

Monday Morning, October 19, 2015

Atom Probe Tomography Focus Topic

Room: 230A - Session AP+AS+MC+MI+NS-MoM

Atom Probe Tomography of Nanomaterials

Moderator: Daniel Perea, Pacific Northwest National Laboratory

8:20am **AP+AS+MC+MI+NS-MoM1 Correlative Multi-scale Analysis of Nd-Fe-B Permanent Magnet**, *Taisuke Sasaki, T. Ohkubo, K. Hono*, National Institute for Materials Science (NIMS), Japan **INVITED**
(Nd,Dy)-Fe-B based sintered magnets are currently used for traction motors and generators of (hybrid) electric vehicles because of their excellent combination of maximum energy product and coercivity. However, there is a strong demand to achieve high coercivity without using Dy due to its scarce natural resources and high cost. In Nd-Fe-B sintered magnets, thin Nd-rich grain boundary (GB) phase is a key microstructural feature affecting the coercivity. Although Nd-rich phases, e.g. Nd-rich oxides and metallic Nd, located at grain boundary triple junctions affect the formation of the Nd-enriched grain boundary phase during post-sinter annealing, their phase constitution, distribution and orientation relationships are still under debate.

This presentation will introduce examples of advanced characterization works to establish the global microstructural feature that controls the coercivity of Nd-Fe-B sintered magnets, e.g. the clarification of phase constitution and distribution of Nd-rich phases at the grain boundaries by correlative SEM and TEM characterization, and the identification of the structure and chemistry of thin Nd-rich grain boundary phases by high resolution HAADF-STEM and 3D atom probe. We found the coercivity decrease by carbon impurity can be explained by the decrease in the RE (RE: Rare earth) content in the thin Nd-rich grain boundary phase.

9:00am **AP+AS+MC+MI+NS-MoM3 Atom-Probe Tomography of Materials with Dimensions in the Nanometer Range**, *Dieter Isheim*, Northwestern University **INVITED**

Nanometer-sized materials and particles seem to naturally lend themselves for investigation by atom-probe tomography (APT) which provides analytical imaging with subnanometer-scale spatial resolution in three dimensions. The material's characteristic dimensions may already be close to the one required to produce the electric field necessary for analysis by field-evaporation in an atom-probe tomograph and thus analysis seems straight forward. In practice, however, controlled manipulation and positioning of these nanoparticles or nanowires for APT analysis proves challenging since the support structure of an APT tip must be strong enough to resist the mechanical stresses exerted by the high electric fields involved. Additionally, the nanoparticles should ideally not be altered or damaged in the preparation process. These requirements can be met by modern processing techniques that combine suitable deposition methods for packaging nanoparticles in structures that are either ready for analysis, or suitable for subsequent APT tip preparation by a standard technique. Focused-ion-beam (FIB) microscopes equipped with a micro- or nanomanipulator and gas injection systems for electron- or ion-beam induced deposition provide a versatile platform for packaging, cutting, joining, and manipulating nanostructured materials, and thus to capture and target nanoparticles or specific microstructural features for APT analysis. This presentation explores these techniques to characterize a variety of nanometer sized and nanostructured materials, including nanodiamond particles and catalytically grown silicon nanowires.

9:40am **AP+AS+MC+MI+NS-MoM5 Exploring Atom Probe Tomography for Energy Storage and Conversion Materials**, *Pritesh Parikh*, University of California, San Diego, *A. Devaraj*, Pacific Northwest National Laboratory, *S. Meng*, University of California, San Diego

The Sun forms the largest and most abundant source of energy on earth, yet it is not exploited to its full potential. Solar energy is a burgeoning field with a real chance to replace fossil fuels. The intermittent presence of sunlight can be mitigated by combining energy conversion devices such as solar panels with energy storage devices, namely Li ion batteries. A true solution is possible with the integration of both solar panels and batteries. With the general impetus towards adopting renewable sources for large scale energy storage and supply, fundamental studies on solar panels and batteries will provide new clues to design the next generation of energy devices. A Perovskite solar cell is one such technology that has the potential of high efficiency and low processing costs but a clear understanding of the role of different materials and their individual interactions is still lacking. The ability to identify and understand interfaces and multiple layers in a

complex device such as solar cells and batteries is the need of the hour. Here we report on laser assisted atom probe tomography of energy storage and conversion devices to identify the spatial distribution of the elements comprising the various layers and materials. Recent progress and significant challenges for preparation and study of perovskite solar cells and battery materials using laser assisted atom probe tomography will be discussed. This opens up new avenues to understand complex multi-layer systems at the atomic scale and provide a nanoscopic view into the intricate workings of energy materials.

10:00am **AP+AS+MC+MI+NS-MoM6 Atom Probe Tomography of Pt-based Nanoparticles**, *Katja Eder, P.J. Felfel, J.M. Cairney*, The University of Sydney, Australia

Pt nanoparticles are commonly used as catalysts in fuel cells. There are a lot of factors which influence the activity of a catalyst, including the surface structure and geometry [1], d-band vacancy of the metal catalyst [2], the type of metal oxide support [3] and the oxidation state of the surface [4]. It is not yet fully understood in which way these factors influence the activity of the catalyst, since it is experimentally very difficult to get atomic scale information about the distribution of the atoms within such particle with conventional methods like transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) and others. Models available which try to explain the structure-activity relationships therefore vary widely and there is much debate in the scientific literature about the underlying mechanisms of catalysis. For this reason it is crucial to conduct more research with methods that are able to obtain chemical information with a resolution on the atomic scale. In the past few years atom probe tomography (APT) has successfully been used in several studies to analyse nanoparticles [4-6]. APT provides a 3D reconstruction of the original specimen, which gives information about the chemical composition and the microstructure at a very high resolution. This method will enable us to have a closer look at the surface and interfaces as well as the composition of individual nanoparticles and solute atoms. In this talk we will present APT results of Pt nanoparticles, describing our efforts to prepare specimens with a reasonable yield and improved throughput compared to earlier studies, as well as some of the approaches used to overcome the difficulties that this challenge presents.

[1] A.R. Tao, S. Habas, P. Yang, *Small*, 4 (2008) 310-325.

[2] M.-K. Min, J. Cho, K. Cho, H. Kim, *Electrochimica Acta*, 45 (2000) 4211-4217.

[3] T. Akita, M. Kohyama, M. Haruta, *Accounts of chemical research*, (2013).

[4] T. Li, E.A. Marquis, P.A.J. Bagot, S.C. Tsang, G.D.W. Smith, *Catalysis Today*, 175 (2011) 552-557.

[5] Y. Xiang, V. Chitry, P. Liddicoat, P. Felfel, J. Cairney, S. Ringer, N. Kruse, *Journal of the American Chemical Society*, 135 (2013) 7114-7117.

