivalent hydride, $UNiZnH_{2.3}$, which is antiferromagnetic (below 50 K). This opened a possibility to study systematically the onset of antiferromagnetism in the system UNiZn-UNiAl and variations of properties of related hydrides. We found that the magnetic order in the precursors sets in between 10 and 30 at.% Al. The Sommerfeld coefficient of electronic specific heat γ increases from 94 mJ/mol.K^2 in UNiZn and reaches 360 mJ/mol.K^2 in the critical area and then it decreases for a higher Al concentration to 164 mJ/mol.K^2 in UNiAl, which is known as a mid-weight heavy fermion. [3]. The hydrides exhibit lower γ-values. γ = 100 mJ/mol.K^2 in the UNiZn hydride decreases monotonously to 67 mJ/mol.K^2 in the hydride of UNiAl. The situation implies that reducing the 5*f*-*p* hybridization even more, we may proceed with strengthening of magnetism in the sense of further increasing T_N and decreasing γ. The natural counterpart of UNiAl is UNiGa with the same structure type but larger X-ligand. However, no attempt to synthesize a hydride of UNiGa was successful in the past. In the present work we undertook a study of the hydrides of quasi-ternary system UNiAl-UNiGa [4], and found that the H absorption can be reached even for high Ga concentrations. Physical properties of Ga-substituted hydrides are currently explored.

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9:40am **AC+MI-WeM6 Radiation damage: Experimental Investigation of Aluminum Containing Helium Bubbles at Static High Pressure in a Diamond Anvil Cell*, Itzhak Halevy,*** Physics Department*; B. Glam,* NRC Soreq, Israel*; S. Maskova,* Charles University, Prague, Czech Republic*; D. Moreno,* NRC Soreq, Israel*; S. Eliezer,* NRC Soreq Shalom Eliezer2, Israel

High pressure investigation of the crystallographic structure and bulk modulus of aluminum containing helium bubbles is presented. The targets were obtained by melting pure aluminum with 0.15% wt.^{10}B powder. The solid targets were neutron irradiated in the Soreq nuclear reactor to get homogeneous helium atoms inside the aluminum boron 10 matrix according to the reaction $^{10}B+n \rightarrow {}^7Li+{}^4He$. The irradiated aluminum was heat treated for accumulation of helium atoms into nanometric bubbles by diffusion . The helium bubbles formation in Al–^{10}B metal was observed by TEM.

The crystallographic structure and the bulk modulus of aluminum loaded up to pressure of 39 GPa in a diamond anvil cell (DAC) were studied in different samples: (1) Al-^{10}B, (2) Irradiated Al-^{10}B with helium bubbles (3) The irradiated Al-^{10}B foil with helium bubbles that was used for TEM observation.

The data was analyzed by the X'Pert Plus (Philips) Rietveld analysis software packages. The high-pressure energy dispersive X-ray diffraction studies were taken at the X17-C beam-line of the National Synchrotron Light Source (NSLS) at BNL [1]. The energy dispersive data was collected with a high purity germanium detector at a fixed Bragg angle ($2\Theta \sim= 12^{\circ}$). The high-pressure X-ray powder diffraction measurements were taken at discrete pressure steps in the range of 0– 35 GPa. The data wascollected by the EDS technique, using the white beam of the superconducting wiggler magnet at the X17-C beam-line. Typical data collection time was about 10 min. Inthe lower range of the high-pressure range, angle dispersive measurements were carried out in transmission configuration using the image plate technique. The data was analyzed using acommercial Rietveld analysis software packages [2].

The Pressure as function of V/V_0 was fitted by Vinet equation to yield the B-$_0$ and B_0' of the EOS. B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0 at zero pressure. For our pure Al B_0=68.6GPa while B_0' was kept at 3.6 .

Our early work with SEM and TEM showed He bubals as the sample was radiated.

Quantum Design SQUID equipment was used for magnetic studies of bulk Al-15wt.% B and pure Al. Magnetic measurements were performed in the temperature range 2-300 K and fields up to 7 T.

Results of the susceptibility measurements, *c*(*T*), are summarized . The susceptibility is field independent in the whole temperature range studied. All "samples" have similar weak temperature dependence, with *c*-values somewhat below $1*10^{-10}m^3$/mol.

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11:00am **AC+MI-WeM10 AVS Gaede Langmuir Award Talk: Multiplets and More for Core-Level Spectra***, **Paul Bagus**[*],* University of North Texas **INVITED**

Multiplets are an essential aspect of electronic spectroscopies and they must be taken into account to correctly describe these spectra. In particular this is true for the core-level spectra of open-shell systems including both X-Ray Photoelectron Spectroscopy, XPS, and Near-edge X-Ray Adsorption Fine Structure, NEXAFS. Unfortunately, the significance of multiplets for the interpretation and analysis of XPS and NEXAFS is often neglected, quite possibly because of the complex mathematical formalism that is required obtain formal expressions for the multiplets and their energies. In this talk, the focus will be on using the familiar rules for the quantum mechanical addition of angular momentum and for multiplet energies, as given, for example, by Hund's rules, to provide a qualitative guide to the importance of these splittings. The combination of these qualitative guides with rigorous electronic structure calculations of energies and intensities allows us to understand the origins of the XPS and NEXAFS features in terms of the chemical and physical interactions in a system. This combination also allows us also to understand how ligand field mixings modify atomic descriptions of these core-level spectra. For XPS, we show that the value of multiplet splittings to identify oxidation states depends on the choice of core-level ionized. [1] For NEXAFS, we show that decomposing a spin-orbit split level, or multiplet, into its composition in terms of Russell-Saunders, RS, multiplets gives insight into the origin of the often complex features of the spectra.[2] This is because the selection rules are stricter for the RS multiplets. The role of "shake" excitations from occupied bonding orbitals into un-occupied anti-bonding orbitals will also be considered. Several examples for the spectra of heavy metal oxide systems will be presented to illustrate the value of the methods described.

We acknowledge support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE.

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11:40am **AC+MI-WeM12 Complex Magnetism of Gd Intermetallics: Ab-initio Theory and Experiment.***, **Leon Petit**,* Daresbury Laboratory, UK*; D. Paudyal, Y. Mudryk, K.A. Gschneidner, V.K. Pecharsky,* Ames Laboratory, Iowa State University*; M. Lueders, Z. Szotek,* Daresbury Laboratory, UK*; J.B. Staunton,* Warwick University, United Kingdom of Great Britain and Northern Ireland

Using an ab-initio electronic structure theory which includes disordered local moments and strong f-electron correlations, we have investigated the magnetic ordering and critical temperatures of Gd-intermetallics.[1] The theory correctly finds GdZn and GdCd to be simple ferromagnets and predicts a remarkably large increase of Curie temperature with pressure (+1.5 K $kbar^{-1}$) for GdCd, confirmed by our experimental measurements . In our calculations for GdMg, a transition from ferromagnetic to AF1 is observed with increasing pressure, whilst a canted magnetic state is seen to emerge from either the ferromagnetic or anti-ferromagnetic state with lowering the temperature. Replacing 35% of the Mg atoms with Zn removes this transition, in excellent agreement with long-standing experimental data. We conclude that despite being filled and situated at low binding energies, the non-lanthanide metal d-states strongly influence the electronic structure at the Fermi level as well as the magnetic ordering.

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12:00pm **AC+MI-WeM13 Thermodynamics of the Doped Sm($Co_{1-x}Fe_x$)$_5$ Alloys: *Ab Initio* Study***, **Alexander I. Landa**, A. Söderlind, E.A. Turchi,* Lawrence Livermore National Laboratory

$SmCo_5$ (in the hexagonal $CaCu_5$–type structure) magnets exhibit enormous uniaxial magnetocrystalline anisotropy (K_1 ~ 17.2 MJ/m_3) substantially higher than for the $Nd_2Fe_{14}B$ (Neomax) magnets (K_1 ~ 4.9 MJ/m3), and $SmCo_5$ magnets have almost twice higher Curie temperature (T_c ~ 1020 K) than $Nd_2Fe_{14}B$ magnets (T_c ~ 588 K). However the world market of permanent magnets is currently dominated by Neomax magnets (~ 62 %), which possess the highest energy performance with a record energy product of 470 kJ/m_3 that is twice as high as the energy product of $SmCo_5$ magnets, of 231 kJ/m_3. Although $SmCo_5$ magnets are more suitable for high temperature applications than Neomax, due to their relatively low energy performance $SmCo_5$ magnets occupy only ~ 3% of the world market. From a cost point of view, it would be beneficial to substitute Co atoms with Fe because Fe in the Earth's crust is ~ 2000 times more abundant than Co and consequently much cheaper. In addition, Fe is a ferromagnetic metal with the largest magnetization at room temperature. However $SmFe_5$ is unstable, and does not appear in the equilibrium Sm-Fe phase diagram. Our presentation show results of *ab initio* Density Functional Theory based on the Exact Muffin-tin Orbital (EMTO) method for the heat of formation of Sm($Co_{1-x}Fe_x$)$_5$ alloys doped with different metals (Me). The Coherent Potential Approximation (CPA) implemented in the *ab initio* EMTO method allows us to gradually substitute the Co atoms by Fe atoms on the Cu-types sites of the $CaCu_5$–type structure. Previous neutron diffraction studies of Th(Co_{1-x}Fex)$_5$ alloys show that the larger Fe atoms prefer to occupy the 3g-type sites whereas the smaller Co atoms prefer to occupy the 2c-type sites. EMTO-CPA calculations reveal very small region ($x \le 0.05$) of stability of Sm($Co_{1-x}Fe_x$)$_5$ alloys. The Full-Potential Linear Muffin-tin Orbital (FPLMTO) calculations for $SmCo_5$ and $SmFe_5$ end points of $SmCo_5$-$SmFe_5$ phase diagram give similar results to those given by the EMTO method. We calculate the heat of formation of the pseudo-binary $SmFe_3(Me_{1-x}Co_x)_2$ alloys where Fe atoms occupy all the 3g-type sites and the occupation of the 2c-type sites gradually changes from pure Me ($SmFe_3Me_2$ compound) to pure Co ($SmFe_3Co_2$ compound) within the CPA. Our calculations show that $SmFe_3(Me_{1-x}Co_x)_2$ alloys could remain stable until approximately half of Me atoms are substituted by Co atoms. This work performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344. This research is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

Biomaterial Interfaces
Room 101A - Session BI+MI-WeM

Biosensors and Diagnostics

Moderators: Daniel Graham, University of Washington, Tobias Weidner, Max Planck Institute for Polymer Research, Germany

8:00am **BI+MI-WeM1 Bacteriophage-Derived Surfaces for the Targeting of Pathogenic Bacteria***, **Stephane Evoy**,* University of Alberta, Canada

Bacterial pathogens cause a high level of morbidity and mortality, specifically for infants, young children, elderly and immunocompromised individuals. Antibodies have been exploited as molecular probes in order to impart specificity to bacterial biosensing platforms. Antibodies however suffer from degradation and reliability issues. The high specificity of phages offers a potent alternative for the targetting of pathogens. More specifically, recombinant phage receptor binding proteins (RBPs) responsible for phage-host specificity can be used as biological probes and present numerous advantages over the use of whole phage.

We successfully coupled phage RBP Gp047 from phage NCTC12673 onto magnetic beads. These beads were then employed for the extraction of Campylobacter cells from food matrices. Recovery rates were greater than 80% in samples spiked with as low as 10^2 cfu mL^{-1} of cells. Phage lysins have also been employed as capturing probes. We coupled recombinant lysin Gp10 from the mycobacteriophage L5 onto magnetic Dynabeads 280 for the capture of *Mycobacterium avium* subsp. *paratuberculosis* (MAP) cells from complex media. The study employed skim cow milk spiked with MAP cells, skim milk spiked with both MAP and *Escherichia coli* cells and Middlebrook 7H9 medium spiked with MAP cells as test matrices. The functionalized beads were incubated with the spiked sample, separated, cleaned, and subjected to DNA extraction. The resulting solution was analyzed by real time PCR. The entire test was completed within 24 hours.

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[*] **Gaede Langmuir Award Winner**

The capture process significantly increased the PCR sensitivity and demonstrated high specificity towards MAP cells.

Further, we demonstrated the use of cysteine-tagged P22 phage RBPs on gold surface for the specific SPR detection of *Salmonella enterica serovar Typhimurium*. These results demonstrate that N-teminus Cys tagged proteins capture bacteria efficiently compared to the C-terminus Cys tagged protein due to preferential orientations. Finally, micromechanical devices have also been proposed for the detection and enumeration of bacteria. We designed and developed a microresonator array optimized for such detection. This large array-based design offers a large total area for the capture of cells, while maintaining the ability to detect the attachment of a single cell anywhere on the array. The devices were functionalized with phage GST-Gp48 tail-spike proteins to impart specificity of detection. We successfully employed these arrays for the specific detection of *Campylobacter jejuni* from clean buffer. The devices did not show any sensitivity to *Escherichia coli* bacteria confirming the specificity of detection .

8:20am **BI+MI-WeM2 Biomolecule Sensing at Attogram Levels via Nanophotonic-Optomechanical Resonators*, Anandram Venkatasubramanian,*** University of Alberta, Canada*; V.T.K. Sauer, S.K. Roy,* National Institute of Nanotechnology, Canada*; D. Wishart, W.K. Hiebert,* University of Alberta, Canada

The Gas chromatography (GC) – Mass spectrometry (MS) system is the industry benchmark in chemical analysis. However the need for complex instrument such as the ionizer makes the Mass spectrometry unsuitable for portable detection applications. Recent demonstrations with nano-optomechanical (NOMS) resonators at atmospheric pressure show they are promising for portable GCs, matching the mass detection limits of NEMS sensors in only the first generation. Owing to their superior displacement sensitivity compared to NEMS, NOMS may have competitive advantages going forward. In this regard, a free space interferometry system was used for NOMS sensing of biomolecules. The primary motivation to develop sensors for portable applications is to develop point of care diagnostic devices for health monitoring. As the state of our health is a product of our interactions with our environment, metabolomics is useful in health monitoring. Among the different human biofluids, urine is “favoured” due to their precise potrayal of metabolic breakdown products, sterility and easy to obtain large volumes. Hence we have demonstrated multiple component (5 +) biomolecule detection from derivatized human urine metabolomes (HUM) as they elute from the GC. Derivatized HUMs such as ethyl malonic acid (EMA) were tested as a single component sample to obtain the limit of detection. From the results it was observed that the minimum detectable mass was about 20 attograms with a concentration threshold of 25 µM with EMA, which is in the normal physiological range in human adults. T o the best knowledge of the authors, this is the first time a NOMS based gas sensor has been used in conjunction with a gas chromatographic system and has demonstrated physiological range of detection of biomolecules.

8:40am **BI+MI-WeM3 Hole-mask Colloidal Lithography Method to Fabricate Chiral Metal-Nanoparticles for Plasmon Enhanced CD Measurements*, Gunnar Klös,*** Aarhus University, Denmark*; D.S. Sutherland,* Aarhus, Denmark

Hole-mask colloidal lithography is a well studied method [1] for a reliable high throughput fabrication of metal nanoparticles (NP). The plasmonic resonances and their electromagnetic near field dependencies of such NPs are widely used as bio-sensors , e. g. for high sensitivity refractive index sensing [2]. Rather recently it was also shown that the near field interactions of planar plasmonic chiral NPs can be used for sensitive chiroptical measurements of very dilute amounts of chiral material [3], allowing structural characterization of even small amounts of many biomolecules. So far the fabrication of such chiral NPs is based on time-consuming techniques such as e-beam lithography [4].

Here, I present a novel method for the fabrication of chiral Au nanocrescents based on a modified version of hole-mask colloidal lithography. This reliable and efficient method utilizes the shrinking of the hole due to the material evaporated through it, adding an additional parameter to the control over the shape of the resulting NP.

The method allows the fabrication of nanocrescents with an outer diameter of 100nm-200nm that show plasmonic responses similar to previous Au structures [2]. Furthermore, when analyzed with circular polarized light, they show a considerable circular dichroism response. Hence, this fabrication method is a promising technique for the time- and cost-efficient production of sensitive biosensors for the structural analysis of chiral materials.

[1] Bochenkov, V. E. and Sutherland, D. S. ” *NanoLett*, Vol. 13, 1216-1220, 2013.

[2] Guerreiro, J. R. L. et al. *ACS nano*, Vol. 8, No. 8, 7958–7967, 2014.

[3] Hendry, E. et al. *NNANO*, Vol. 5, 783-786, 2010.

[4] Hentschel, M. et al. *NanoLett*, Vol. 12, 2542-2547, 2012.

9:00am **BI+MI-WeM4 Neuraminidase Assay using Glycan-Functionalized Graphene Field-Effect Transistors*, Kaho Kamada,*** *T. Ono, Y. Kanai,* Osaka University, Japan*; Y. Ohno,* Tokushima University, Japan*; K. Maehashi,* Tokyo University of Agriculture and Technology, Japan*; K. Inoue,* Osaka University, Japan*; Y. Watanabe,* Kyoto Prefectural University of Medicine, Japan*; T. Kawahara, Y. Suzuki,* Chubu University, Japan*; S. Nakakita,* Kagawa University, Japan*; K. Matsumoto,* Osaka University, Japan

A lot of the anti-influenza virus drugs such as Tamiflu® and Relenza® prevent the viruses from infecting to the next cell. Influenza viruses enter the host cells of the throat and trachea by binding to the host cell’s surface receptor molecules which contains sialic acid. After the proliferation into the cell, the viruses cleave the sialo oligosaccharides by the action of the enzyme neuraminidase (NA), and propagated viruses are detached from the cells on the infection to the next cell. Therefore, it is possible to suppress the chain of propagation of virus by inhibiting the NA. Currently, the evaluation of antiviral drugs has been conducted mainly using cultured cells, there are problems in accuracy and quantitative property. In addition, it is difficult to evaluate the mechanism of reaction. Therefore we aim to build a useful new biological model platform for drug evaluation and drug discovery research. We modified sialoglycoprotein chain on the graphene surface, and fabricated the glycan-functionalized Graphene Field-Effect Transistors (G-FET), which reproduce cell surface environment on the graphene. The reaction behavior of the virus is highly detected as the current by the G-FET. So we can quantitatively evaluate drug reaction by the physical indicators. As a first step here, we electrically measured NA reaction by the glycan-functionalized G-FET.

G-FET was produced by evaporating the electrodes on graphene obtained by the exfoliation method. 1-Pirenbutan acid succinimidyl ester as a linker, was modified human sialoglycoprotein chain having a modified amino group on the graphene channel. After dropping the NA on it, we measured time course of the neuraminidase reaction monitored by the graphene-FET.

When dropping the NA, the current value is decreased exponentially. This is because the sialic acid negatively charged was disconnected from the sugar chain, and the hole carriers induced on graphene were decreased. The rate of decrease in current value with neuraminidase dropping is in good agreement with the activity value obtained by the absorption method (A NA molecule cuts the 1.7 of molecules per second). This shows that the rate constant obtained from electrically measurement by G-FET reflects the enzyme reaction rate.

This study has received the support of JST・CREST.

9:20am **BI+MI-WeM5 Surface-sensitive Imaging of Supported Membranes and Single Lipid Vesicles for Medical Applications*, Fredrik Höök,*** Chalmers University of Technology, Sweden **INVITED**

Measurements of ligand-binding events to membrane-protein receptors in a near-natural environment display an opportunity in mechanistic studies of membrane receptors. Furthermore, the residence time of drug-target interactions is being increasingly recognized as a key parameter in evaluating drug efficacy, but is hampered by the technical challenge to perform such studies for membrane proteins. However, with membrane proteins embedded in nanoscale lipid vesicles and detection methods with single molecule sensitivity, such information can be gained in a broad dynamic range, as requested in both drug-screening and diagnostic applications. A diverse set of tools with single-nanoparticle sensitivity is now available, to which we recently contributed a concept that enables simultaneous fluorescent and scattering-based label-free imaging of thousands of surface-bound nanoscale entities [Agnarsson B et al., ACS Nano, 2015]. The principle is based on the use of lipid vesicles as enhancer elements in optical waveguide based fluorescence and label-free evanescent-wave scattering microscopy, making the concept compatible with analysis of both water-soluble and cell-membrane bound receptors. The concept is currently evaluated as a diagnostic assay for biomarker detection and in drug-screening applications, previously explored by us using conventional total internal reflection fluorescence (TIRF) microscopy

[Gunnarsson et al., Anal Chem (2015)]. The use of scattering microscopy in the context of single-enzyme detection in complex biological fluids will be presented, with focus on single-molecule biomarker detection in cerebrospinal fluid from individuals suffering from Alzheimer's disease [Angew Chemie, 2015]. A new means to utilize the two-dimensional fluidity of supported cell-membrane derived lipid bilayers in microfluidic designs for nanoparticle size determination and sorting applications will also be presented [Simonnson et al., JACS, 2011 and Pace et al., Anal Chem, 2015].

11:20am **BI+MI-WeM11 Non-invasive Thermal Sensing using Thermographic Phosphors*, **Firouzeh Sabri**,* University of Memphis*; S. Allison,* EMCO*; P. Parajuli,* University of Memphis

F. Sabri[1], S. W. Allison[2], and P. Parajuli[1]

1. University of Memphis, Department of Physics and Materials Science

2. Emerging Measurements Co.

Thermal measurements involving thermographic phosphors, whether in the form of powder, crystal, or glass, continues to be of interest for a wide range of applications and temperature ranges. The investigation of phosphor-doped polymer films is a promising avenue for thermometry applications. Phosphor thermometry has been investigated recently for non invasive thermal assessment of biological and biomedical surfaces. For thermographic phosphors to be useful for biomedical applications they must first be encapsulated in a biocompatible, biostable, and transparent "host" that would allow optical access to the embedded phosphors. The work here demonstrates the feasibility of thin film thermographic phosphor-based thermometry where La_2O_2S:Eu particles have been embedded in a clear silicone encapsulant at different concentrations. The composite materials were prepared by means of spin-coating technology and the effect of spin speed and spin time on the thickness and distribution of the powder was investigated. . In order to improve the thermal conductivity of the composite material, a layer of carbon has been incorporated into the multilayer structure. The results presented will compare the excitation-emission behavior of the composite materials mentioned above with the properties of pure powder, at various temperatures. The effect of the tensile properties of the composite material on the excitation/ emission behavior of the materials will also be discussed. Measurements were conducted at low temperatures and at elevated temperatures and the decay characteristics were investigated as a function of temperature.

11:40am **BI+MI-WeM12 Imaging Time-of-Flight Secondary Ion Mass Spectrometry to Characterize Tumor Progression and Regression**, ***Lara Gamble**, B.M. Bluestein, D.J. Graham,* University of Washington*; F. Morrish, D. Hockenbery,* Fred Hutchinson Cancer Research Center

The tumor microenvironment has been associated with regulating tumor cell growth, metastatic potential, and chemotherapeutic drug resistance. However, very few techniques are capable of directly probing the tumor microenvironment on the micron scale. A new perspective is required to interpret and characterize this complex environment. Using imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a mouse model with Myc-dependent inducible and regressible pancreatic β-cell neoplasia, it is possible to relate changes in the composition and distribution of metabolic related molecules with tumor development. Myc, one of the most frequently deregulated oncogenes in human cancers, contributes to tumorigenesis through various mechanisms, including the deregulation of cell proliferation and growth, protein and mitochondrial biogenesis, and metabolic alterations. Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction. 4 µm cryosections were serially cut, with one used for H&E staining, one for ToF-SIMS analysis, and another for immunohistochemistry. ToF-SIMS data was acquired on an IONTOF TOF V with pulsed 25 keV Bi_3^+ ion beam. Principal component analysis (PCA) of ToF-SIMS image data separated regions of tumor cells from stroma within the first principal component and revealed subtle differences in chemistry between the tumor and surrounding tissue. ToF-SIMS data suggests a preferential uptake of fatty acids 18:3, and 18:2 within the tumor. The tumor also shows an increased localization of sphingomyelin fragments and vitamin E compared to the surrounding tissue. PCA was also applied to selected tumor regions to spatially and chemically analyze within the tumor and compare chemistries between different tumor sizes. Distinct chemical differences were identified between control and 6 day Myc activated β-cell islet tissues using multivariate analysis techniques. The results from C14:0 and phosphatidylcholine fragments present within the tumor are suggestive of *de novo* fatty acid synthesis. This work further demonstrates the high resolution capability of ToF-SIMS as the data clearly reveals intra-tumor chemical heterogeneity as localized high intensity regions, but histologic correlations are needed to discern the purpose and function of these structures.

12:00pm **BI+MI-WeM13 $SrI_2(Eu^{2+})$Gamma Camera for SPECT Imaging in Medical Applications**, ***LaNell Williams**, M. Groza, E. Rowe, J. Butler,* Fisk University*; T. Peterson,* Vanderbilt University*; A. Burger,* Fisk University

The detection of gamma rays for nuclear imaging has become increasingly important in designing non-invasive imaging tools for biological research and modeling. Although imaging techniques such as computed tomography (CT) and Positron Emission Tomography (PET) have been previously used, and improved spatial resolution and sensitivity continue to be an issue. Thus, improvements in these detection devices are needed to create better images for more accurate modeling in research [Cressey, 2011]. Scintillators such as Cesium Iodide (CsI), and Sodium Iodide (NaI) have been used for many imaging techniques for their ease of growth, energy resolution, and overall effectiveness as a gamma ray detectors. In more recent studies, Strontium Iodide doped with Europium ($SrI_2(Eu^{2+})$ has shown to be a promising scintillator compared to NaI and CsI. Because of's $SrI_2(Eu^{2+})$ improved energy resolution (~2.7%), fast decay time (~1.2 µs) and light yield (110,000 photons/MeV), it is an ideal replacement for technologies that have used previously been made with NaI and CsI. [Cherepy, 2008]. In addition, $SrI_2(Eu^{2+})$ also has an emission centered around 420 nm making it an ideal scintillator to be used with silicon photomultipliers that provide lower energy consumption than the standard photomultiplier tube. The improved energy resolution of $SrI_2(Eu^{2+})$ in a gamma camera will result in an promising detector for nuclear imaging.

Thin Film
Room 105A - Session TF+MI+NS-WeM

ALD and Nanostructures

Moderators: Sean King, Intel Corporation, Mariadriana Creatore, Eindhoven University of Technology, Netherlands

8:00am **TF+MI+NS-WeM1 Scalable Manufacturing of Nanostructured Materials by Gas-Phase Deposition Techniques**, ***Ruud van Ommen**,* Delft University of Technology, Netherlands **INVITED**

Core-shell nanoparticles and other nanostructured particles have high potential in applications such as catalysis, energy storage and pharma. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Current liquid-phase and gas-phase synthesis methods often lack the high precision required or do not lend themselves to large-scale production. Gas-phase coating can be used to provide the surface of a particle with either a thin continuous coating or a decoration of nanoclusters. Coating techniques that can be used are chemical vapour deposition (CVD) [1], atomic layer deposition (ALD) [2], and molecular layer deposition (MLD) [3].

When carried out in a so-called fluidized bed, gas-phase coating is an attractive way of producing nanostructured particles with excellent scale-up potential. In such a system, the particles are suspended in an upward gas flow. We can do this both for nanoparticles and micron-sized particles. Nanoparticles – contrary to what is typically observed for larger particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. I will discuss the challenges related to coating of nanoparticles using CVD, ALD, and MLD with such a system. Moreover, I will give a number of examples of the applications of nanostructured particles produced in this way.

[1] Valdesueiro, D., Meesters, G., Kreutzer, M., and van Ommen, J.R., 'Gas-phase deposition of ultrathin aluminium oxide films on nanoparticles at ambient conditions', Materials 8: 1249-1263 (2015).

[2] Goulas, A. and van Ommen, J.R., 'Atomic layer deposition of platinum clusters on titania nanoparticles at atmospheric pressure', Journal of Materials Chemistry A 1(15): p. 4647-4650 (2013).

[3] Vasudevan, S.A., Xu, Y., Karwal, S., van Ostaay, H.G.M.E., Meesters, G.M.H., Talebi, M., Sudhölter, E.J.R., and van Ommen, J.R., 'Controlled release from protein particles encapsulated by molecular layer deposition', Chemical Communications 51: 12540-12543 (2015).

8:40am **TF+MI+NS-WeM3 Surface Passivation of InP Nanowires by Atomic Layer Deposition**, ***Lachlan Black**, Y. Cui, A. Cavalli, M.A. Verheijen, E.P.A.M. Bakkers, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

III/V semiconductor nanowires offer a variety of novel properties that make them of interest for electronic and optoelectronic device applications, including enhanced light trapping/concentration, reduced material use, and relaxation of lattice-matching constraints, which enables novel heterostructures and growth on inexpensive substrates. However, the greatly increased surface-to-volume ratio of nanowires compared to planar devices significantly increases the importance of surface recombination and hence of effective passivation of the nanowire surface.

In this work, we focus on nanowires of InP, a material of particular interest for optoelectronic devices. In contrast to the situation for GaAs, the bare or natively oxidised surface of InP presents relatively few electronically active defect states to facilitate surface recombination. However, in order to form InP device structures it is necessary to deposit an insulating dielectric layer on part of the InP surface, and this tends to result in significant depassivation of the surface, to the extent that the performance of InP devices is commonly limited by surface recombination.

Atomic layer deposition (ALD), as a relatively “soft” deposition technique capable of forming well-controlled, high-quality dielectric layers, would seem to offer the best chance of successfully passivating InP nanowire surfaces. ALD can be performed at low substrate temperatures, which is important to avoid phosphorus out-diffusion and resulting damage of the InP surface, while its excellent conformality allows for uniform deposition on nanowire surfaces. Nevertheless, previous attempts to passivate InP surfaces by ALD have encountered similar difficulties to other techniques in achieving low surface recombination for deposited dielectric layers of appreciable thickness.

In this work, we demonstrate successful dielectric passivation of InP planar and nanowire surfaces in the presence of a relatively thick (>10 nm) ALD Al_2O_3 layer deposited from trimethylaluminium (TMA), through the use of a thin phosphate interlayer deposited at low temperature in the same system from trimethyl phosphate (TMP), in both cases using an O_2 plasma oxidant. Time-resolved photoluminescence measurements show that carrier lifetimes are increased relative to the native surface for both planar and nanowire InP samples (e.g. from 1.6 to 2.4 ns for one nanowire sample), in contrast to a strong depassivation observed following ALD of Al_2O_3 and other dielectrics on the bare InP surfaces. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) are used to elucidate the composition and structure of the deposited phosphate layers.