[6] D.J. Larson, A.D. Giddings, Y. Wu, M.A. Verheijen, T.J. Prosa, F. Roozeboom, K.P. Rice, W.M.M. Kessels, B.P. Geiser, T.F. Kelly, *Ultramicroscopy*, (2015).

10:40am **AP+AS+MC+MI+NS-MoM8 APT & TEM Observations on Local Crystallization of NbO₂ used in Switching Devices**, *J.-H. Lee*, Pohang University of Science and Technology (POSTECH), Samsung Electronics, Republic of Korea, *J.-B. Seol*, *C.-G. Park*, Pohang University of Science and Technology (POSTECH), National Institute for Nanomaterials Technology (NINT), Republic of Korea **INVITED**

Threshold switching is the basis of electrical or thermal-driven phase change mechanism of oxide layer. That is, some oxide can change their conductivity from the level of insulators to that of metals with above certain current density. Although the mechanism responsible for threshold switching is not fully understood at present, it can be used as a switching device for the solution of sneak leakage problem. In order to apply the bipolar switching materials as the active layer of Resistive-switching Random Access Memory (RRAM), selection device which can minimize the sneak leakage current is needed. Among various candidates, we chose Nb-oxide for the selection device due to its superior compatibility with semiconductor structure. We have elucidated the mechanism of threshold switching of the amorphous NbO₂ layer by using in-situ transmission electron microscopy (TEM) technique combined with atom probe tomography (APT).

In this study, we proved that through an ex-situ experiment using TEM the threshold switching of amorphous NbO₂ accompanies local crystallization. The change in I-V characteristics after electroforming was examined by evaluating the concentration profile. APT combined with in-situ TEM probing technique was performed to understand the threshold switching in

amorphous NbO₂. The local crystallization in amorphous NbO₂ was validated by the observed difference in time-of-flight (ToF) between amorphous and crystalline NbO₂. We concluded that the slower ToF of amorphous NbO₂ (a-NbO₂) compared to that of crystalline NbO₂ (c-NbO₂) is due to the resistivity difference and trap-assisted recombination.

11:20am **AP+AS+MC+MI+NS-MoM10 Correlating Atom Probe Tomography with High-Resolution Scanning Transmission Electron Microscopy and Micro-Photoluminescence Spectroscopy: The Case of III-Nitride Heterostructures**, *Lorenzo Rigutti*, University of Rouen
INVITED

Correlating two or more microscopy techniques on the same nanoscale object may yield a relevant amount of information, which could not be achieved by other means. In this contribution, we present several results of correlated studies of micro-photoluminescence (μ -PL), high-resolution scanning transmission electron microscopy (HR-STEM) and laser-assisted atom probe tomography (APT) on single nano-objects containing AlGaInN quantum well and quantum dot systems. We will show how this approach can be applied to the study of heterostructure interface definition, presence of defects, carrier localization and optical emission in III-N quantum confined systems [1]. Furthermore, we will show how the use of complementary techniques may be extremely helpful for a correct interpretation of atom probe results [2]. The possible implementation of micro-photoluminescence as an in-situ technique within the atom probe itself will finally be discussed [3].

[1] L. Rigutti et al., Nano letters (2014), 14, 107–114.

[2] L. Mancini et al. J. Phys. Chem. C (2014) 118, 24136-24151.

[3] L. Rigutti et al., Ultramicroscopy (2013), 132, 75-80.

Monday Afternoon, October 19, 2015

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+2D+MI+NS+TF-MoA

Design and Discovery (Bio and Other Interfaces)
Moderator: Sean Jones, National Science Foundation (NSF), Lynnette Madsen, National Science Foundation (NSF)

3:00pm **MG+2D+MI+NS+TF-MoA3 Rational Accelerated Design of Polymer Dielectrics, Rampi Ramprasad, University of Connecticut**
INVITED

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass 'standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection.

3:40pm **MG+2D+MI+NS+TF-MoA5 Method to Make a Stable Copper-Carbon Alloy, Ivan Shchelkanov, D.N. Ruzic, I. Jasiuk, University of Illinois at Urbana Champaign**

Modern industry demands advanced materials with enhanced properties. To expand a range of available materials the covetic alloy is studied. Covetic is a novel alloy invented and patented by Third Millennium Metals, LLC (TMM). This is a new hybrid material made of a carbon and a metal, where the carbon forms a super lattice structure inside a metal. The base metal can be copper, aluminium, lead, tin or other low-melting point metals. In normal conditions the metal does not wet and does not form chemical bond with the carbon. However, the amount of carbon in the covetic alloy exceeds carbon solubility in the metal by several orders of magnitude. Such a composition is achieved by supplying a current to a volume of molten metal while it is being blended with micron size carbon particles. The alloy is prepared in vacuum.

The process of covetic formation is influenced by chemical composition of the base metal, a cast volume temperature change rate, external electric and magnetic fields, compound viscosity, surface and interphase tension coefficient, density, and thermal and electric conductivities of the metal and carbon particles. A part of the process of covetic alloy formation, which involves carbon particles dissolving, can be compared to phenomena occur in dust plasma. This assumption provides a possibility to visualise processes of microparticles spatial distribution and decomposition into single atoms with subsequent formation of a carbon super lattice inside the metal lattice.

The current work focuses on: the electric current influence on the alloy structure formation and carbon atoms distribution inside the metal; copper covetic hardness, conductivity, and tensile strength change as a function of carbon composition; and a phenomenological model for covetic alloy formation.

4:00pm **MG+2D+MI+NS+TF-MoA6 Development of Nanoporous Solid Phase Microextraction (SPME) Fibers by Sputtering, Matthew Linford, C.V. Cushman, B. Singh, A. Diwan, Brigham Young University**

Solid phase microextraction (SPME) is a solventless, fast, easy and relatively inexpensive sample preparation technique that integrates sampling, extraction and preconcentration of samples such as food, waste water, air, and biological fluids in one step. However, commercial SPME coatings may be expensive, show relatively short lives, extract limited numbers of compounds, and have relatively low thermal and mechanical stability. The aim of this study is to develop an SPME device that is thinner, robust, long lasting, has higher mechanical strength, greater thermal and solvent stability, and is devoid of the other drawbacks of commercial coatings. We describe a new method for the preparation of nanoporous SPME coatings via the oblique-angle sputtering of silicon and subsequent

functionalization with silanes. The thickness of the sputtered coatings was controlled by varying the sputtering time. To increase the density of -OH groups on the surfaces, the coatings were treated in piranha solution and then reacted with n-octadecyldimethylmonomethoxysilane to render the surfaces hydrophobic. The coatings were robust and were characterized at each step in the process using XPS, water contact angle goniometry, spectroscopic ellipsometry, and scanning electron microscopy. Our sputtered, silanized fiber yielded comparable and/or better extraction efficiencies than a commercial 7 μm PDMS fiber, especially for higher molecular weight species. In the case of a series of primary alcohols, and aldehydes, our fiber outperformed the commercial PDMS fiber by a factor of 2 - 3. In the evaluation of two real world samples: a sea water extract and beer, our fiber showed unique selectivity. Our 1.1 μm fiber yielded comparable signals to 65 μm PDMS-DVB and 85 μm CAR-PDMS commercial fibers for higher molecular weight analytes. For a ~2.2 μm fiber, the performance of our fiber increased substantially.