9:00am **TF+MI+NS-WeM4 Selectivity and Nucleation Effects in Atomic Layer Deposition of Copper for Plasmonic Nanostructures***, **Jie Qi**, B.G. Willis,* University of Connecticut

Plasmonic nanostructures made of conducting metals such as copper, silver, and gold have been intensively investigated due to their capability for enabling optics beyond the diffraction limit and making it possible to manipulate visible and near-IR radiation at the nanometer scale. The interaction between metallic nanostructures and incident light induces large enhancements of the local electromagnetic fields via the excitation of localized surface plasmon resonances (LSPRs). These confined and enhanced fields have many exciting applications in optical detection, cancer therapeutics, biological and chemical sensors, spectroscopy, catalysis, and photovoltaics. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size, shape, composition, and surroundings of the nanostructures. Selective area atomic layer deposition (SA-ALD) offers a promising nanofabrication technique to further tune the properties of plasmonic nanostructures with composition and thickness control at an atomic level. Successful application of SA-ALD requires good control of nucleation and surface morphology evolution, as well as good selectivity. Unfortunately, there are very few studies that report selectivity and/or nucleation characteristics, and their dependence on growth conditions.

In this work, we investigate the growth characteristics of Cu SA-ALD for tuning plasmonic nanostructures. Pd nanostructures are fabricated by electron-beam lithography and used as template layers. Samples are analyzed by AFM, high-resolution SEM, and image processing to investigate nuclei size and density, and morphology evolution. It has been found that nucleation is greatly affected by deposition temperature and co-reactant H_2 partial pressure. Poor nucleation leads to a rough surface with randomly distributed nanoparticles, while good nucleation leads to smooth, conformal growth over the entire feature. Sample surface pretreatments are found to be more critical for initiating growth on nanostructures compared to planar films, which might be related to residual impurities from photoresist layers or other contaminants from nanofabrication processing. Several preparation cleaning methods have been investigated for their effects on Cu film nucleation and growth selectivity including: UV-Ozone, O_2 plasma, annealing in H_2, annealing in He, boiling in water, and dipping in dilute HF.

9:20am **TF+MI+NS-WeM5 Metal Oxide Aerogel Patterning by CO_2 Laser Etching of ALD-coated Carbon Nanotube Macro-Structures***, C. Aksu, P.D. Bradford, **Jesse Jur,*** North Carolina State University

Patterning techniques of metal oxide foam architectures embedded within an ALD-coated carbon nanotube interconnected matrix are defined. Three dimensionally interconnected networks of carbon nanotube are produced from spinnable vertically aligned CNT arrays in which CNTs make. Atomic layer deposition is used to functionalize the surface of the CNTs in the array. Prior work has demonstrated that the CNT networks can be sacrificially removed to form aerogel architectures of the ALD material. In this study, we present a simple and scalable method to fabricate macro-sized structures of ALD alumina foams embedded in the carbon nanotube foam architecture via a CO2 continuous wave laser etching. Specifically, we have demonstrated the ability to ALD modify the CNT in large macro-structures (>1 cm2) and subsequently remove the CNT from specified areas, leading to the complex hybrid alumina-CNT periodic structures. The effects of ALD coating thickness are inspected by in-situ heating transmission electron microscopy methods and by high resolution scanning electron microscopy. Factors relating to manufacturability (i.e. etching speed and power) and dimension stability (i.e. laser etch size) are defined to identify scale-up opportunities.

9:40am **TF+MI+NS-WeM6 Tungsten ALD in Porous Carbon Nanotube Forests***, K. Hinton, N. Hollingworth, D.D. Allred, **Richard Vanfleet,*** Brigham Young University

We have deposited tungsten on carbon nanotube (CNT) forests by CVD (WF_6 & H_2) and ALD -the silane reduction of WF_6. Resulting structures are studied by scanning electron and transmission electron microscopy. We observed that the CNT forest provides a scaffolding for the nucleation and growth of the tungsten. Such structures may be a useful avenue for metal MEMS that does not require extensive etching. The present study may provide insight into the mechanisms of ALD in highly porous structures. In conventional ALD on surfaces which are largely planar, the amount of reactants needed to completely cover the surface does not change much from step-to-step. In contrast the surfaces of carbon nanotube forests consist of cylindrical tubes largely oriented perpendicular to the sample surface. Thus, the surface area increases with deposition. This is in addition to the changes in surface area associated with incubating early stage nucleation sites. When beginning with adequate tungsten or silane one might expect to move to starvation mode as the number of cycles increases if the amount of each reactant is kept constant. We see evidence for tungsten starvation in our research results. For low number of cycles the CNT fibers have a spatially uniform nucleation of tungsten. For low amounts of WF_6 or low “soak” times, as cycles increase, growth on the top surface and sidewalls of the carbon nanotube forest outpaces growth within the structure. Post deposition cross-sections show distinct bands witnessing the starvation of tungsten growth in the interior as more of the tungsten is deposited on regions that have direct access to the WF_6 gas. EDX analysis across such a cross-section shows distinct plateaus in the amount of tungsten present corresponding to the bands.

11:00am **TF+MI+NS-WeM10 Rational Design of Hyperbranched ZnO Nanowire Systems for Superomniphobic Surfaces Enabled by ALD***, **Ashley Bielinski**, M. Boban,* University of Michigan, Ann Arbor*; Y. He,* Pacific Northwest National Laboratory*; E. Kazyak,* University of Michigan, Ann Arbor*; C. Wang,* Pacific Northwest National Laboratory*; A. Tuteja, N.P. Dasgupta,* University of Michigan, Ann Arbor

Semiconductor nanowires (NWs) are powerful 1D building blocks for a range of technologies including electronics and optics, sensors, mechanical resonators, and energy conversion [1]. NW arrays are synthesized with careful control of morphology and composition using both top-down and bottom-up approaches. However, the hierarchical assembly of these NWs into heterogeneous systems remains challenging, largely due to lack of deterministic control of feature size, shape and position in 3D assemblies. Here we demonstrate that Atomic Layer Deposition (ALD) is a powerful tool for modifying interfaces to control the fabrication of ordered hyperbranched NW systems. Hierarchical branched NWs bridge the nano and micro length scales, while providing an exponential increase in surface area. Examples have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum in order to optimize the structure requires development.

Nanoscale patterning techniques for NW placement, while slow and costly on planar substrates, often become impossible on high aspect ratio structures. Solution-based techniques offer scalability and lower cost, but the results are often disordered and difficult to tune. Our approach uses ALD to catalyze the nucleation of NWs on the substrate during hydrothermal growth. ALD is essential for this approach because it deposits conformal films on ultra-high aspect ratio substrates, with atomic-scale control of film composition and structure. We've demonstrated that by varying the thickness of ALD ZnO films, their crystallographic orientation, roughness, and surface stress can be controlled [2]. These catalyst seed layers allow us to tune the NW array morphology, including density and orientation, over a range of substrate materials and geometries.

We further show that ALD can overcome challenges that arise when transitioning from simple NW arrays to complex branched structures [3]. First, amorphous ALD TiO_2 over-layers are used to reduce nanowire density creating space for subsequent levels of hierarchy. Next, ALD interlayers are used to block the crystallinity of the previous level of ZnO NWs to allow for non-epitaxial deposition of the subsequent ALD seed layer, forming core-shell NWs. These new techniques were used to grow hierarchical branched NW arrays, which were shown to be superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids using ALD to control the array properties.

[1] Dasgupta, N. P.; et al. *Adv. Mater.***2014**, *26* (14), 2137–2184.

[2] Bielinski, A. R.; et al. *Chem. Mater.***2015**, *27* (13), 4799–4807.

[3] Bielinski, A. R.; et al. *Submitted***2016**

11:20am **TF+MI+NS-WeM11 Bio-Templated *Morpho* Butterfly Wings by ALD for Photocatalysis***, **Robin E. Rodriguez**, D. Das, S.P. Agarwal,* University of Michigan, Ann Arbor*; W. Shang, T. Deng,* Shanghai Jiao Tong University, China*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Hierarchical nanostructures found in biology have unique properties that inspire bio-mimetic engineering. These natural nanostructures present design principles of bottom-up nanomanufacturing for materials with tunable properties. For example, structural coloration is a phenomenon observed in a wide range of natural materials that take advantage of nanoscale hierarchical structures to tune their reflection and absorption properties through periodic diffraction and photonic resonances. Here we demonstrate *bio-templating* via Atomic Layer Deposition (ALD) as an approach to manufacture atomically-precise synthetic materials that manipulate the natural structural coloration found in *Morpho* butterfly wings for enhanced photocatalytic activity.

Until recently, conventional approaches to bio-templated nanomaterial synthesis have been limited in their ability to create highly conformal 3-D interfaces between temperature- and chemically-sensitive bio materials and functional thin films. ALD is uniquely suited for scalable and conformal bio-templating, which allows us to use the nanoscale structural complexity that nature provides to tune the interfacial properties of natural systems by coating them with functional materials. By varying the geometric and optical properties of the surface, ALD is able to tune structural coloration to manipulate the light absorbing and photocatalytic properties of natural materials with nanostructured surfaces.

Morpho butterflies are particularly interesting examples of structural coloration, which occurs due to hierarchical nanostructures on their wing surfaces. The combination of strong photonic resonances and high surface area in these wings represent an ideal template for photocatalysis. To demonstrate this, proof-of-concept tests were performed on *Morpho* wings coated by ALD of TiO_2 and ZnO. Electron microscopy images showed conformal coating of the wing geometries at the nanoscale. The structural coloration of the butterfly wings could be tuned using this approach, which was modeled using finite-difference time-domain simulations of the modified wing geometry. The viability of this approach was further demonstrated in the photocatalytic degradation of methylele blue dyes in water, which led to an increase in photocatalytic activity relative to planar thin film samples. The ALD deposited materials show superior photocatalytic activity which was attributed to enhanced light absorption and increased surface area from the butterfly's hierarchical structures.

Actinides and Rare Earths Focus Topic
Room 103C - Session AC+MI-WeA

Actinide and Rare Earth Theory (2:20-3:40 pm)/Nuclear Power, Waste Remediation and Applications (4:20-6:20 pm)

Moderators: Paul Bagus, University of North Texas, Leon Petit, Daresbury Laboratory, UK, Alexander I. Landa, Lawrence Livermore National Laboratory, Melissa Denecke, University of Manchester, UK, David Geeson, AWE, UK, Stefan Minasian, Lawrence Berkeley National Laboratory (LBNL)

3:00pm **AC+MI-WeA3 First-Principle Calculations of Magnetic Properties of Actinide Complexes***, **Hélène Bolvin**,* IRSAMC, Université de Toulouse III **INVITED**

The calculation of properties of open-shell 5f molecules is a challenge for the methods of quantum chemistry : these complexes have many low lying configurations, spin-orbit effects are important and correlation effects must be taken into account. The SO-CASPT2 method gives results that compare well to experimental data : it is a two-step wave function based method. The multiconfigurational nature of the wave functions is described by starting with a CASSCF calculation, correlation effects are calculated by 2nd order theory and spin-orbit effects are introduced in the very last step by a state interaction procedure.

We will show by several examples how calculations have become a complementary tool to the experimental data in order to get information about the nature and the magnetization of the ground and excited states.

1. calculation of EPR parameters : the ground state and excited states of actinyl complexes depend strongly on the nature of the equatorial ligands. All calculations are rationalized using a model based on crystal field theory. [1,2,3]

2. calculation of the susceptibility of aquo An(III), An(IV), An(V) and An(VI) cations and comparison to the LS coupling scheme. [4]

3. calculation of the pNMR shifts in the An(Et-DPC) $_{3}^{3-}$ series and comparison with the lanthanide series. The variation in temperature of this shift will be discussed.

[1] D. Paez Hernandez, H. Bolvin J. Electron. Spectrosc. Relat. Phenom. 194, 74 (2014).

[2] F. Gendron, D. Paez Hernandez, F. P. Notter, B. Pritchard, H. Bolvin, J. Autschbach Chem. Eur. J. 20, 7994 (2014).

[3] F. Gendron, B. Pritchard, H. Bolvin, J. Autschbach Inorg. Chem. 53, 8577 (2014).

[4] M. Autillo, L. Guerin, H. Bolvin, P. Moisy, C. Berthon Phys. Chem. Chem. Phys. 18, 6515 (2016).

4:20pm **AC+MI-WeA7 Observations of Actinide-mineral Precipitation in Solution by *In Situ* Electron Microscopy***, E.C. Buck, **Michele Conroy**, J.A. Soltis,* Pacific Northwest National Laboratory **INVITED**

In this presentation, the history of Pu contamination at the Hanford site will be reviewed, including the various disposal locations, the quantities of Pu and co-contaminants disposed, and recent research efforts designed to unravel the chemical form of Pu in the environmental samples. Microanalytical information will also be presented for the sediments at the Z-9 site. The information will include the chemical characterization of the sediments at two bore holes drilled at the Z-9 sites. Although the majority of the plutonium is present as oxide, using both electron microscopy (EM) and x-ray absorption spectroscopy evidence was found for the formation of nano-sized mixed Pu and iron phosphate hydroxides that are structurally related to rhabdophane-group minerals. The Pu-phosphate formation may depend on the local microenvironment in the sediments, availability of phosphate, and hence the distribution of these minerals may control long-term migration of Pu in the soil. The presentation will also focus the role of *in-situ* EM can play in understanding nanoparticle formation and its subsequent interaction with substrates.

Iron (II) minerals, when in isolation, will control the fate of Pu; however, in a sediment with clay, calcite, and other soil minerals present as we observed in the Z9 sediments, other phases and elements may have a significant impact on the Pu chemistry. Nevertheless, the complexity found in the natural environments may lead to the formation of phases that may not be predicted in laboratory set-ups. Understanding the chemistry of Pu in complex media requires tools that can probe micro-environments. We have been exploring the use of *in-situ* EM to investigate the precipitation of Pu. All designs of cells for *in-situ* electron microscopy incorporate a membrane that prevents evaporation of the liquid sample in the microscope vacuum. We will describe other observations of Pu behaviour, morphology, and compositional changes studied with these new EM methods.

5:40pm **AC+MI-WeA11 PES Study of Surface Passivation in U-Zr Alloys***, **Ladislav Havela**, M. Paukov,* Charles University, Prague, Czech Republic*; F. Huber, T. Gouder,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements

High temperature *bcc* structure of Uranium (γ-U) can be retained to low temperatures by alloying with different *d*-metals. Such alloys are used, due to enhaced resitance to radiation damage and better mechanical properies comparing to α-U, as nuclear fuels. Alloying leads also to reduced surface reactivity. Such "stainless" uranium is much more resitant to oxidation, and reaction with hydrogen gas needs high H_2 pressures. This raises questions about phenomena at the surface of such alloys. We performed a photoelectron spectroscopy study of the alloy $U_{0.80}Zr_{0.20}$, prepared by rapid solidification (splat cooling). The concentration of 20% Zr was chosen as the lowest concetration which still gives a safe margin for single-phase *bcc* phase. In particular, we studied the properties of the surface exposed to oxidation and/or annealing.