Tuesday Morning, October 20, 2015

Magnetic Interfaces and Nanostructures

Room: 230A - Session MI-TuM

Oxides, Fluorides, and Spin Structures

Moderator: Greg Szulczewski, The University of Alabama

8:00am **MI-TuM1 Magnetic Interactions at Perovskite Oxide Interfaces**, *Yayoi Takamura, B. Li, R.V. Chopdekar*, University of California, Davis, *E. Arenholz*, Lawrence Berkeley National Laboratory, *A. Mehta*, SLAC National Accelerator Laboratory, *M.D. Biegalski, H.M. Christen*, Oak Ridge National Laboratory **INVITED**

Perovskite-structured oxides possess a wide range of intriguing and technologically relevant functional properties including ferromagnetism, ferroelectricity, and superconductivity. Furthermore, the interfaces of perovskite oxides have been shown to exhibit unexpected functional properties not found in the constituent materials. These functional properties arise due to various structural and chemical changes as well as electronic and/or magnetic interactions occurring over nanometer length scales at the interfaces, and they have the potential to be harnessed to enable new, more versatile, and energy efficient devices. In particular, magnetic exchange coupling at ferromagnetic/antiferromagnetic (FM/AFM) and FM/FM interfaces are crucial due to their applications in magnetic technologies such as magnetic read heads and nanostructured permanent magnets. In this talk, we report on a unique spin-flop coupling observed at FM $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO)/AFM $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ (LSFO) interfaces and contrast these interfaces to FM/FM interfaces consisting of hard FM $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ (LSCO) and soft FM LSMO where exchange-spring behavior has been observed. Detailed structural and magnetic characterization of the individual layers was carried out using a combination of resonant x-ray reflectometry and element-specific soft x-ray magnetic spectroscopy, which provide more insight into interfacial effects over conventional characterization techniques such as bulk magnetometry. Our results indicate that the complex interplay between the charge, lattice, spin and orbital degrees of freedom at perovskite oxide interfaces provides a versatile route to control magnetic switching behavior as required for advanced magnetic device applications.

8:40am **MI-TuM3 X-ray Imaging of Magnetism at the Nanoscale**, *Stefano Bonetti*, Stockholm University, Sweden, *R. Kukreja, Z. Chen*, Stanford University, *F. Macia, J.M. Hernandez*, Universitat de Barcelona, Spain, *A. Eklund*, KTH Royal Institute of Technology, Sweden, *D. Backes*, New York University, *J. Frisch*, SLAC National Accelerator Laboratory, *Y. Acremann*, Laboratorium für Festkörperphysik, ETH Zürich, Switzerland, *J. Katine*, HGST, *G. Malm*, KTH Royal Institute of Technology, Sweden, *S. Urazhdin*, Emory University, *A.D. Kent*, New York University, *Ohldag, J. Stöhr, H.A. Dürr*, SLAC National Accelerator Laboratory **INVITED**

In this talk, I will describe the new scanning x-ray transmission microscope instrument that we recently built at the Stanford Synchrotron Radiation Lightsource (SSRL), at the SLAC National Accelerator Laboratory. In a single experiment, we are now able to measure extremely small magnetic, elemental and chemical signals at the nanoscale (with 35 nm resolution), in buried layers. We can also achieve a temporal resolutions of 50 ps, and synchronize our instrument to a microwave generator in order to detect excitations of up to 10 GHz in frequency. In order to show the capabilities of our technique, I will present two of our most recent results.

At first, I will discuss our successful attempt to directly image the injection of spins from a thin film ferromagnet into a non-magnetic Cu layer, when a bias current is fed through the ferromagnet/non-magnet interface. The elemental and chemical specificity of x-rays allows us to distinguish spin accumulation on Cu atoms located at the interface from those within the bulk of the Cu film. Spin accumulation in the film gives rise to an average transient magnetic moment per Cu atom of $3 \times 10^{-5} \mu_B$ around the Fermi level, which we explain using Mott's two current model. We also find a greatly enhanced transient moment on the Cu interface atoms, which we attribute to enhanced spin dependent scattering via localized interface states.

Then, I will present the first time-resolved x-ray images of the spin-wave soliton generated by spin-torque when a spin-polarized current is injected from a nano-contact into an extended magnetic layer, a 5-nm thick permalloy ($\text{Ni}_{80}\text{Fe}_{20}$) film. The circular polarization of the photons, tuned at the resonant L_3 absorption edge of Ni, allows for selectively probing the dynamics of the magnetization in the film. By synchronizing the spin waves oscillations to the RF cavity of the synchrotron, we are able to create a phase resolved map of the magnetic excitation, i.e. a spin-wave "movie." The unprecedented combined temporal and spatial resolution, and the ability to look through the thick metal electrodes that provide the current

necessary to excite the dynamics, reveal intriguing details of the spin-wave dynamics. In particular, we observe the emergence of a novel localized spin-wave soliton with a nodal line, i.e. with p -like symmetry, qualitatively different from the predicted solitonic excitation with essentially cylindrical symmetry (i.e. s -like).

Our studies provide a deeper understanding of magnetism at the nanoscale, and highlight the importance of nanoscale time-resolved techniques to tackle the challenges of modern magnetism.

9:20am **MI-TuM5 Complex Fluorides: A New Class of Multiferroic and Magnetoelectric Materials**, *David Lederman, A. KC, T.A. Johnson, C. Cen, A.H. Romero, P. Borisov*, West Virginia University **INVITED**

Transition metal fluoride antiferromagnets have been used to study the fundamental properties of exchange bias and magnetism at the interface between antiferromagnets and ferromagnets. The highly ionic nature of these compounds makes them ideal candidates for studying fundamental magnetic properties. Less studied are multiferroic fluoride compounds such as the orthorhombic BaMF_4 or the perovskite NaMF_3 materials, where M is a transition metal. Recent theoretical and computational work has suggested that the some of the BaMF_4 compounds should be magnetoelectric and that the perovskite fluoride compounds in particular should have large canting of the antiferromagnetic structure which results in strong weak ferromagnetism. In this talk I will describe recent work in the growth of thin films of these materials using molecular beam epitaxy. Their magnetic properties were measured using SQUID magnetometry and their ferroelectric properties were measured using scanning probe microscopy and direct ferroelectric polarization measurements. For the BaMF_4 compounds, we were able to confirm that the Ni and Co compounds are multiferroic, while the Fe compound is definitely not multiferroic. I will also discuss the growth of NaMnF_3 thin films and their magnetic and dielectric properties as a function of temperature and magnetic fields.

11:00am **MI-TuM10 Spin-Dependent Size of Interband Hybridization Gap: The Interplay of Adlayer and Substrate States in Pb/Cu(111)**, *Markus Donath, S.N.P. Wissing, K.T. Ritter, A.B. Schmidt, P. Krueger*, Muenster University, Germany

In view of spintronics applications, spin-polarized valleys are a key issue to realize spin-polarized currents. To date, spin-polarized valleys have been discovered in surface states at high-symmetry points in momentum space (see, e.g., [1]). We propose and have discovered an alternative way of producing spin-polarized valleys via hybridization gaps induced by spin-orbit interaction. So far, spin-orbit-influenced hybridization led to spin-dependent avoided band crossings, yet with no energy gap of spin-dependent size, i.e., no spin-polarized valleys.

We investigated the unoccupied electronic structure of Pb/Cu(111) by spin- and angle-resolved inverse photoemission. In these studies, we discovered a hybridization gap with spin-dependent size, about 200 meV for the one and even larger than 500 meV for the other spin direction, although not in a fundamental band gap at the Fermi level. Yet more importantly, we revealed the mechanism behind the formation of this spin-dependent valley-like gap structure by a tight-binding model based on *ab initio* calculations: The way of how adlayer and substrate states interact [2].

[1] K. Sakamoto et al., Nat. Commun. **4**, 2073 (2013).

[2] S.N.P. Wissing et al., Phys. Rev. B (Rapid Communications), accepted (2015).

11:20am **MI-TuM11 Energy Dispersion and Spin Structure of Unoccupied Electronic States of BiTeI: A Matter of Surface Termination?**, *Christian Langenkämper*, K. Miyamoto, A.B. Schmidt, P. Krüger, M. Donath*, Westfälische Wilhelms-Universität Münster, Germany

Recently, a new class of "Rashba materials" has been discovered: Non-centrosymmetric materials like MoS_2 [1] and BiTeI [2] show a lifting of the spin degeneracy in the electronic structure due to the bulk Rashba effect. So far, studies on BiTeI are limited to the occupied band regime and its Rashba-type spin dependence. For future applications, e.g. opto-spintronics, a substantiated knowledge about the complete spin-dependent electronic structure, occupied as well as unoccupied, is needed.

We present a combined experimental and theoretical study on the unoccupied electronic structure of BiTeI along the Γ -K direction. In our spin-resolved inverse photoemission measurements, we found a strong influence of the sample quality on the energy dispersion around the Γ point. Based on band structure calculations, we attribute this effect to different

* Falicov Student Award Finalist

surface terminations, Te or I. Due to band bending, the different terminations have a direct consequence for the band dispersion. This effect is not observed at K, where the spectra do not depend on the surface quality. We will discuss this result in the context of *ab initio* band structure calculations. - In addition, we studied the spin structure of the bands along Γ -K. Around the Γ point, we found in-plane spin polarization in agreement with previous photoemission experiments for the occupied states [2]. Upon approaching K, the direction of the spin polarization rotates from in-plane to fully out-of-plane in accordance with the crystal symmetry.

[1] Suzuki *et al.*, Nature Nanotechnology **9**, 611 (2014)

[2] Ishizaka *et al.*, Nature Materials **10**, 521 (2011)

11:40am **MI-TuM12 Abnormal Asymmetric Domain Expansion and Skyrmion Bubble Stability in Thin Films with Strong Dzyaloshinskii-Moriya Interaction**, *Lucas Caretta, M. Mann, A.J. Tan, G.S.D. Beach*, Massachusetts Institute of Technology

The Dzyaloshinskii-Moriya interaction (DMI) at heavy-metal/ferromagnet interfaces can stabilize chiral spin textures [1]. It has recently been shown that field-driven bubble domain expansion in perpendicularly-magnetized thin films is asymmetric under the application of an in-plane field, which can be used to quantify the DMI effective field in the domain wall (DW) [2]. We have imaged domain expansion in Pt(3nm)/Co(0.9nm)/Pt(x)/GdOx(3nm) films using wide-field Kerr microscopy to characterize this behavior systematically as a function of DMI strength. In the case of null or weak DMI, realized when top and bottom Pt layers are of similar thickness, the in-plane field dependence of the DW velocity is well-described by the simple expansion model derived in Ref. [2]. However, in the case of strong DMI, we find a strongly nonmonotonic behavior due to flattening of the DW, minimizing Zeeman energy and DMI energy. Moreover, we show that when the ratio of the DMI effective field to the perpendicular anisotropy field is large, expanding bubble domains leave behind fine-scale dendritic structures, consisting of coupled 360 degree DWs. These dendritic structures can be manipulated to form stable skyrmion bubbles. We show that the stability of skyrmion bubbles is a strong function of the applied in-plane field near the DMI field. The skyrmion bubble annihilation field becomes deterministic at large in-plane fields.

1. A. Fert *et al.*, Nat. Nano., **8**, 152-156 (2013)

2. S.G. Je *et al.*, PRB **88**, 214401 (2013)

12:00pm **MI-TuM13 Control and Characterization of Magnetic Domain Patterns in Complex Oxide Microstructures**, *Michael Lee, T. Wynn, R.V. Chopdekar*, University of California, Davis, *E. Folven, J. Grepstad*, Norwegian University of Science and Technology, *A. Scholl, A. Young*, Lawrence Berkeley National Laboratory (LBNL), *S. Retterer*, Oak Ridge National Laboratory, *Y. Jia, B. Li, Y. Takamura*, University of California, Davis

Future memory devices must achieve improved storage density, stability, and low power consumption. To this end $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) is a promising material due to the confluence of many scientifically interesting functional properties, including ferromagnetism, colossal magnetoresistance, and high spin-polarization. The ability to tune these properties through a number of different stimuli is equally encouraging. In order to utilize LSMO the magnetic behavior of nanostructures must be well characterized, but due to the vast array of energetically competitive interactions present, size effects play a significant role in oxide nanostructures.

In this work we investigated the evolution of domain structure as a function of temperature in micromagnets patterned into epitaxial films of LSMO via x-ray photoemission electron microscopy (XPEEM). Results showed transitions from vortex to Landau patterns in circular patterns (2 μm in diameter) indicating that saturation magnetization and magnetocrystalline anisotropy (K_1) have different dependence on temperature. Additionally, squares (also 2 μm) with edges aligned along the hard magnetization axis began in the Landau state dictated by shape anisotropy, but developed distinct inner and outer flux closure structures as K_1 becomes stronger at lower temperatures. This could mean the creation of magnetic domain structures in devices that have more fine-tuned and efficient behavior. The presence of these novel spin-textures has been used to extract approximate fundamental magnetic parameters for LSMO at micro- and nano-dimensions. We have developed a method to extract values of K_1 from simulations of the observed XPEEM images. Parameters obtained from circular micromagnets were used to simulate other experimentally observed magnetic domain structures and confirm the validity of the procedure. This is a new analysis technique making it possible to locally measure magnetic properties in structures that would otherwise be difficult or impossible to characterize.