The surface in the initial state is Zr-rich (approx. 85% Zr), and the Zr excess is only slowly removed by Ar-ion sputtering. In the cleaned state the U-4*f* spectra indicate that the degree of the 5*f* localization is not changed between the α-U and γ-U phases, which can be understood considering that the U-U spacing even in the γ-U phase remains far below the Hill limit. Also the valence-band spectra in UPS exhibit only small differences with respect to pure U, which adopts the α-U phase.

Exposing the clean surface of $U_{0.80}Zr_{0.20}$ to O_2, one observes relatively rapid oxidation. The dose of 5 Langmuir of O_2 converts 35-40% of metal into a dioxide, while Uranium oxidizes slightly more than Zirconium.

Isochronal annealing for 900 s leaves the clean surface unchanged for temperatures below 500 K. However, above this temperature the concentration of Zr in the surface layer fast increases. Repeated cleaning and annealing cycles lead to the same picture of surface enriched by Zr. The oxide formation of such surface is much more sluggish. This is true particularly for U, which has difficulty to form UO_2. The oxidation can be stimulated by elevated temperatures, pointing to the fact that such oxidation is modulated by diffussion of O thrugh the Zr overlayer. Still for 100 L of O_2 at 473 K the large part of U remains in metallic state and the amount of oxide is lower than for room-temperature oxidation of stoichiometric surface after 5 L O_2. The finding demosntrates that the U-Zr alloys are coated by Zr or Zr-rich film when exposed to 500-600 K and such film leads to a passivation of the surface.

This work was supported by the Czech Science Foundation under the Grant 15-01100S. The work at ITU was supported by the European FP7 TALISMAN project, under contract with the European Commission.

6:00pm **AC+MI-WeA12 XPS and SIMS Study of the Surface and Interface of Aged C^+Implanted Uranium***, **Art Nelson**, S. Donald, J. Siekhaus,* Lawrence Livermore National Laboratory

Core-level photoelectron spectroscopy in combination with X-ray excited Auger peak energies were blended with secondary ion mass spectrometry depth profiling to investigate the surface and interfacial chemistry of oxidized C^+ ion implanted polycrystalline uranium exposed to air for over 10 years at ambient temperature. Implantation of 33 keV C^+ ions into U^{238} with a dose of 4.3×10^{17} cm^{-3} produced a physically and chemically modified surface layer that was characterized and shown to initially prevent air oxidation and corrosion of the uranium. The evolution of the previously characterized surface and interfacial layers were now examined by using a combination of the C KLL and U NOV Auger peak energies with the associated chemical shift of the C 1s and U 4f photoelectron lines that defines the Auger parameter resulting in a reliable method for conclusively determining oxidation states independent of binding energy calibration. Results showed definitive Auger line-shapes and were used to produce a chemical state (Wagner) plot for select surface oxide and interfacial carbide. In addition, valence band spectra were used to explore the electronic structure of the aged carbide surface and interface layer. Furthermore, the time-of-flight secondary ion mass spectrometry depth profiling results for the aged sample confirmed an oxidized UC layer over the carbide layer/U metal interface.

The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Thin Film
Room 105A - Session TF+EM+MI-WeA
Thin Films for Microelectronics

Moderators: Paul Poodt, Holst Centre / TNO, Netherlands, Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France

2:20pm **TF+EM+MI-WeA1 Impact of ALD VO_2 Film Thickness on the Electrical and Optical Properties of the Metal-Insulator Phase Transition***, **Virginia Wheeler**, B.P. Downey, J. Roussos, M. Currie, A. Giles, C. Ellis, J. Tischler, J. Caldwell, D.J. Meyer, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 films are known to undergo a metal-insulator phase transition (MIT) at a critical temperature (T_c = 68°C) near room temperature which results in significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties; thus attracting interest in a variety of new electronic, optoelectronic, and photonic applications. Atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar, as well as three-dimensional, high surface area nanostructures, which could be used to integrate VO_2 films into complex electronic and optical devices for additional functionality. In this work, VO_2 electrical devices and VO_2 coated SiC-based nanoresonantors are used to investigate the impact of film thickness on electrical and optical properties.

The influence of VO_2 thickness on electrical performance was investigated using a simple two-terminal device structure. Sheet resistance measurements as a function of temperature revealed that the R_{off}/R_{on} ratio increased with increasing VO_2 thickness, up to R_{off}/R_{on} of ~7000 for a 92 nm film. Similarly, the T_c increased slightly with increasing thickness (T_c = 66°C for 35nm, 73°C for 92nm), while all films show relatively low hysteresis (ΔT<8°C). Initial small-signal rf measurements using the 92 nm ALD VO_2 film demonstrated a cut-off frequency of greater than 1 THz, indicating the potential for rf-switch applications into millimeter wavelength frequencies using these ultra-thin ALD films, and the potential of these films to be conformally integrated into complex circuits with an ALD process.

For applications in the infrared, surface phonon-polariton-based SiC nanoresonators exhibiting strong, narrowband absorption features within the 10-12.5 µm range were coated with different thickness ALD VO_2 films. Since these films are transparent to infrared light below the Tc and reflective above the Tc, conformally coating these SiC nanostructures provides a way to add functionality to these structures by modulating the amplitude of the resonances with temperature. Initial results show that the magnitude of the resonance suppression increases with increasing VO_2 thickness and a VO_2 film thickness greater than 16nm is required to fully inhibit the signal. It was also determined that the SiC resonances become increasingly shifted and broadened with increasing thickness of the VO_2 coating. These results suggest that VO_2 can add active tunability and integrated switching to optical structures.

2:40pm **TF+EM+MI-WeA2 Study of Ru Silicidation with and without Sub-nm ALD TiN and TaN Barrier/nucleation Layers for Ru Interconnect Applications***, **Sonal Dey**,* SUNY College of Nanoscale Science and Engineering*; K.-H. Yu, S. Consiglio, K. Tapily, C.S. Wajda, G.J. Leusink,* TEL Technology Center, America, LLC*; J. Jordan-Sweet, C. Lavoie,* IBM T.J. Watson Research Center*; A.C. Diebold,* SUNY College of Nanoscale Science and Engineering

With continual shrinkage of the feature size in devices, contribution of the Cu interconnects, liners, and barrier layers to the RC time-delay is becoming a significant obstacle at the 10 nm technology node and below. Ru is a potential candidate to replace Cu as an interconnect material for ultra-scaled line widths where scaling effects on Cu line resistance become increasingly problematic. Ru has already been demonstrated to be useful as the seed layer for Cu electroplating but has been shown to be an inadequate barrier to prevent Cu diffusion into surrounding BEOL dielectrics and requires the use of an additional barrier layer such as a Ta-based nitride. In addition, TaN deposited by PVD is reaching a limit in its ability to conformally coat aggressively scaled structures in the sub 10 nm node. Accordingly, in this study we evaluated the thermal stability of thin Ru films (3 nm) with and without ultra-thin (~0.5 nm) highly conformal ALD TiN and TaN films as nucleation and/or barrier layers for Ru interconnect applications in advanced technology nodes. Si (100) substrates were chemically cleaned to remove the native oxides followed by deposition of ultra-thin ALD TiN and TaN barrier films. $TiCl_4$ and $Ta(NCMe_3)(NEtMe)_3$ precursors, along with NH_3, were used for deposition of the TiN and TaN layers, respectively. Using $Ru_3(CO)_{12}$, 3 nm of Ru was deposited by CVD on top of these refractory metal nitride films and also directly on Si. We also used PVD Cu (25nm)/Si as a control stack for our experiments. The diffusion kinetics of metal-silicide formation was evaluated using in-situ rapid thermal anneal (RTA) synchrotron x-ray diffraction (XRD) measurements and a Kissinger-like analysis to determine the transition temperatures of the metal-silicidation in these stacks and the effective activation energy (E_a) using three different ramp rates (0.3, 3, and 10 °C/s). The Ru/Si stack showed higher E_a = 2.48 eV as compared to the Cu/Si stack (E_a = 1.88 eV). A 0.5 nm thick TaN (E_a = 2.88 eV) was found to act as a more effective barrier as compared to 0.5 nm thick TiN (E_a = 2.64 eV). Scanning electron microscopy (SEM) data shows that both TaN and TiN act as nucleation layers for the growth of Ru microstructure on top. A fewer number of pin holes was observed for Ru films deposited on TaN although there was not significant change on the wettability properties of the Ru film with either TiN and TaN nucleation layers underneath. Additional physical and chemical characterization with XPS and TOF SIMS were also performed to gain understanding of the film stack properties before and after silicide formation.

3:00pm **TF+EM+MI-WeA3 2D - Material and Process Challenges of the Ultimate Thin Films in Nanoelectronics***, **Stefan de Gendt**,* KU Leuven, IMEC, Belgium*; S. Brems, D. Chiape,* IMEC, Belgium*; M. Heyne, K. Verguts,* KU Leuven, IMEC, Belgium*; R. Philipson,* KU Leuven, Belgium*; C. Lockhart de la Rosa, A. Delabie,* KU Leuven, IMEC, Belgium*; S. De Feyter,* KU Leuven, Belgium*; C. Huyghebaert,* IMEC, Belgium **INVITED**

Graphene has emerged as one of the promising candidates for post-Si electronics, both for channel (Logic, RF, sensors) and interconnect applications. Further, other two-dimensional (2D) materials such as transition metal dichalcogenides (MX2, with M a transition metal of group 4–7 and X a chalcogen) have versatile properties that complement or even supersede those of graphene. Both categories however share similar problems, related to the absence of good quality synthesis processes, subsequent layer transfer processes and doping and contacting challenges. To tackle the **first challenge** – growth – chemical vapor deposition (CVD) is widely considered to be the most economically viable method to produce both graphene and MX2 materials for high-end applications. However, in most cases, this deposition technique typically yields undesired grain boundaries in the 2D crystals, which drastically increases the sheet resistance of the layer. Strategies w.r.t. template and process development will be presented. Further, given growth temperature and template, direct growth on devices is often unfeasible, thus a **second challenge** relates to the requirement for a transfer process. For graphene, several transfer process possibilities have been evaluated, but up to now, the graphene transfer suffers from contamination often coming from the temporary support layer and/or etching products, wrinkle formation during bonding, crack formation during graphene handling, ... Moreover, with improvement in 2D quality the release from the growth template is hindered due to increased adhesion forces. At least for MX2 materials, the transfer challenge can be avoided through area selective growth. A process based on a reductive two step CVD process will be presented, whereby in a first step the metal precursor (WF6) is reduced to a lower oxidation state through sacrificial reaction with Si. Subsequently, the metallic film is allowed to react with a sulphur precursor (H2S). Challenges are again related to the (poly)crystallinity of the films and the control of lateral 2D versus crystal 3D growth. Last but not least, a **third challenge** related to 2D materials resides in the contacting and doping of these materials. Different strategies have been proposed to achieve doping, but in this presentation we will demonstrate the self-assembly of organic molecules physisorbed on top bulk and thin 2D layers as a means to achieve controlled doping.

4:40pm **TF+EM+MI-WeA8 Atomic Layer Deposition of Stoichiometric $TaSi_2$ on Si(001)***, **JongYoun Choi**, S.W. Park,* University of California San Diego*; R. Hung,* Applied Materials Inc.

Transition metal disilicides are of great interest in Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) due to their ability to tune the work function at the metal contact in the source/drain regions. Various kinds of transition metal silicides such as $TiSi_2$, $NiSi_2$ and WSi_2 have been studied in previous decades, however, nanoscale studies of $TaSi_2$ are relatively scarce. Previously, Lemonds *et al.* successfully demonstrated atomic layer deposition (ALD) of tantalum silicide ($TaSi_x$) on SiO_2 using TaF_5 and Si_2H_6. In this work, it is demonstrated that using similar reaction conditions $TaSi_2$ can be grown by ALD process on oxide-free clean Si(001). The growth rate of $TaSi_2$ on Si(001) was monitored *in-situ* using a Quartz Crystal Microbalance (QCM) during the deposition. This enabled optimization of the TaF_5 and Si_2H_6 dosing to avoid chemical vapor deposition (CVD) components. Scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), scanning tunneling spectroscopy (STS) and atomic force microscopy (AFM) have been used to investigate the atomic and electronic structure of Si(001) surface after $TaSi_2$ thin film deposition. HF cleaned Si(001) was used for the substrate. The chemical composition was determined by XPS after ALD to be that of a stoichiometric $TaSi_2$ film formed on the Si substrate. The key variables in forming stoichiometric $TaSi_2$ are the ratio of the precursors and the surface temperatures. In the ALD process, a 100x fold excess of Si_2H_6 is required to prevent formation of TaOx; in addition, the surface temperature must be above 240C. These requirements for excess Si_2H_6 and a high surface temperature are likely due to high activation barrier to break the residual Ta-F bonds on the surface after the TaF_4 half pulse since the Ta-F bonds are stronger than the Si-H bonds.

5:00pm **TF+EM+MI-WeA9 Different Approaches for Enhancing the Thermal Stability of $Ge_2Sb_2Te_5$ Thin Films by Carbon Addition***, **David Adams**, K. Childs, T. Gurrieri, W. Rice,* Sandia National Laboratories

Different forms of carbon-doped $Ge_2Sb_2Te_5$ chalcogenide thin films have been evaluated for potential use in phase change memory and thermal sensor applications. This includes films sputter deposited from single, carbon-doped targets and refined multilayers made by sequential deposition of chalcogenideand C layers. In both forms, the crystallization temperature (T_{cryt}) and the resistance change through crystallization vary with carbon content. Doped chalcogenide films sputter deposited from single targets exhibit increased T_{cryt} as the concentration of C is made larger. For example, films having ~7 at.% C exhibit a T_{cryt} that is approximately one hundred and fifteen degrees above that of undoped $Ge_2Sb_2Te_5$. Films with reduced C content, in the range 1-6 at.%, show intermediate crystallization temperatures. Multilayers fabricated by the sequential deposition of thin chalcogenideand C layers behave much like films grown from single targets, provided that multilayer periodicity is made small, < 3 nm. The crystallization temperature of multilayers also increases with C concentration and a prompt transition to a crystalline phase is observed when the carbon content is low. Interestingly, multilayers made with ≥ 9 at.% C do not transition abruptly to a crystalline state. Instead, a transformation occurs over a broad range of elevated temperature. Each form of chalcogenide thin film exhibits a decreased resistivity upon crystallization. In most cases, resistivity is reduced by 5 decades upon transforming to a face centered cubic structure or a subsequent hexagonal close packed lattice at higher temperature. The changes to microstructure and thickness associated with phase change will also be described. These film properties are investigated by cross-section and plan view electron microscopy.