Novel spin-textures have been observed as a direct result of studying materials systems that express magnetocrystalline anisotropy. Using the newly developed technique, approximate values of magnetocrystalline anisotropy have been uncovered for the micromagnets studied to more clearly describe the magnetic behavior of LSMO nanostructures. The outcome of this project will improve the quality of future research due to a deeper understanding of the delicate balance of energies.

Thin Film

Room: 111 - Session TF+EM+MI+MS-TuM

ALD for Alternative Devices

Moderator: Paul Poodt, Solliance/TNO, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+MI+MS-TuM1 FAST-ALD™ with Close Proximity (CP) Plasma for Low Temperature Applications: Nano-Composite Layer (NCL) Stacks for Flexible Substrates**, *SangIn Lee*, Veeco **INVITED**

The stress of the film is an important factor in mechanical stability and reliability of the devices, especially flexible electronic applications and microelectro-mechanical systems (MEMS), because it causes mechanical cracks, delamination and degradation in reliability of the device. Moreover, mechanical integrity of nano-scaled devices requires not only the physical properties of the individual films such as thermal expansion coefficient and elastic modulus, but also integral structural properties such as interface adhesion, and therefore residual stress of the film need to be managed.

Veeco's proprietary ALD technology, Fast Array Scanning Technology (FAST-ALD™) with Close-Proximity (CP) Plasma, has unique characteristics that are differentiated from other spatial ALD technologies. CP-plasma in FAST-ALD™ provides very uniform radical streams onto the substrate without plasma-induced damages and substrate heating enabling FAST-ALD™ to provide plasma-ALD films and stable polymeric MLD films from CP Plasma which cannot be obtained from conventional plasma process, for high-quality films at extremely low temperature for use in stress-sensitive device applications such as low-k films on Si wafers or flexible functional films on plastic substrates.

Stresses in inorganic ALD layers can be offset by either carbon-incorporated dielectric (CID) interlayers or polymeric MLD interlayers. The relative percentage of the inorganic ALD film to CID interlayer can be changed to tailor the stress of the stacked film to the device requirements. In this experiment, the combinations of an inorganic dielectric layer (Al_2O_3) with CID interlayers as part of nano-laminates, obviously in the same philosophy with polymeric MLD interlayers, nano-composite layer (NCL) stacks were deposited at 80°C to control the stress of the stacks from tensile to compressive state and vice versa, by changing the thickness and atomic content of Al_2O_3 layer and materials. By changing the ratio of the thickness in NCL stacks, 4:2 stacked film (4 Al_2O_3 layers and 2 CID layers as a sub-stack) and 1:1 stacked film (1 Al_2O_3 layer and 1 CID layer as a sub-stack) with total 30nm thickness show very low tensile stress and compressive stress of +58MPa and -89MPa, respectively, indicating the potential application of these free standing film stacks to nano-scaled devices and/or environmentally sensitive devices. NCL stack shows higher immunity to cracks and competitive barrier properties than that of the single ALD layer. NCL concept approaches can be applied to semiconductor in low-k pore sealing and oxidation barrier in the backend-of-line (BEOL) and cutting-edge devices with flexible substrates.

8:40am **TF+EM+MI+MS-TuM3 Atmospheric Roll-to-Roll Spatial Molecular Layer Deposition for flexible barriers**, *Fieke van den Bruele, F. Grob, P. Poodt*, Holst Centre / TNO, Netherlands

Proper encapsulation of devices such as OLEDs and thin-film photovoltaics is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10⁻⁶ g/m²/day. To achieve these very low WVTRs, very high quality barrier layers are required, being pinhole free over the entire device area. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much.

The recent development of roll-to-roll and large-area Spatial ALD technology has spurred the interest in ALD for encapsulation and barriers. Thin layers of inorganic material (10-20 nm) made with (spatial) ALD have sufficiently low intrinsic WVTR but often do not meet the requirements for barriers because they are very sensitive to particles and roughness that lead to defects. Thick inorganic films are less sensitive to particles, but suffer

from stress and can have a limited flexibility. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x , Al_2O_3) with an organic layer that acts as stress relief layer but has no additional barrier functionality. One of those proposed interlayers for stress relief and flexibility are organic materials deposited through Molecular Layer Deposition (MLD). A well-studied example are the Alucones, prepared by reacting trimethyl aluminum with an alcohol. There are several reports on the barrier properties of Al_2O_3 – Alucone multilayer stacks, but the results seem to be inconclusive.

Assessing the flexibility these MLD layers are is not straightforward as measuring the mechanical properties of these very thin layers is difficult. We use a simple, qualitative method to test the flexibility of these MLD layers, by combining bending test with a polymer etch test to visualize cracks and other defects in the MLD film caused by bending. Preliminary results show that the flexibility of MLD layers, like their organic counterparts, largely depend on film thickness and can suffer from instability.

The next step in making MLD barriers is upscaling towards large-area and roll-to-roll production. We will present the results of our atmospheric roll-to-roll spatial MLD of alucones on polymer foils. Furthermore, an outlook to full-industrial scale R2R ALD/MLD production of barriers will be discussed.

9:00am **TF+EM+MI+MS-TuM4 Low Temperature, Temporal and Spatial Atomic Layer Deposition of TiO_2 using Titanium Tetra-isopropoxide as Precursor**, *Morteza Aghaee*, Eindhoven University of Technology, Netherlands, *P.S. Maydannik*, Lappeenranta University of Technology, Finland, *P. Johansson*, Tampere University of Technology, Finland, *M. Creatore*, Eindhoven University of Technology, Netherlands, *T. Homola*, *D.C. Cameron*, Masaryk University, Czech Republic, *J. Kuusipalo*, Tampere University of Technology, Finland

Spatial atomic layer deposition (S-ALD) is a technique which has been shown to lead to high quality moisture barrier films (e.g. Al_2O_3) in a roll-to-roll process¹. However, TiO_2 is expected to outperform Al_2O_3 because of its higher stability against long-term degradation than Al_2O_3 . For high throughput S-ALD at low temperature, highly reactive precursors with high vapour pressure are necessary. Titanium chloride is typically used but has the disadvantages of residual chlorine incorporation in the film and generation of corrosive by-products. Titanium tetra-isopropoxide (TTIP) is a valid alternative because of its high vapour pressure at room temperature compared to other titanium organometallic compounds². TTIP has not previously been used as a precursor for S-ALD.

In this work, a preliminary investigation has been carried out on the temporal ALD approach consisting of alternating exposure of a polyethylene naphthalate (PEN) substrate to the precursors TTIP and water, ozone or oxygen-fed plasma. The deposition was carried out at a substrate temperature of 80-120°C. The highest growth rate (0.056 nm/cycle) and refractive index (2.33) values have been obtained by using an O_2 -fed plasma. The water vapour transmission rates have been found to be lower than $5 \times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ at 38°C, 90% RH conditions for a film thickness of 20 nm. For the water process, WVTR values were found to be in the range of 10^{-3} for a 40 nm film.

Based on these results, a low pressure S-ALD process was developed using a Beneq TFS200R system. Titanium dioxide films were successfully deposited by TTIP and water as S-ALD precursors in the same temperature range as temporal, and their properties were characterised in terms of growth per cycle, refractive index and chemical composition. The growth rate saturated at precursor exposure time of 230 ms at every deposition temperature, which was slightly higher than the growth rate in temporal ALD mode at the same temperature range. Similar properties (refractive index and chemical composition) to temporal ALD have been obtained by adopting S-ALD.

¹ P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Soderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, and X. Zeng, *J. Vac. Sci. Technol. A* **32**, 051603 (2014).

² M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, T. Homola, M. Creatore, D. C. Cameron, Submitted to *J. Vac. Sci. Technol.* (2015)

9:20am **TF+EM+MI+MS-TuM5 Spatial Atomic Layer Deposition into Flexible Porous Substrates**, *Kashish Sharma*, University of Colorado at Boulder, *D. Routkevitch*, *N. Varaksa*, In Redox, *S.M. George*, University of Colorado at Boulder

Spatial atomic layer deposition (S-ALD) is important for ALD commercialization. S-ALD has been successfully demonstrated on flat substrates. In this work, S-ALD was examined on flexible porous substrates using anodic aluminum oxide (AAO) membranes and Li ion battery

electrodes. The AAO membranes were coated with ZnO ALD using diethylzinc and ozone as the reactants. The Li ion battery electrodes were coated with Al₂O₃ ALD using trimethylaluminum and ozone as the reactants. These experiments utilized a rotating cylinder reactor for S-ALD that is scalable to roll-to-roll operation [K. Sharma et al., , 01A132 (2015)].

ZnO S-ALD into the pores of AAO membranes depends on gas transport that is determined by the pore diameter, pore aspect ratio and reactant pulse duration. The reactant pulse duration is defined by the substrate speed in S-ALD. Different reaction conditions and AAO membrane characteristics were explored using energy dispersive spectroscopy (EDS) to measure the Zn coverage profiles. Substrate speeds were defined by rotating cylinder rates of 10, 100 and 200 revolutions per minute (RPM). The AAO pore diameters were 50, 100 and 150 nm.

For AAO pore lengths of 10 microns, the EDS analysis revealed that uniform Zn coverage profiles were obtained at 10 RPM. The Zn coverage profiles were less uniform at higher RPM values and smaller pore diameters. These results indicate that S-ALD into porous substrates is feasible. However, the uniformity of the ALD coverage will depend on reaction parameters and the characteristics of the porous substrate. In addition, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Li ion battery electrodes on flexible metal foil were coated with Al_2O_3 ALD using the S-ALD reactor at 10-100 RPM. Initial coin-cell testing has demonstrated that enhanced capacity stability of these cathode electrodes is obtained after 2-5 Al_2O_3 ALD cycles.

9:40am **TF+EM+MI+MS-TuM6 Accurate Precursor and Reactant Delivery for Quantitative Atomic Layer Deposition**, *Masafumi Kitano*, Stanford University, *M. Nagase*, *N. Ikeda*, Fujikin Incorporated, Japan, *P.C. McIntyre*, Stanford University

Atomic layer deposition (ALD) has been widely discussed in the literature from various points of view. Typically, the amount of the precursor and reactant supplied into the ALD chamber is dictated only by controlling valve operation time, and is not quantitatively defined. To achieve a more quantitative ALD process, we have developed new flow rate control system (FCS) which can accurately dose precursor and reactant into an ALD reactor. This FCS consists of an orifice plate, pressure sensor, thermal sensor, and piezo control valve. It can be heated to 250°C to achieve sufficient vapor pressure for most precursors used in ALD of various inorganic compounds and elements. The FCS controls the flow rate under critical expansion conditions (or choked flow conditions); the flow rate through the orifice is proportional only to the upstream pressure of the orifice.[1,2] The piezo control valve accurately controls the upstream pressure and, thus, the flow rate. This mode of operation makes it possible to control the dosing of precursor and reactant by simply operating an endpoint valve placed close to the ALD reactor, because the upstream pressure is controllable whether the gas flow is running or not.

We have demonstrated an ALD process with trimethylaluminum (TMA) and water vapor (H_2O) reaction for Al_2O_3 deposition using the FCS to accurately control dosing into the ALD reactor. Excellent uniformity and reproducibility of deposition, and high quality dielectric properties of the resulting Al_2O_3 films have been achieved. The critical doses of TMA and H_2O into the chamber have been found to achieve surface saturating ALD of Al_2O_3 on a silicon substrate.

[1] A. Guthrie, R. K. Wakerling, "Vacuum Equipment and Techniques" McGraw-Hill book company, Inc., pp17, (1949)

[2] R. H. Perry, D. Green, "Perry's Chemical Engineers' Handbook, Sixth Edition" McGraw-Hill Co., pp5-14, (1984)

11:00am **TF+EM+MI+MS-TuM10 ALD for Capacitor Technologies**, *Ramakrishnan Rajagopalan*, *C. Randall*, The Pennsylvania State University

Atomic layer deposition (ALD) is a powerful processing technique that can be used to modify interfacial processes occurring in electrochemical capacitors. Charge storage mechanism in electrochemical capacitors is either due to electrostatic double layer formation or pseudocapacitive faradaic interactions at electrode/electrolyte interfaces. The talk will present an overview of our efforts in developing pseudocapacitive vanadium oxide thin films using ALD approach on high surface area carbon electrodes. The deposition process is dependent upon the carbon properties such as surface functionalization and porosity. We will report our investigation of deposition of ALD films on nanostructured carbon electrodes with controlled porosity in mesopores (<20 nm) to ultramicropore (0.8 nm to 2 nm) ranges. ALD also facilitates the possibility of combining electrochemical effects with dielectric effects. ALD of dielectrics such as Al_2O_3 on electrodes used in aqueous, organic and lithium based electrolytes can mitigate the issues relating to electrochemical stability due to solvent decomposition reactions and leakage performance with limited effect on the ESR performance of the capacitor. There is also possibility of designing novel solid state capacitor structures that synergistically integrates the

electrical double layer interactions due to ions with dielectric energy storage.