This work was supported by Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

5:20pm **TF+EM+MI-WeA10 Comparison of Electromigration and Resistivity in On-chip Co and Cu Damascene Nanowires***, **C.-K. Hu**, J. Kelly, J.H-C. Chen, H. Huang, Y. Ostrovski, R. Patlolla, B. Peethala, P. Adusumilli, T. Spooner,* IBM Research Division, Albany*; L. Gignac, S. Cohen,* IBM Research Division, T.J. Watson Research Center*; R. Long, G. Hornicek, T. Kane, G. Lian, M. Ali,* IBM Systems*; V.M. Kamineni, F. Mont, S. Siddiqui,* GLOBALFOUNDRIES

Cu metallization has been used for back end of the line (BEOL) on-chip interconnections since 1997. However, scaling Cu BEOL dimensions has increased Cu resistivity and degraded electromigration (EM) reliability. The Cu effective resistance has increased rapidly as the interconnect size has reduced and the ratio of liner area to total interconnect cross sectional area has increased. This size effect was caused primarily by increasing the probability of electron scattering with interfaces and grain boundaries. The EM lifetime degradation was caused by an increase in the volume fractions of diffusing atoms at interfaces and grain boundaries and a decrease in the void volume required to cause EM failure. It is estimated that ~ 70% of interconnect metal area could be occupied by the liner in the 5 nm technology node for reliable Cu metallization. To this end, an alternate metal, Co, was investigated. Multi-level Co BEOL was fabricated using typical 10 nm node technology wafer processing steps. A Co dual damascene process was used to fill the interconnect trenches and holes. The present Co resistivity study showed a similar size effect in Co as in Cu. This can be explained by the fact that the slope of resistivity vs. interconnect size is proportional to the product of the electron mean free path and resistivity, with the two slopes being about the same for Cu and Co. The effective resistivity difference between Co and Cu becomes small when no liner is used in Co lines. EM in 22 nm to 88 nm wide Co lines was tested using sample temperatures from 376^{o}C to 425^{o}C. Two–level EM structures consisted of either Co M1 to Co V1 to Co M2 or W CA to Co V0 to Co M1. The EM stress conditions for Co were far more severe than those for Cu. For comparison, EM in 24 nm wide Cu lines with a Co cap was also included. These data showed that both Co and Cu BEOL were highly reliable EM.

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

5:40pm **TF+EM+MI-WeA11 UV/VUV Curing Process for Low-k Organosilicate Dielectrics***, **Huifeng Zheng**, X. Guo, D. Pei, W. Li, J. Blatz, K. Hsu, D. Benjamin,* University of Wisconsin-Madison*; Y. Lin, H. Fung, C. Chen,* National Synchrotron Radiation Research Center, Taiwan, Republic of China*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

Porous SiCOH films are of great interest in semiconductor fabrication due to their low-k properties. Post-deposition treatments of SiCOH thin films are required to decompose labile pore generators (porogens) and to ensure optimum network formation to improve the electrical and mechanical properties of low-k dielectrics. The goal of this work is to optimize the vacuum-ultraviolet spectrum to identify those wavelengths that will have the most beneficial effect on improving dielectric properties and minimizing damage without the need for thermal heating of the dielectric. Vacuum ultraviolet (VUV) irradiation between 8.3-8.9 eV was found to increase the hardness and elastic modulus of low-k dielectrics at room temperature. Combined with UV exposure of 6.2 eV, it was found that this UV/VUV curing process compares favorably with current UV curing. The results also show that UV/VUV curing can overcome many of the drawbacks of UV curing and improve properties of dielectrics more efficiently without the need for high-temperature heating of the dielectric.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

6:00pm **TF+EM+MI-WeA12 Effects of Cesium Ion Implantation on the Mechanical and Electrical Properties of Organosilicate Low-k Films***, **Weiyi Li**, D. Pei, X. Guo, M.-K. Cheng, S. Lee,* University of Wisconsin-Madison*; Q. Lin,* IBM Research Division, T.J. Watson Research Center*; S.W. King,* Intel Corporation*; J.L. Shohet,* University of Wisconsin-Madison

The effects of cesium (Cs) ion-implantation on uncured plasm a-enhanced chemical-vapor-deposited (PECVD) organosilicate low dielectric constant (low-k) (SiCOH) films have been investigated and compared with the effects of ultraviolet (UV) curing. The mechanical properties, including the elastic modulus and hardness, of the films were improved by up to 30% with Cs implantation, and further up to 52% after annealing at 400°C in a N2 ambient for one hour. These improvements in mechanical properties are either comparable with or better than the effects of UV-curing. These improvements are attributed to an enhancement of the Si-O-Si network structure. The k-value of the SiCOH films increased slightly after Cs implantation, and increased further after annealing. These increases are attributed to two carbon-loss mechanisms, i.e. the carbon loss due to Si-CH3 bond breakage from implanted Cs ions, and the carbon loss due to oxidation during the annealing. The time-zero dielectric breakdown strength was improved after the Cs implantation and the subsequent annealing, and were shown to be better compared with the UV-cured SiCOH films. Within the investigated range of implantation dose, an optimal dose can be found to achieve the best effects. These results indicate that Cs ion implantation has the potential to be a supplement to or a substitution for the incumbent UV curing method for processing SiCOH low-k films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359.

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Thin Film

Room 104E - Session TF+MI-WeA

Thin Films for Magnetic and Optical Applications

Moderator: Subhadra Gupta, University of Alabama

2:20pm **TF+MI-WeA1 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Heterostructures via Magnetic anisotropy Dispersion***, **Colin Rementer**, Q. Xu, P. Nordeen, G.P. Carman, Y. Wang, J.P. Chang,* University of California Los Angeles

Iron-gallium (FeGa) is one of the most promising magnetic materials for use in composite multiferroics due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in MHz range or below.[1] In order to make it suitable for high frequency (GHz) applications, metalloid dopants have been used to soften magnetic materials and enhance their frequency dependent properties, but at the cost of the saturation magnetization as well as magnetoelastic properties.[2] A viable approach to circumvent this trade-off problem is to integrate a magnetic material with complementary properties into magnetic heterostructures. In this work, multilayer laminates were fabricated with FeGa and NiFe, a material with excellent properties in high frequency regimes.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets with compositions $Fe_{85}Ga_{15}$ and $Ni_{81}Fe_{19}$ (at%) into multilayers with layer thicknesses ranging from 3-50 nm, with FeGa being used as the first and last layer in the stack. XPS confirmed the composition and showed there was no intermixing of the layers. Static magnetic properties were evaluated via SQUID magnetometry, and it was found that the incorporation of NiFe layers reduced the coercivity by up to 85%, from 30 Oe to 4 Oe. FMR studies showed a reduction of the linewidth of up to 50%, from 70 Oe to 38 Oe. It is believed that this effect is largely due to the decrease of magnetic anisotropy dispersion in the multilayers.[3] The multilayer films maintained a high magnetostriction of up to 190 ppm, on the same order of magnitude as giant magnetostrictive materials such as thin film Terfenol-D.[4] FeGa/NiFe heterostructures have been shown to be an excellent candidate for strain-coupled microwave multiferroics.

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2:40pm **TF+MI-WeA2 Magnetic Anisotropy of $CoFe_2O_4$ Nanotubes Synthesized by Radical-Enhanced ALD***, **Puilam(Cyrus) Cheung**, J. Chang,* University of California Los Angeles

Multiferroic materials, exhibiting ferroelectricity and ferromagnetism simultaneously, have attracted interests for energy efficient multifunctional applications at nanoscale such as memories, antennas and actuators. While room temperature single-phase multiferroic materials such as bismuth ferrite provide insufficient magnetoelectric effect, composite systems have enhanced magnetoelectric properties by combining piezoelectric materials and magnetostrictive materials through strain. However, such strain-mediated approach in thin film composites is limited by interfacial area and substrate clamping. Ferromagnetic nanowires, on the other hand, provides a new degree of freedom in manipulating magnetic properties through shape anisotropy.

In this work, cobalt ferrite ($CoFe\text{-}_2O_4$) nanotubes were grown on anodic aluminum oxide membranes using radical enhanced atomic layer deposition (RE-ALD) to study magnetic shape anisotropy. The deposition was achieved using metal tmhd precursors (tmhd = 2,2,6,6,tetramethyl-3,5-heptanedionato) and oxygen radicals at 200˚C. The ALD growth rate of cobalt ferrite was 0.18nm/cycle. Nanotubes array were formed inside the cylindrical pores of the membrane with diameter of 18nm, 35nm and 80nm. The morphology and magnetic properties of the nanotubes were studied using scanning electron microscopy, SQUID and energy dispersive X-ray spectroscopy. It was observed that as the wall thickness of the nanotube increases from 16nm to 32nm, the magnetic easy axis was switched from perpendicular to parallel to the nanowires axis, with a doubled saturation magnetization of $5.12x10^5$ emu. The out-of-plane anisotropy field was observed to be 18.7% higher than that from in-plane axis, indicating the out-of-plane axis was magnetically more favorable. As cobalt ferrite nanowires were formed, the preferential easy axis was reversed, which could potentially be implemented in manipulating of magnetization orientation if coupled to a piezoelectric material for device applications.

3:00pm **TF+MI-WeA3 Magnetic Anisotropy and Relaxation in Spintronic Materials***, **Claudia Mewes**, T. Mewes, J. Beik Mohammadi, A. Farrar, K. Cole,* The University of Alabama **INVITED**

Functional materials with optimized properties, such as the magnetic anisotropy and magnetic relaxation rate, are crucial for the next generation of spintronic devices. Therefore technological progress in this area depends heavily on the successful search for new materials as well as on a deeper understanding of the fundamental mechanisms of the magnetic relaxation and the magnetic anisotropy. This talk will focus on different aspects which can influence the magnetic relaxation as well as the magnetic anisotropy within a confined device setting.

For many spintronic applications the use of thin films with perpendicular anisotropy is often essential for the functionality of the device. For example the use of thin films with perpendicular anisotropy in spin transfer torque magnetic random access memories (STT MRAMs) leads to a reduction of the current density needed to switch the device state. In addition to the perpendicular anisotropy it is often crucial to have materials with a low magnetization relaxation rate. Therefore many spintronic applications rely on ultra-thin magnetic films with a low magnetization relaxation in which the perpendicular anisotropy is created through surface anisotropy. This approach is very sensitive to the interface morphology and chemical environment. In this talk I will discuss the effect of spatial fluctuations of the first order perpendicular anisotropy in thin films and its influence on the effective anisotropy for these materials.

Similar to the magnetic anisotropy the magnetic relaxation in thin ferromagnetic films can be affected by neighboring layers. Spin pumping is a well-known contribution that has to be taken into account for practical applications using multilayer structures. More recently a strong unidirectional contribution to the relaxation in exchange bias systems has been observed experimentally. To describe this phenomenon theoretically we use the formalism of an anisotropic Gilbert damping tensor that takes the place of the (scalar) Gilbert damping parameter in the Landau-Lifshitz-Gilbert equation of motion. In this talk I will discuss this approach to study the modified magnetization dynamics under the influence of unidirectional damping.

ACKNOWLEDGMENTS

C.K.A. Mewes acknowledges support by the NSF-CAREER Award No. 1452670, T. Mewes acknowledges support by the NSF-CAREER Award No. 0952929.

4:20pm **TF+MI-WeA7 Vacuum Furnace Annealing Block Copolymers for Bit Patterned Advanced Media***, **Allen Owen**, S. Gupta,* University of Alabama

Hard disk drive storage media is trending towards both smaller physical size and greater storage capacity, there by increasing the areal density of the magnetic storage media. Bit patterning shows potential as a method for increasing this areal density. A block copolymer template can be used to provide an etch mask for bit patterning a magnetic thin film. A statistical design of experiments was carried out to optimize the effect of nanopatterning via ion milling Co/Pd multilayers for PS-PFS block copolymers. The design of experiments varied the etch angle and etch time during ion milling. Samples that were sputter-deposited with Co/Pd multilayered thin films were spin-coated with PFS block copolymer and vacuum furnace annealed at 140 °C for 48 hours at a pressure of ~5 x 10^{-5} Torr. After vacuum furnace annealing, the films were ashed in oxygen plasma to remove the PS, leaving the PFS spheres as masks for the subsequent ion milling. The stack used was Pd5/$[Co0.3Pd1.0]_{14}$ /Pd 5 nm sputter deposited onto a Si substrate. The as deposited coercivity was ~1.3 kOe. After ion milling for 2 min at an angle of 45°, the coercivity was found to be ~0.6 kOe. Ion milling at 45° for 4 min resulted in a coercivity of ~0.07 kOe. This is in comparison with previous experiments using thermal annealing in atmosphere and solvothermal annealing with heptane, where the coercivity increased at ~4 min at the same 45° ion milling angle. The difference can be explained by the fact that for the previous experiments, the stack used was Ta5/$[Co0.3Pd1.0]_{14}$/Ta5 nm. The Ta capping layer must be more resistant to ion milling than Pd, which means the ion milling times must be adjusted to transfer the bit pattern to the media.

4:40pm **TF+MI-WeA8 Atomic Layer Deposition Enabled Synthesis of Miltiferroic Composite Nanostructures***, **Jeffrey Chang**, A. Buditama,* University of California at Los Angeles*; A. Rosenberg,* Stanford University*; L. Kornblum,* Yale University*; S.H. Tolbert,* University of California at Los Angeles*; K.A. Moler,* Stanford University*; C.H. Ahn,* Yale University*; J.P. Chang,* University of California at Los Angeles

Multiferroic materials, which exhibit controllable ferromagnetic (ferroelectric) properties via electric (magnetic) field, are of great interest due to their potential in enabling new device applications. Due to the scarcity of single-phase multiferroics in nature and their weak responses at room temperature, composite multiferroics are proposed to realize robust multiferroic behaviors by coupling the functional properties from the constituent phases. A strain-mediated coupling strategy is achieved by interfacing magnetostrictive ferromagnets with piezoelectric materials, where the interfacial area per volume, as well as the material crystallinity, play important roles in the attainable functional properties. With the aim of enhancing the composite magnetoelectric behavior by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, shows considerable potential in achieving high quality multiferroic composites with industrial scalability.

In this work, lead-free ferroelectric/antiferromagnetic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) thin films were grown on $SrTiO_3$ (001) substrates by ALD using tmhd-based metalorganic precursors(tmhd =2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature process capability at ~200°C. The growth rates for BFO and CFO are ~3.3Å/cycle and ~2.4Å/cycle, respectively. The BFO films showed epitaxial single crystalline growth in (001) pseudocubic orientation after being annealed under 650°C, while the CFO films are oriented polycrystalline due to the lattice mismatch between the film and substrate. The BFO piezoelectric properties were confirmed using piezo force microscopy, while tunable CFO magnetic properties were demonstrated by thickness-related strain relaxation measurements.

Multiferroic composite nanostructures were synthesized by implementing ALD processes with different substrates. Room-temperature magnetoelectric behaviors ($\alpha \approx 64\times10^{-3}$ Oe cm/V) and tunable magnetic anisotropies were observed in the BFO/CFO system with 2-2 and 1-3 orientations, respectively. The microscopic magnetic domain structures were characterized by the scanning SQUID systems. 0-3 CFO/PZT composites were enabled by using mesoporous PZT structures. The change in lattice parameters after poling was observed by high-resolution XRD measurements, showing that the strain interactions lead to the magnetoelectric behavior in the composite. Besides, the integration of the BFO/CFO system onto Si platforms demonstrated the versatility of the ALD processes, illustrating a path for integrating novel multiferroic materials into current industrial processes by ALD.