11:40am **TF+EM+MI+MS-TuM12 Compositionally and Functionally Graded Hybrid Layer for High-Performance Adhesion, Yichuan Ding, R.H. Dauskardt, Stanford University**

Reliable bonding of organic/inorganic interfaces continues to be one of the most important challenges in multilayer devices including microelectronic, photovoltaic and display technologies. Hybrid molecular materials which contains both organic and inorganic components has been shown to be well suited for bonding organic/inorganic (metals, metal-oxides, nitrides, ...) interface, mitigating moisture degradation and even stress migration. The hybrid films (less than 100nm) made of two primary precursors, an epoxysilane and a zirconium alkoxide, have been deposited via solution based synthesis, with low cost and high throughput. By optimizing sol-gel chemistry and processing conditions, we achieved an impressive tenfold improvement in interfacial adhesion at the epoxy/Si substrate interface, and have proven the suppression of moisture degradation at the interface.

In this work, we emphasized on our newly developed spray deposition technique with more versatility and better suited to large-scale manufacturing. We utilized both bilayer coating and dual-sources spray strategies to create highly compositionally and functionally graded hybrid film compared with films achieved via traditional dip-coating. XPS depth profiling shows highly graded hybrid films with independent compositional control within 80nm can be achieved via spray coating in the dry regime. We took advantage of the compositional control brought by spray coating to unravel the structure-property relationships in the multi-functional hybrid films by varying components/parameters to fine tune the molecular structure of the resulting film and relate that to its properties obtained from our advanced thin-film mechanical testing techniques together with other chemical characterization techniques (XPS, FTIR, NMR and GCMS). The evolution of the hybrid molecular network during film process and how molecular level details of the hybrid film has a large effect on its mechanical properties were better understood.

Tuesday Afternoon, October 20, 2015

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MC+MI+NS+SP+SS+TF-TuA

Electronic and Magnetic Properties of 2D Materials

Moderator: Thomas Mueller, Vienna University of Technology, Austria, Xiaobo Yin, University of Colorado Boulder

2:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA1 Direct Capacitive Probe of Isospin Order in Graphene Bilayers, Andrea Young**, University of California at Santa Barbara **INVITED**

Bilayer graphene is a highly tunable electronic system in which electric fields can be used to control both the carrier density as well as the electronic structure. Like its monolayer cousin, the bilayer graphene Landau levels are characterized by approximate spin and valley degeneracy; unlike monolayer, however, the three dimensional structure of the bilayer allows control of the sublattice splitting with a perpendicular electric field. This feature has been used extensively to probe the phase diagram of interacting electrons, particularly within the zero energy Landau level, revealing a number of interacting states characterized by spin and/or valley order. Typically, however, the spin or valley order is inferred indirectly by varying conjugate fields and inferring the order from the resulting changes in conductivity. Here I will describe a technique capable of resolving layer-polarization directly through high sensitivity capacitance measurements. The measurements confirm the known features of the bilayer graphene phase diagram, while revealing several new phases and a series of sharp features associated with phase transitions between states of different layer polarization. These features suggest a new mechanism for inversion symmetry breaking in Bernal stacked bilayer graphene.

3:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA3 Patterning Hydrogenated Graphene via Electron Beam Irradiation, Woo-Kyung Lee, K.E. Whitener, J.T. Robinson, P.E. Sheehan**, Naval Research Laboratory

We demonstrate that electron-beam irradiation selectively removes hydrogen atoms from hydrogenated graphene (HG) prepared by the Birch reduction.¹ Hydrogen removal can pattern the surface with two different functionalities. First, we show that partially-hydrogenated graphene (Phg) on a SiO₂ substrate is ferromagnetic, and that the local magnetic strength can be tuned using e-beam irradiation. An e-beam lithography system enables us to modulate or eliminate the permanent magnetization over a large area to produce a patterned magnetic array. Secondly, since removal of the hydrogens converts the highly electrically insulating HG back into conductive graphene, we can write chemically isolated, dehydrogenated graphene nanoribbons (GNR) as narrow as 100 nm. These GNRs have a low sheet resistance ($\geq 31.5 \text{ K}\omega/\square$), only 10x that of the pristine graphene, and their Dirac points before and after e-beam irradiation appear at comparable gate voltages.

1. W.K. Lee et al., *Advanced Materials*, 27, 1774 (2015).

3:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA4 Large-Area Low-Pressure Synthesis of Single-Layer MoS₂ Films and Schottky-Barrier Formation upon Metal Deposition, Michael Gomez, J. Martinez, M. Valentin, L. Bartels**, UC Riverside

Using a high vacuum CVD process we are able to synthesize large area monolayer MoS₂ films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to 2cm² in size that are uniform and free of oxides. The films have pronounced photoluminescence intensity and are in Raman spectroscopy indistinguishable from exfoliated material. Metal contact formation to these films was investigated under UHV conditions utilizing X-Ray Photoelectron Spectroscopy. These measurements permit us to follow the formation of a Schottky Barrier with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS₂ valence band under metal deposition.

4:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA7 Accelerating the Discovery of Alternative Fuel Catalysts through Intelligent Computational Framework, Altaf Karim**, COMSATS Institute of Information Technology, Pakistan **INVITED**

In today's modern world of high performance computing, properties of materials can be predicted with high accuracy before these materials are

ever made. In this scenario my focus has been on the development of state of the art computational framework based on intelligent/ smart self-learning algorithms for the design and discovery of catalytic materials. By giving some examples, I will describe how this enterprise of the predictive multi-scale modeling/simulation has been passing through the stages of its evolution and how these complex algorithmic species integrated themselves into an intelligent python, which is helping scientists design & discover new materials for alternative fuel catalysis. In practice, our computational framework develops databases of candidate catalysts. Further this framework enables a set of algorithms to screen across a broad range of multi metallic catalytic materials with variable reactivity, selectivity, and stability while searching for materials with desired combination of properties required for the optimal catalytic performance for alternative fuel production. I would also explain that how our computational tools in catalyst design deal with the multi-component microstructures of catalysts composed of multi-element nano chunks. In order to tune up the rate limiting processes we can take advantage of the multi-element nano chunks. For example, on many catalytic surfaces the diffusion is rate limiting process for larger organic molecules. To enhance the diffusion such molecules on such surfaces, nano chunks of other materials (on which the diffusion of the organic molecules is comparatively higher) can be integrated in the catalyst's surface, which improves the overall performance of the catalyst in terms of overall reactivity and also selectivity. In addition to that our tools also help us to filter out, from the databases, stable multi-component microstructures of artificially engineered catalysts.

5:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA9 Probing Massive Dirac Electrons in Bilayer Graphene, Feng Wang**, University of California at Berkeley **INVITED**

Electrons in monolayer graphene are described by massless Dirac electrons, which exhibit unique quantum phenomena due to the pseudospin and Berry phase of the massless electrons. In this talk, I will discuss our effort in probing massive Dirac electrons in gapped bilayer graphene. In particular, I will discuss the topologically protected 1D conducting channel at the domain boundary of AB-BA bilayers, which can be attributed to the quantum valley Hall edge states in gapped bilayer graphene.