5:00pm **TF+MI-WeA9 Thin Film Challenges for High Performance Ir Plasmon Enhanced Photodiodes: from Simulation to Focal Plane Array Integration and Characterization***, **François Boulard**,* Univ. Grenoble Alpes, France*; O. Gravrand,* Univ. Grenoble Alpes,France*; D. Fowler,* Univ. Grenoble Alpes, France*; G. Badano,* Univ. Grenoble Alpes, France*; P. Ballet,* Univ. Grenoble Alpes, France*; M. Duperron,* Univ. Grenoble Alpes, France*; L. Adelmini, R. Espiau de Lamaestre,* Univ. Grenoble Alpes, France **INVITED**

For several decades now, Surface Plasmons (SP) have been increasingly studied for applications in many fields from chemistry, biology, to materials science. In the IR sensor community, the use of SPs to concentrate and channel light offers new possibilities to increase sensitivity or modify spectral response. However, the incorporation of metallic nanostructures in technologically mature components is challenging. This paper deals with the design and integration of a sub-wavelength photonic structure to add spectral functionalities to mid wave and longwave IR HgCdTe photodiodes. Based on simulation and experimental results, tradeoffs to reach the full potential of SP enhancement are discussed. The relationship between the metallic grating geometry and the excited optical mode is illustrated using numerical simulations. The agreement between the simulated and measured spectral response and dispersion relation on a test photodiode array is shown. The influence of the absorber, passivation, and adhesion layer properties and thicknesses on the resonance intensity and photodiode noise is experimentally illustrated. Finally, results of multicolor midwave IR focal plane arrays with shot noise limited operation and less than 0.3% defective pixels are presented.

6:00pm **TF+MI-WeA12 Watching Thin-film Aluminum Oxidize***, **David Allred**, M. Miles, S. Thomas, S. Willett, M.J. Greenburg, A. Vance, R.S. Turley,* Brigham Young University

In three years NASA will be in the midst of its decadal review, establishing priorities for the 2020s. Very likely one of the chief astrophysical missions will contain a LUVOIR (large, UV-optical-IR) telescope. This space-based observatory will likely contain the largest mirrors ever flown and will probe the cosmos seeking to address key questions of the origin, current status and evolution of our universe. These investigations will profit from a truly broad-band mirrors. Thus, the reflective coating will almost certainly be aluminum. To be viable, the top surface of such a space mirror needs to be bare without the tarnish layers that naturally form in air. This could open up the 11-15eV band for space-based astrophysics without sacrificing IR, visible and UV reflectance. We report on two techniques aimed at clarifying the oxidation mechanism for Al. First, we have used VUV (>10 eV) reflectometry of bare, freshly deposited aluminum mirrors as they age in controlled atmospheres, and second, variable-angle, spectroscopic ellipsometry is shown to be capable of measuring changes at the angstrom level in multilayers consisting of aluminum, protected by various vacuum-applied barrier layers. These ultrathin barrier layers included polymers such as parylene and inorganic films, such as MgF_2 and AlF_3. For example, we saw that the growth in oxidation thickness of aluminum protected by a 7nm MgF_2 film is logarithmic over a period of time of more than 1000 hrs.

2D Materials Focus Topic
Room 103B - Session 2D+MI-ThM

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

Moderators: Paul Sheehan, US Naval Research Laboratory, Zhaohui Zhong, University of Michigan, Ann Arbor

8:00am **2D+MI-ThM1 Mechanics and Fracture of 2D Materials with Defects and Grain Boundaries***, **Zhao Qin**, G.S. Jung,* Massachusetts Institute of Technology*; S. Wang,* University of Oxford, UK*; F.J. Martin-Martinez,* Massachusetts Institute of Technology*; J.H. Warner,* University of Oxford, UK*; M.J. Buehler,* Massachusetts Institute of Technology

Two dimensional materials including graphene, silicene, MoS2 and so forth represent ideal materials composed of a single layer of atoms organized in a lattice form. Their unique geometry and intriguing mechanical and thermal properties make them perfect candidates for nano scale engineering applications. The robustness of the materials, especially those with defects is important to prevent their catastrophic failure and contribute to their durability in usage. Here we combine both large-scale molecular dynamics simulations based on reactive force fields and experiments via transmission electron microscopy to investigate their fracture behavior under extreme mechanical loading conditions. We focus on how defects and grain boundaries in 2D materials affect the critical conditions and the dynamics process of their fracture. Our results reveal that certain forms of atomic defects and grain boundaries are beneficial to enhance the mechanical strength of 2D materials that are subjected to cracks. For example, we find that poly-crystalline graphene under fracture releases up to 50% more energy than the pristine graphene. We find that grain boundaries increase the critical energy release rate to fracture by reducing stress concentration and making branches near the crack tip. We find atomic defects can cause crack deflections during crack propagation, effectively extending the crack length during propagation and thus increase the energy dissipation. Together, these molecular irregularities taking place at the atomic scale level can significantly affect the lattice characteristics of the 2D materials at larger scale levels and thereafter enhance their fracture toughness, making its crack propagation different from pristine ones, and such a mechanism explains the reduced crack propagation speed by adding vacancies as what is seen in experiments.

8:20am **2D+MI-ThM2 Effects of Non-local Screening and Effective Mass Anisotropy on Excitons in 2D Materials***, I.I. Oleynik, **Joseph Gonzales**,* University of South Florida

The optical excitations in semiconductors are substantially influenced by electron-hole interactions resulting in formation of excitons. Although the exciton binding energies in the bulk are much smaller that the fundamental band gaps, the excitonic effects in 2D materials are significantly amplified due to combined effect of quantum confinement and non-local screening of electron-hole interactions in two dimensions. An effective mass theory of 2D excitons, which takes into account the combined effect of the anisotropy and non-local 2D screening, is used to systematically investigate the variation of monolayer exciton binding energies E_x across a representative set of layered chalcogenides, both isotropic, such as $MoTe_2$, $MoSe_2$, WSe2, and WS_2, and anisotropic including phosphorene, TiS_3, ReS_2, and $SnSe_2$. The markedly different values of E_x are correlated with corresponding variations in atomic polarizabilities of constituent atoms.

8:40am **2D+MI-ThM3 2D Materials: A New Platform for Strong Light-Matter Interactions***, **Ajit Srivastava**,* Emory University **INVITED**

A recent addition to low-dimensional materials are monolayer transition metal dichalcogenides (TMDs), such as WSe_2, with an atomically thin, honeycomb lattice and optical band gaps. In addition to spin, charge carriers in TMDs exhibit a “valley” degree of freedom which can be optically addressed using circularly polarized light, opening up exciting possibilities for “valleytronics". Another curious aspect of TMDs lies in the non-trivial geometry of their band structure which gives rise to equal but opposite Berry curvature, an effective magnetic field in the momentum space. Owing to unusually strong Coulomb interactions in truly 2D limit, optical spectra of monolayer TMDs is dominated by tightly bound excitons which are expected to strongly couple to light and form stable polaritons - half light, half matter excitations.

In this talk, I will begin by presenting our recent results on valley Zeeman effect, where in analogy to spins, valleys shift in energy with magnetic field. Next, I will discuss our theoretical results on how the non-trivial geometry of Bloch bands modifies the excitonic fine structure of TMDs resulting in an orbital Zeeman effect in reciprocal space and a Lamb-like shift of levels. Finally, I will present our recent results on the observation of microcavity polaritons confirming the strong light-matter interactions in these materials. The presence of valley degree of freedom, non-trivial geometry of bands, and the possibility of introducing non-linearities in form of quantum emitters makes polaritons in TMDs particularly appealing for studying correlated many-body physics and topological states of matter.

9:20am **2D+MI-ThM5 Electronic Transport and Localization in Nitrogen-Doped Graphene Devices Using Hyperthermal Ion Implantation***, **Adam Friedman**, C.D. Cress,* Naval Research Laboratory*; S.W. Schmucker,* National Research Council postdoc working at Naval Research Laboratory*; J.T. Robinson, O.M.J. van 't Erve,* Naval Research Laboratory

Chemical alteration of graphene facilitates doping and may add a usable transport gap. For most published studies, atomic species (e.g., fluorine or hydrogen) are chemically bonded to the surface out-of-plane, breaking the sp^2 symmetry and replacing it with an sp^3 bond. These methods produce functionalized graphene, rather than substitutionally-doped graphene, where the former is typically only chemically stable for days (e.g., fluorine) or weeks (e.g., hydrogen) or less, depending on environmental conditions. Hyperthermal ion implantation offers a controllable method of producing high-quality substitutionally doped graphene with nitrogen, an n-type dopant that has great potential for graphene electronics and spintronics applications where high carrier concentration, uniform doping, and minimal vacancy defect concentration is desired [1]. Here we examine the transport properties of monolayer graphene sheets as a function of implantation beam energy and dose. We observe a transition from weak (metal) to strong (insulator) localization that varies as a function of carrier concentration, and we find that the transition is suppressed near the Dirac point for higher amounts of nitrogen [2]. For nominally equivalent doses, increased N ion energy results magnetoresistance magnitude increases, reaching a value as approximately -5.5% at 5,000 Oe, which we discuss in the context of dopant concentration and defect formation. We use a model for the temperature dependence of the conductivity that takes into account both temperature activation, due to the formation of a transport gap, and Mott variable-range hopping, due to the formation of defects, to further study the electronic properties of the doped films as a function of dose and N ion energy. We find that the temperature activation component dominates the behavior, further indicating that the implanted nitrogen, rather than defects, is responsible the observed result.

[1] C.D. Cress, et al. ACS Nano 10, 3714 (2016).

[2] A.L. Friedman, et al. Phys. Rev. B, 93 161409(R) (2016).

9:40am **2D+MI-ThM6 Metal Contacts to Transition Metal Dichalcogenide Films: Understanding and Avoiding the Formation of a Schottky-like Barrier***, M. Gomez, J. Martinez, M. Valentin, E. Preciado, V. Klee, C. Merida, **Ludwig Bartels**,* University of California - Riverside

We utilize a combination of X-ray photoelectron spectroscopy, transport measurements and optical as well as acoustic excitation to study the impact of the formation of metal contacts to transition metal dichalcogenide films on the electronic structure of the films. Photoelectron spectroscopy permits us to follow the formation of a Schottky-like barriers with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS_2 valence band during metal deposition. Our findings indicate that single layer MoS_2 films adopt the character of the metal (Fermi-level pinning) resulting in a Fermi-level position in the MoS_2 semiconducting gap that is – depending on the metal work function –indicative of a *p*-type semiconductor, even though the native carriers in an MoS_2 film are electrons. As a consequence, metal-TMD-metal junctions may best be understood as *p-n-p* junctions. Numerous ancillary measurements support this hypothesis.

11:00am **2D+MI-ThM10 Multilayer Graphene Suspension Over Millimeter Size Openings and Mechanical Testing***, **Joseph Rowley**, R.F. Davis, R.R. Vanfleet,* Brigham Young University*; J. Abbott,* Moxtek, Inc.

Because of it's high ultimate tensile strength, a single atomic layer of graphene has been able to suspend micron size holes reliably. However, to extend into regimes where devices have dimensions measured in millimeters, a single layer of graphene is insufficient. Films made from a few layers of graphene, although not as strong as pristine single layer graphene, have been shown to still retain a high level of strength. Using chemical vapor deposition on a nickel catalyst, we have fabricated many layer graphene films and suspended these membranes over millimeter size holes. Mechanical properties were measured on suspended films using a custom bulge test instrument.

11:20am **2D+MI-ThM11 Modeling Excitons in Transition-Metal Dichalcogenides***, F. Tseng,* NRC Research Associate*; E. Simsek,* George Washington University*; **Daniel Gunlycke,*** Naval Research Laboratory

Using a triangular lattice exciton (3ALE) model, we explore exciton states in semiconducting monolayer transition-metal dichalcogenides. We show that the hydrogen model for excitons breaks down due to lattice effects and that the excitons are neither Wannier nor Frenkel excitons and instead span an intermediate size regime. The model is formulated on sparse form in direct space, leading to a computationally efficient N log(N) scaling and the ability to calculate over lattice grids with tens of thousands of sites, more than sufficient to converge exciton states in this intermediate exciton regime. In this presentation, we will also discuss the Coulomb potential generated from a dielectric substrate and how the exciton binding energies could be tuned by the thickness and permittivity of an oxide layer.

11:40am **2D+MI-ThM12 Characterization of Collective Ground States in Single-layer $NbSe_2$***, **Miguel M. Ugeda,*** CIC nanoGUNE, Spain*; A.J. Bradley,* University of California at Berkeley*; Y. Zhang,* Advanced Light Source, Lawrence Berkeley National Laboratory*; S. Onishi, W. Ruan, Y. Chen, C. Ojeda-Aristizabal,* University of California at Berkeley*; H. Ryu,* Advanced Light Source, Lawrence Berkeley National Laboratory*; M.T. Edmonds, H.Z. Tsai, A. Riss,* University of California at Berkeley*; S.K. Mo,* Advanced Light Source, Lawrence Berkeley National Laboratory*; D. Lee, A. Zettl,* University of California at Berkeley*; Z. Hussain,* Advanced Light Source, Lawrence Berkeley National Laboratory*; Z.X. Shen,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; M.F. Crommie,* University of California at Berkeley **INVITED**

Layered transition metal dichalcogenides (TMDs) are ideal systems for exploring the effects of dimensionality on correlated electronic phases such as charge density wave (CDW) order and superconductivity. In bulk $NbSe_2$ a CDW sets in at T_{CDW} = 33 K and superconductivity sets in at T_c = 7.2 K. Below T_c these electronic states coexist but their microscopic formation mechanisms remain controversial. In this tal I will present the electronic characterization study of a single 2D layer of $NbSe_2$ by means of low temperature scanning tunneling microscopy/spectroscopy (STM/STS), angle-resolved photoemission spectroscopy (ARPES), and electrical transport measurements (1). I will show that 3x3 CDW order in $NbSe_2$ remains intact in 2D. Superconductivity also still remains in the 2D limit, but its onset temperature is depressed to 1.9 K. Our STS measurements at 5 K reveal a CDW gap of $\Delta = 4$ meV at the Fermi energy, which is accessible via STS due to the removal of bands crossing the Fermi level for a single layer. Our observations are consistent with the simplified (compared to bulk) electronic structure of single-layer $NbSe_2$, thus providing insight into CDW formation and superconductivity in this model strongly-correlated system. Furthermore I will show that CDW order is also present in 2D semiconducting TMDs around 1D mirror twin boundaries (2).

(1) M. M. Ugeda, et al., Nature Physics 12, 92 (2016).

(2) S. Barja, et al., Nature Physics, in press (2016).

Advanced Ion Microscopy Focus Topic
Room 104A - Session HI+MI+NS-ThA

Ion Beam Based Imaging and Nanofabrication

Moderators: Jacques Gierak, LPN-CNRS, Shinichi Ogawa, AIST, Japan

2:20pm **HI+MI+NS-ThA1 Mask Repair Technology using Gas Field Ion Source***, **Anto Yasaka**, F. Aramaki, T. Kozakai, O. Matsuda,* Hitachi High-Tech Science Corporation, Japan **INVITED**

We developed a new ion beam based mask repair system using a gas field ion source (GFIS). For conventional photomasks, nitrogen ions were used to repair defects, while hydrogen ions were used for EUVL masks. We evaluated the performance of the mask repar system on MoSi based phase shift masks and EUV masks. The results demonstrates that GFIS technology is a reliable solution of repairing defects on high end photomasks for 1Xnm generation and beyond.

3:00pm **HI+MI+NS-ThA3 Application of an Advanced Bi Cluster LMIS for TOF-SIMS Analysis at the Nano-scale***, F. Kollmer, W. Paul, D. Rading, R. Moellers,* ION-TOF GmbH, Germany*; N.J. Havercroft,* ION-TOF USA*; E. Niehuis, **Julia Zakel**,* ION-TOF GmbH, Germany

In recent years, the application of cluster primary ions has become standard for all kinds of TOF-SIMS applications. Organic surfaces, in particular, benefit from the cluster bombardment due to a more efficient emission of molecular species compared to mono-atomic bombardment. However, the ultimate spot size so far has been obtained by Ga based liquid metal ion sources. In our contribution we will show that a Bi based cluster LMIS has the potential to outperform the established Ga LMIS even in terms of TOF-SIMS imaging at the highest lateral resolution.

We will discuss fundamental emission properties such as energy spread and virtual source size for the main species of a Bi cluster LMIS. Via a consistent optimisation of emission parameters and an adaption of the ion-optical column, a lateral resolution in the 20 nm range can be achieved. At this scale it seems that we are approaching the physical limits since not only the primary ion beam spot size, but also the size of the sputter cascade as well as the signal intensity limit the obtainable useful lateral resolution. Further progress requires the combination of the SIMS data with complimentary imaging techniques of higher lateral resolution or sophisticated sample preparation methods such as bevelling of the surface region with an FIB column.

In this respect we will show that a combined TOF-SIMS Scanning Probe Microscopy (SPM) provides the required information on the nanometer level. Moreover, information on surface topography and other physical properties of the scanned surface area can be obtained in-situ. The investigated samples include inorganic reference samples, alloys, biological samples, hybrid sample systems and thin films.

3:20pm **HI+MI+NS-ThA4 Nanoscale Imaging and Characterization of Interface Driven Assembly of Soft Materials via He-Ion Beam Microscopy***, **Matthew Burch**, A. Belianinov, D. Chang, Y. Luo, K. Hong, O.S. Ovchinikova,* Oak Ridge National Laboratory

The ability to directly image and characterize nanoscale structures and features of soft materials is key to understanding the role growth, interfaces and extrinsic stimuli have on the functionality of these materials. In particular, the arrangement and architecture of bottlebrush block copolymer systems is of interest, as material properties depend greatly on the organization and interfaces of these polymers during growth. However, due to the insulating nature of these materials, directly imaging surface features at the nanoscale using traditional electron microscopy based techniques is challenging. Alternatively, He-ion beam microscopy (HIM) has been developed to the level where it can now characterize and directly image the nanoscale surface features of these soft materials directly.

In this work, He-Ion microscopy is utilized to investigate the nanoscale structures of copolymer systems. In particular, the ordered periodic structures of bottle brush copolymer thin film systems are investigated to understand how different substrates and growth conditions impact the final periodic lamella and domain structures. Of particular interest is how the interface driven separation leads to different short range molecular and long rage surface ordering. Furthermore, we will discuss how surface ordering of the copolymers effects the functionality of the material by correlating HIM imaging results with local probing of electromechanical and electrochemical using scanning probe microscopy.

Acknowledgements

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

4:00pm **HI+MI+NS-ThA6 Advances in *Ex Situ* Lift Out and Manipulation Techniques for FIB Applications***, **Lucille Giannuzzi***, EXpressLO LLC

The focused ion beam (FIB) *ex situ* lift out (EXLO) technique was the first lift out technique developed for transmission electron microscopy (TEM), surface science, and other site specific analysis of materials [1,2]. EXLO is well known for its ease, speed, and reproducibility, and is perfectly suited for manipulation of thick or electron transparent thin specimens for site specific microscopy or analytical characterization. EXLO is also perfectly suited for manipulation of electron transparent specimens to MEMS carrier devices used for *in situ* TEM holders. Micromanipulation techniques also aid in specimen preparation for particulates and fibers that require subsequent FIB milling. A review of EXLO and advances of the technique using a new slotted grid specimen carrier will be presented. This new grid negates the need for a carbon film specimen support and allows for additional specimen FIB milling or other post processing after manipulation [3].

[1] L.A. Giannuzzi et al., Mat. Res. Soc. Symp. Proc. 480 (1997) 19-27.

[2] F.A. Stevie et al., *Surf. Interface Anal.* 31 (2001) 345–351.

[3] L.A. Giannuzzi et al., *Microsc. Microanal*. 21 (2015) 1034-1048.

4:20pm **HI+MI+NS-ThA7 Helium Ion Microscopy Imaging of Carbon Nanofoams from Hydrothermal Carbonization of Sucrose***, **Natalie Frese**,* Bielefeld University, Germany*; S.T. Mitchell, A. Bowers, K. Sattler,* University of Hawaii*; A. Gölzhäuser,* Bielefeld University, Germany

Carbon nanofoam is considered as potential hydrogen storage material as well as cathode material for metal-air batteries. It is known that carbon nanofoam contains both sp^2- and sp^3-bonded carbon atoms. However, there is still a lack of knowledge about the atomic structure of this material. In this work, different types of carbon nanofoams were produced by low-temperature hydrothermal processing of carbon precursor materials. It was found that the produced foams have a low density and are uniform in their appearance. Helium-ion microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy were used to characterize the foam samples. The results show good consistency between the micro- and nanostructure as well as the elemental composition. We conclude that hydrothermal processing of carbon precursor materials is an effective method to produce high-quality carbon nanofoams of graphitic nature.

4:40pm **HI+MI+NS-ThA8 Nanofabrication Limits in Layered Ferroelectric Semiconductors via He-ion Beam***, **Alexei Belianinov**, A. Ievlev, V. Iberi, H. Hysmith, M.A. Susner, M. McGuire, S. Jesse, S.V. Kalinin, O.S. Ovchinnikova,* Oak Ridge National Laboratory

Manipulating matter at progressively finer and ultimately atomic scales enables new functionality and effectively drives nanoscience. Currently, well understood, robust resist-based lithography, carries the brunt of nanofabrication, however local electron, ion and physical probe methods are improving as well, driven largely in part of their ability to fabricate without multi-step preparation processes that contaminate the sample with processing resists and solvents. Furthermore probe based methods extend beyond nanofabrication to nanomanipulation and imaging, vital ingredients to rapid transition to testing and manufacturing of layered 2D heterostructured devices.

In this work we demonstrate chemical and physical changes induced by a helium ion beam in a Helium Ion Microscope (HIM) with the surface of bulk copper indium thiophosphate (CITP) $CuM_{III}P_2X_6$ (M = Cr, In; X= S, Se) library of compounds of varying copper concentration; from 4–100%. Physical changes in micro- and nano-fabrication are explored via Atomic Force Microscopy, (AFM), and chemical changes are probed by Secondary Ion Mass Spectrometry, (SIMS). Our work illustrates controlled loss of ferrielectric domains, and nanostructure growth with material volumes scaling to the dosage of the helium ion beam. The nanostructures are oxygen rich, sulfur poor, with the copper concentration virtually unchanged. Effects of varying copper concentration on the quality of the fabricated nanostructures, as well as the differences in their chemical make-up will be discussed.

Acknowledgements

Research was supported (A. B., V. I., A. I., H. H., S. J. S. V. K. O. S. O) and partially conducted (AFM, HIM, SIMS) 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, US Department of Energy. This work was also supported (M. S., M. M.) and partially conducted (material growth) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

5:00pm **HI+MI+NS-ThA9 Focused Ion Beam Technology Challenges for Circuit Edit***, **Yuval Greenzweig**, Y. Drezner, A. Raveh,* Intel Corporation

The challenges of Circuit Edit (CE) using focused ion beam (FIB) are driven by the perpetual down-scaling of minimum features per VLSI process technology generation. The recent emergence of FIBs with much reduced probe sizes relative to Ga LMIS based tools, may provide a long-needed revitalization of FIB nanomachining capabilities such as FIB image resolution and machining acuity, necessary for nanomachining tasks such as CE. However, other requirements must go along, driving preferences of ion species, ion energies, and requirements for system performance in several areas.

Among the challenging requirements of CE is the task of milling in a controlled and planar fashion through layers of parallel metal lines with intervening dielectric, and end-pointing on a metal layer of choice. The end-pointing is based on the real-time secondary electron (SE) image during ion milling, and the requirement is leaving most of the target metal intact. If linear dimensions of features, such as minimum metal widths, reduce by a factor $\boldsymbol{\alpha}$ from one VLSI generation to the next, then maintaining quality realtime milling images, i.e., sufficient resolution and signal to noise, requires milling vertically through a layer proportional to $\boldsymbol{\alpha}^{-2}$ relative to the previous generation - same number of ions, but in a smaller pixel. On the other hand, the vertical thickness of the metals has also decreased by a, causing the etching to scale as $\boldsymbol{\alpha}^{-3}$ relative to the thinner new metal thicknesses. Previous VLSI process generation scaling factors have been approximately $\boldsymbol{\alpha} = 0.7$, so that the severity of this challenge has been getting worse by ~3X for several generations and is now at the feasibility limit. To improve on this, SE emission and collection efficiency must improve, and in particular SE collection efficiency of normally emitted SEs, which are the bearers of the information from the bottom of these milling boxes. The figure of merit representing this challenge is the SE yield times the SE detector collection efficiency, divided by the sputter yield (or etch rate), this provides opportunity for GFIS sources.

Other challenges of the CE application which providing preferences of ion species and ion energy will be discussed.

5:20pm **HI+MI+NS-ThA10 Ion-milling of Graphene Nanostructures While Supported and Unsupported: Considerations of Graphene Contamination, Substrate Scattering and Beam Tailing***, J. Swett,* Lockheed Martin Space Systems Company*; V. Iberi, D. Cullen, **Adam Rondinone**,* Oak Ridge National Laboratory

Graphene and other 2D materials offer novel characteristics and opportunities compared to traditional thin films. Common nanofabrication techniques including e-beam and nanoimprint lithography can be used to pattern atomically thin 2D systems but the multi-step processes they utilize result in exposure of the film to solvents and resists, and hence degradation of the material's novel electronic properties. Herein we demonstrate that helium and neon-ion milling are effective tools for the creation of very fine features with arbitrary geometries in supported and unsupported graphene, to include conductive structures, arrays of pores, and engineered defects. Properties of graphene, including contamination levels, play an important role in determining millability, as do instrumental parameters such as beam tailing and substrate scattering.

Acknowledgement

This research was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

5:40pm **HI+MI+NS-ThA11 Interaction of Gas Field Ionized Nitrogen with Silicon***, **Marek Schmidt**, Y. Oshima, L.T. Anh, X. Zhang, T. Kanzaki, M. Akabori,* Japan Advanced Institute of Science and Technology, Japan*; A. Yasaka,* Hitachi High-Tech Science Corporation, Japan*; M. Muruganathan, T. Shimoda, H. Mizuta,* Japan Advanced Institute of Science and Technology, Japan

A larger number of gas molecules (among them helium, nitrogen and neon) can be ionized by the gas field ion source (GFIS) and used as projectiles in focused ion beam (FIB) systems. Among them, the nitrogen stands out as it forms a very strong covalent bond. It is not yet fully understood how this N_2 molecule behaves during field ionization and sample interaction, i.e. if and when the bond is broken. Previously, it has been shown that cross section studies are very useful in analyzing beam/sample interaction [1]. Here, we report scanning transmission electron microscopy (STEM) analysis of cross sections extracted from silicon bombarded with ionized N_2 molecules. The extracted implantation depths for ion energies of 25 and 16 keV are compared with theoretical values and suggest that the bond is broken during sample interaction. We use first principle molecular dynamics simulation to support this finding, in particular that the covalent bond is broken within the first few atomic layers of the impinged silicon target.

All nitrogen ion implantation was carried out in the GFIS-FIB nanofabrication system [2] located at the Japan Advanced Institute of Science and Technology. Line implantation was carried out on cleaned silicon. Following the cross section preparation STEM observation was conducted. For the 25 keV beam, an implantation depth of ~75 nm is observed, while this decreases to ~35 nm for the case of 16 keV. These values match the theoretically predicted values for the case that two nitrogen atoms are ionized with a single charge (N_2^+), and split upon impact. The splitting is also predicted by the molecular dynamics simulation we conducted.

These results help to give a clearer picture of the nitrogen ionization in a GFIS and the resulting beam. After ionization of the N_2 molecule through electron tunnelling into the atomically sharp emission tip, the ion is accelerated to the energy $E = E_0$and focused onto the sample. Upon interaction with the sample surface, the covalent bond is momentarily split. Consequently, each of the nitrogen atoms has only half of the energy $E = E_0/2$. The ion charge is dissipated in the substrate by transfer of an electron.

The help of M. Uno with the usage of the GFIS-FIB is acknowledged. The authors thank M. Ito for the help with TEM cross section preparation. This work is supported by the Center Of Innovation (COI) program of the Japan Science Technology Agency.

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6:00pm **HI+MI+NS-ThA12 Spatially Controlled Ripple Formation in the HIM using Low Voltages and High Temperatures***, **Gregor Hlawacek**, L. Sottili, M. Engler, S. Facsko,* Helmholtz-Zentrum Dresden Rossendorf, Germany

Ripple formation is a well known phenomenon that is observed for many materials under low energy ion bombardment. Often broad beam noble gas ion irradiation using energies of a few keV is employed to create these self-organized patterns on various metal, semiconductor and insulator surfaces. In addition to the fundamental interest in the formation and evolution of these structures they can be utilized in a number of new applications. Creating nano scale periodic roughness can be of interest for various microfluidic applications or to control friction in new MEMS and NEMS devices. However, these applications are not realized at their full potential today as the required sub micron patterning which can not easily be realized using broad beams.

Here, we present for the first time ripple patterns that have been created on the GaAs(001) surface using 5 keV Ne ions and elevated temperatures of up to 600 K in a Helium Ion Microscope (HIM). We will present the home built sample heater that can be loaded through the load lock of the Carl Zeiss Orion NanoFab and describe the influence on the device performance, as well as HIM operation at 5 keV.

The evolution of the ripple wavelength changes from 30 nm at low 1e17 Ne/cm² to 80 nm at 1e18 Ne/cm². The orientation of the ripples with respect to the shape can be changed by rotating the pattern on the surface and the influence of the geometrical constrains of the irradiated area on the ripple pattern is studied.

Spectroscopic Ellipsometry Focus Topic
Room 104C - Session EL+AS+EM+MI+TF-FrM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Morten Kildemo, Norwegian University of Science and Technology, Nikolas Podraza, University of Toledo

8:20am **EL+AS+EM+MI+TF-FrM1 Magnetoopticalproperties of Metals, Half-Metals, and Garnets Probed by Vector-Magneto-Optical Generalized Ellipsometry***, **Heidemarie Schmidt**,* Technische Universität Chemnitz, Nano-Spintronics Group, Germany **INVITED**

Magnetotransport measurements are a standard technique for the electrical characterization of single layers on insulating substrates. However, magnetotransport measurements require electrical contacts and known current paths, which excludes application to multilayer stacks. Motivated by the recent development of fast Mueller matrix ellipsometers, we have set-up a vector magnetooptical generalized ellipsometer (VMOGE) with an 0.4 T octupole magnet [1] and have investigated magnetooptical response of a single layers and multilayer stacks in a magnetic field of arbitrary orientation and magnitude up to 0.4 T at room temperature. We assume that the off-diagonal element of the magnetooptical dielectric tensor of every magnetizable layer in the multilayer stack is a product of the magnetic field independent and wavelength dependent complex magnetooptical coupling constant and the magnetic field dependent and wavelength independent magnetization of the layer. As an example, the complex magnetooptical coupling constant of nominally 10, 20, and 30 nm thick ferromagnetic Ni films obtained from modelling corresponding VMOGE data is discussed. It was challenging to identify the magnetization direction of Ni films from different sets of magnetic field dependent Mueller matrix elements [2]. In the future knowledge of complex magnetooptical coupling constant of all magnetizable materials in a multilayer stack will allow for modelling and optimizing the magnetooptical response of given stack. As a second example, the modelled complex magnetooptical coupling constant of capped, ferromagnetic Fe, Ni20Fe80, Co, Ni80Fe20, and Ni thin films on ZnO substrates is discussed and related with the spin-dependent electronic bandstructure of given weakly correlated, magnetizable materials [3]. For this comparison the experimental complex off-diagonal elements of the magnetooptical dielectric tensor have been converted into theoretical complex off-diagonal elements of magnetooptical conductivity tensor. Finally, the experimental magnetooptical response of strongly correlated, magnetizable materials [4], e.g. half-metals and garnets, is presented and as an outlook development of new theoretical frameworks for calculating the bandstructure of such strongly correlated, magnetizable materials for a comparison with experiment is motivated. [1] K. M. Mok, N. Du, H. Schmidt, Rev. Sci. Instrum. 82 (2011) 033112; [2] K.M. Mok, C. Scarlat, G. J. Kovács, L. Li, V. Zviagin, J. McCord, M. Helm, H. Schmidt, J. Appl. Phys. 110 (2011)123110; [3] K.M. Mok, G. J. Kovács, J. McCord, L. Li, M. Helm, H. Schmidt, Phys. Rev. B 84 (2011) 094413; [4] G. Kotliar and D. Vollhardt, Physics Today 57 (2004) 53

9:00am **EL+AS+EM+MI+TF-FrM3 *In Situ* Terahertz Optical Hall Effect Measurements of Ambient Doping Effects in Epitaxial Graphene***, S. Knight,* University of Nebraska-Lincoln*; C. Bouhafs, N. Armakavicius, P. Kühne, V. Stanishev, R. Yakimova,* Linköping University, Sweden*; S. Wimer, M. Schubert,* University of Nebraska-Lincoln*; V. Darakchieva,* Linköping University, Sweden*; **Tino Hofmann**,* University of North Carolina at Charlotte

Recently, the cavity-enhanced THz optical Hall effect (THz-OHE) has been demonstrated as non-contact method to obtain free charge carrier properties using low-field permanent magnets [1,2]. A tunable, externally-coupled cavity is used to enhance the THz-OHE signal which allows the accurate determination of a sample's free charge carrier properties even at low magnetic fields. In this work we take advantage of this approach by integrating the permanent magnet into a gas flow cell. We demonstrate for the first time the application of the cavity-enhanced THz-OHE for the *in-situ* characterization of free charge carrier properties of monolayer graphene on Si-face 4H-SiC as a function of ambient conditions. The experiments were performed using a new rotating-analyzer THz ellipsometer at Linköping University. Upon changing the CO_2, H_2O, and O_2 concentration in the cell, large variations in both free charge carrier sheet density N_S and mobility μ are observed for the *n*-type graphene. The lowest N_S was found for the as-grown sample with $N_S = 5.9(1) \times 10^{11}$ cm^{-2} where $\mu = 2507(57)$ cm^2/Vs. The highest N_S was found after purging the sample with nitrogen for 6 hours with $N_S = 2.43(4) \times 10^{12}$ cm^{-2} where $\mu = 1604(23)$ cm^2/Vs. These significant changes are attributed to a redox-reaction of oxygen and water at the graphene surface which results in the extraction of electrons from graphene [3]. This will be discussed in detail in our presentation. We further observe that this doping mechanism is only partially reversible at room temperature upon removal of oxygen, carbon dioxide, and water by purging the cell with nitrogen. In conclusion, we demonstrate *in-situ* THz-OHE as a new and powerful technique to determine ambient-dependent doping mechanisms which is illustrated here using monolayer epitaxial graphene on Si-face 4H-SiC.

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9:20am **EL+AS+EM+MI+TF-FrM4 Excitons at Interfaces in Ellipsometric Spectra***, **Nuwanjula Samarasingha**, C. Rodriguez, J.M. Moya, N.S. Fernando, S. Zollner,* New Mexico State University*; P. Ponath, K. Kormondy, A. Demkov,* University of Texas at Austin*; D. Pal, A. Mathur, A. Singh, S. Dutta, J. Singhal, S. Chattopadhyay,* Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants and ellipsometry spectra of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the E_1 critical points are strongly enhanced by two-dimensional excitons, even at room temperature. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. Excitons also influence the dielectric function of $SrTiO_3$. An exciton is an electron-hole pair bound by the Coulomb interaction, with properties similar to a hydrogen atom. The influence of excitonic absorption on the dielectric function was described by Tanguy.

In a thin epitaxial layer (with a thickness below or near the Bohr radius) on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In a thin type-I quantum well, consisting of a narrow-gap semiconductor grown on a large-gap substrate, both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the dominant absorption peak at 4.2 eV is larger in a 20 nm thick $SrTiO_3$ layer on a $LaAlO_3$ substrate than in bulk $SrTiO_3$. (The band gap of $LaAlO_3$ is larger than that of $SrTiO_3$.)

On the other hand, in a staggered type-II quantum well, either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element (and thus the excitonic absorption) is strongly reduced, because one quasiparticle resides in the quantum well and the other one in the substrate. If a $SrTiO_3$ layer is grown on Si or Ge, the valence band maximum occurs in the substrate, while the conduction band offset is very small. Therefore, the exciton wave function is delocalized (deconfined), which reduces the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin $SrTiO_3$ layers on Si or Ge are much smaller than in the bulk and decrease monotonically with decreasing thickness. A similar effect can be seen for thin ZnO layers on Si as a function of thickness.

The dielectric function of $SrTiO_3$ is not only affected by layer thickness. A very thick polycrystalline $SrTiO_3$ layer on Si has a much lower dielectric function than a single-crystalline $SrTiO_3$ substrate. In this case, we speculate that the magnitude of the dielectric function is related to other Tanguy parameters, perhaps the excitonic binding energy or the exciton decay rate (broadening). To investigate this further, we will perform temperature-dependent ellipsometry measurements on bulk zinc blende GaP, which has a much simpler band structure than wurtzite ZnO or the correlated metal oxide $SrTiO_3$, but shows similar excitonic effects.

9:40am **EL+AS+EM+MI+TF-FrM5 Infrared and Visible Dielectric Properties of $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$***, **Jacqueline Cooke**, N.T. Nunley, T. Willett-Gies, S. Zollner,* New Mexico State University

Using spectroscopic ellipsometry, we determined the dielectric function of LSAT, from the mid-IR to the deep UV (0.03 to 6.5 eV). LSAT is an acronym for the chemical formula $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$, equivalent to $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$. LSAT is a common substrate for epitaxial growth of complex metal oxides. Precise knowledge of the optical constants is useful to investigate the properties of epitaxial films grown on LSAT. We also investigated the band gap and the infrared-active phonons. Czochralski-grown LSAT wafers with (001) surface orientation were obtained commercially (MTI Corp., Richmond, CA). Single-side polished wafers were used for spectroscopic ellipsometry and two-side polished wafers with 0.5 mm thickness for transmission. Between 0.8 and 6.5 eV, we measured the normal-incidence transmission and the ellipsometric angles from 60° to 80° incidence in 2° steps on a J.A. Woollam variable angle of incidence ellipsometer with a computer-controlled Berek waveplate compensator. We also measured in the mid-IR on a rotating compensator FTIR ellipsometer. Transmission measurements show a steep rise of the absorption coefficient (α) between 4.6 and 4.8 eV, where LSAT becomes opaque. Fitting the ellipsometry data with a model containing two Tauc-Lorentz oscillators and 19 Å surface roughness thickness yields an excellent fit to the data. The Tauc gap is 4.9 eV and the high-frequency dielectric constant ε_∞= 4.0. Plotting α^2 versus photon energy yields a direct band gap of 5.8 eV. An Urbach tail extends towards lower energies. The resulting dielectric function is in agreement with previous ellipsometry and minimum-deviation prism measurements. The mid-IR dielectric function shows four ε_2 peaks due to TO phonon absorption. The loss function shows four LO peaks. A fifth TO phonon was seen at 155 cm^{-1} in far-IR ellipsometry. An ideal ABO3 perovskite has only three IR-active TO phonons. FCC ordering on the B-site as in (Sr_2AlTaO_3) adds a fourth phonon. We argue that the TO phonons at 155 and 283 cm^{-1} are vibrations of the tetrahedra against the La/Sr sublattices, respectively (mode splitting due to disorder). On the other hand, the 397 and 442 cm^{-1} modes are B-O bending modes due ordering in the Al/Ta sublattice. Finally, a B-O stretch mode at 664 cm^{-1} and broad two-phonon absorption at 765 cm^{-1} are also found. Fitting the spectra with a factorized TO/LO model yields better results than a sum of Lorentzians, because the individual TO/LO pairs are not well separated. The presence of FCC ordering was also confirmed with x-ray diffraction. We will also discuss temperature dependent ellipsometry and transmission measurements.

10:00am **EL+AS+EM+MI+TF-FrM6 A New Constant of Product of Electronic Scattering Time and Resistivity in Thin Silver Refractive Index Calculation from Ellipsometry and Resistivity Measurements***, **Guowen Ding**, C. Clavero, D. Schweigert, M. Le,* Intermolecular, Inc.

The optical and electrical response of metal thin films is highly affected by electronic scattering with the interfaces and defects. We are able to successfully model the electrical resistivity and near infrared (IR) optical response using a thickness dependent electronic scattering time. We investigated Ag films thickness in the range of 3 nm to 74 nm and determined that the product of electronic scattering time (τ) and resistivity (ρ) remains constant regardless of the thickness ($\tau \times \rho = C$), with a value of 59±2 μΩ cm·fs for Ag films. As a result, determining the constant C for a given thin film will allow to calculate the propreties of the film over a large range of wavelengths while limiting the number of measurements.Our findings enable us to develop a theoretical framework to determine the optical response of metal thin films in the near IR by using single wavelength ellipsometer measurements. An excellent agreement is found between experimental measurements and predicted values. We first reported this constant $\tau \times \rho =C$ for silver, and we posit that such constant concept could be applied for other conducting films. Application of the model presented here will allow rapid characterization of the IR optical response of metal thin films, with important application in a broad spectrum of fundamental and industrial applications, including optical coatings, low-emissivity windows and semiconductor industry.

10:20am **EL+AS+EM+MI+TF-FrM7 Realization of an *In Situ* Mueller-matrix Imaging Ellipsometer for the Real Time Observation of Surface Properties in an Ultra-high Vacuum EUV Facility***, **Pim Muilwijk**, N.B. Koster, F.T. Molkenboer, E. Sligte, te, A.F. Deutz, P. Walle, van der,* TNO Technical Sciences, Netherlands

TNO is realizing EUV Beamline 2 (EBL2), a facility to investigate the effects of Extreme Ultra-Violet (EUV) radiation on surfaces to enable future EUV High Volume Manufacturing (HVM) production. In this facility, samples with sizes up to 152x152x20 mm (6” EUV reticles) can be exposed to EUV radiation of up to 500W equivalent at intermediate focus (IF) under realistic environmental conditions and analyzed by in-situ ellipsometry and XPS. EBL2 consists of EUV source, automated handling system, beam line and an exposure chamber with an in-situ dual wavelength Mueller-matrix imaging ellipsometer.

Light from the dual wavelength light source (405 & 640nm) enters the exposure chamber through a polarizer, configurable retarder and a vacuum window producing a defined polarization state. After reflecting off of the sample, the light exits the exposure chamber through a vacuum window, configurable retarder and polarizer. The sample position is imaged on two camera’s, one for each wavelength. By combining all combinations of 4 polarization illumination states with 4 analyser states the full Mueller matrix of the sample can be recovered.

Calibration is performed in-situ with two insertable polarizers and two different calibration samples. The calibration procedure does not require prior knowledge of the polarizer orientation nor of the calibration samples.

This presentation will focus on the design and realization of the ellipsometer and will also touch upon the process of interpreting the data.

EBL2 will be publicly accessible as a test facility for EUV lithography related research after qualification, which is expected to be finished end of Q1 2017.

10:40am **EL+AS+EM+MI+TF-FrM8 Conducting, Semi-Conducting and Insulating 2D-Materials Characterized by Spectroscopic Imaging Ellipsometry***, **Matthias Duwe**, S. Funke,* Accurion GmbH, Germany*; U. Wurstbauer,* Technical University of Munich, Germany*; A. Matkovic,* University of Belgrade, Serbia*; A. Green,* SUNY College of Nanoscale Science and Engineering*; A. Molina-Mendoza,* Universidad Autonoma de Madrid, Spain*; A. Castellanos-Gomez,* IMDEA Nanoscience, Spain*; P.H. Thiesen,* Accurion GmbH, Germany

Finding thin-film flakes of 2D-materials after the fabrication and identifying their layer thicknesses often is a challenging and time-consuming task. Here, we present various applications of spectroscopic imaging ellipsometry (SIE) to a variety of conducting, semi-conducting, and insulating 2D-Materials such as graphene, molybdenum disulfide (MoS_2), hexagonal boron nitride, and black phosphorus. As a combination of polarization-contrast microscopy and spectroscopic ellipsometry, SIE measurements localize microscopic flakes of the 2D-materials, yield the samples’ optical dispersion functions, and determine the layer thicknesses.

Matkovic et al. [1] characterized monolayers of graphene by SIE, and they obtained the optical dispersion by Fano-resonance modelling. Using this dispersion, SIE offers a straightforward search for and identification of few-layer graphene flakes on various opaque or transparent substrates. As this flake search uses ellipsometric measurements, it depends far less on the used substrate compared to e.g. conventional light-microscopy. In a similar procedure, SIE identified monolayers of insulating hexagonal boron nitride, and it yielded the material‘s optical properties.

SIE measurements on MoS_2 revealed the repercussion of the used substrate [2]. Ellipsometric contrast micrographs showed the lateral variation of the optical parameters for a structured flake. Spectroscopic measurements of the ellipsometric values (Ψ & Δ) obtained from selected regions of interest on the flake yielded the optical dispersion for the in-plane and out-of-plane components of the dielectric function in the visible spectral range.

Finally, we will present imaging Mueller-matrix ellipsometry (IMME) for the characterization of thin-film flakes of the semi-conducting 2D-material black phosphorus. In contrast to MoS_2, black phosphorus also features an optical in-plane anisotropy. IMME-micrographs easily reveal this anisotropy as the Mueller matrix's off-diagonal blocks deviate from zero. By performing spectroscopic Mueller-Matrix mapping and rotational Mueller-matrix measurements combined with atomic force microscopy, we obtained the flake’s layer thickness, the orientations of the optical axes, and the material's optical properties in the visible spectral range.

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