5:40pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA11 Combining Photoemission and Photoluminescence Microscopy to Study Substrate Transfer Process Effects in Chemical Vapor Deposited MoS₂ Monolayers, Olivier Renault, M. Frégnaux**, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *J. Bleuse*, Univ. Grenoble-Alpes & CEA-INAC, France, *H. Kim*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *D. Voiry, M. Chhowalla*, Rutgers University
Within the perspective of integrating two-dimensional transition metal dichalcogenides (2D TMDs) such as molybdenum disulfide (MoS₂), into devices, it becomes of utmost importance to assess the influence of each step of the device fabrication process on the optical and transport properties of the MoS₂ single layer (1L) domains. Particularly at the deposition stage the properties may be influenced by substrate effects [1], and later, transfer processes may further alter the desired properties of TMDs. This requires effective microscopic characterization techniques.

We present a characterization method combining photoemission microscopy (XPEEM and Kpeem) and photoluminescence microscopy to compare the structural, optical and electronic properties of both as-deposited and transferred MoS₂ 1L domains onto different substrates. XPEEM is used with laboratory sources in both direct space imaging for work function and core-level mapping [2] and particularly in the momentum microscopy mode (k-PEEM) to perform parallel angular imaging and retrieve the band structure in a one shot experiment [3]. Micro-photoluminescence spectroscopy at low (5K) and room temperature is used to detect the specific radiative recombination that occurs in MoS₂ 1L (direct band gap semiconductor behavior) and to evidence the eventual presence of midgap states caused by process-induced defects. The results of both characterization techniques will be presented for MoS₂ 1L domains transferred onto silica and gold substrates highlighting the roles of substrate nature (metal or insulant), surface roughness, and the presence of structural defects whether induced by the preparation process or intrinsic such as grain boundaries.

[1] Jin et al. Phys. Rev. Lett. 111 (2013), 106801.

[2] Kim, Renault, et al. Appl. Phys. Lett. 105 (2014) 011605.

[3] Mathieu et al., PRB 83 (2011) 235436.

Magnetic Interfaces and Nanostructures

Room: 230A - Session MI+SA-TuA

Spin Currents, Spin Textures and Hybrid Magnetic Structures

Moderator: Greg Szulczewski, The University of Alabama

2:20pm **MI+SA-TuA1 Spin Hall Effect in Metallic Multilayers**, *Georg Woltersdorf*, Martin Luther University Halle-Wittenberg, Germany, *M. Obstbaum, M. Decker, D. Wei, C.H. Back*, University of Regensburg
INVITED

The discovery of the spin pumping effect and the Spin Hall Effect (SHE) has stimulated the research on dynamics in metallic magnetic nanostructures. Here a comprehensive study of the SHE in metallic multilayers will be presented. We study the direct as well as the inverse SHE. In the case of the direct SHE a dc charge current is applied in the plane of a ferromagnet/normal metal layer stack and the SHE creates a spin polarization at the surface of the normal metal leading to the injection of a spin current into the ferromagnet [1,2]. This spin current is absorbed in the ferromagnet and causes a spin transfer torque. Using time and spatially resolved Kerr microscopy we measure the transferred spin momentum and compute the spin Hall angle. In a second set of experiments using identical samples pure spin currents are injected by the spin pumping effect from the ferromagnet into the normal metal [3]. The spin current injected by spin pumping has a large ac component transverse to the static magnetization direction and a very small dc component parallel to the magnetization direction. The inverse SHE converts these spin current into charge current [4,5]. The corresponding inverse SHE voltages induced by spin pumping at ferromagnetic resonance (FMR) are measured in permalloy/platinum and permalloy/gold multilayers in various excitation geometries and as a function of frequency in order to separate the contributions of anisotropic magnetoresistance and SHE. In addition, we present experimental evidence for the ac component of inverse SHE voltages generated by spin pumping [6,7].

- [1] - K. Ando et al., Phys. Rev. Lett. **101**, 036601, (2008)
- [2] - V. E. Demidov et al., Phys. Rev. Lett. **107**, 107204 (2011)
- [3] - Y. Tserkovnyak, A. Brataas, and G.E.W. Bauer, Phys. Rev. Lett. **88**, 117601 (2002)
- [4] - E. Saitoh et al., Appl. Phys. Lett. **88**, 182509 (2006)
- [5] - O. Mosendz, et al., Phys. Rev. Lett. **104**, 046601 (2010)
- [6] - H. Jiao and Gerrit E. W. Bauer, Phys. Rev. Lett. **110**, 217602 (2013)
- [7] - D. Wei et al. Nat. Comm. **5**, 3768 (2014)

3:00pm **MI+SA-TuA3 Chiral Spin Textures in Ultrathin Ferromagnets**, *Geoffrey Beach*, Massachusetts Institute of Technology
INVITED

Spin orbit coupling at interfaces in ultrathin magnetic films can give rise to chiral magnetic textures such as homochiral domain walls and skyrmions, as well as current-induced torques that can effectively manipulate them [1-3]. This talk will describe the statics and dynamics of chiral spin textures in thin-film nanowires stabilized by the Dzyaloshinskii-Moriya interactions (DMI) at a heavy metal/ferromagnet interface. We show that the DMI depends strongly on the heavy metal, differing by a factor of ~20 between Pt and Ta [2], and describe the influence of strong DMI on domain wall dynamics [1,2] and spin Hall effect switching [3]. We present high-resolution magnetic imaging of static magnetic textures that directly reveal the role of DMI and allow its strength to be quantified [4]. Finally, we will describe how a gate voltage can be used to control interfacial magnetism and magnetic domain walls in nanowires by manipulating interfacial oxygen coordination and magnetic anisotropy at a ferromagnet/oxide interface [5].

- [1] S. Emori, et al., Nature Mater. **12**, 611 (2013).
- [2] S. Emori, et al., Phys. Rev. B **90**, 184427 (2014).
- [3] N. Perez, et al., Appl. Phys. Lett. **104**, 092403 (2014).
- [4] S. Woo, et al., arXiv:1502.07376 (2015).
- [5] U. Bauer, et al., Nature Mater. **14**, 174 (2015).

4:20pm **MI+SA-TuA7 Indirect Modification of Magnetic Surface States by Organic Semiconductor Adsorbates**, *Daniel Dougherty, J. Wang*, North Carolina State University
INVITED

The spin-dependent electronic coupling of organic molecules to magnetic electrode surfaces is now widely acknowledged to be a crucial factor controlling direct spin injection in organic spintronic devices. This suggests the application of known surface chemisorption principles can guide new

developments in this field. However, the kinds of interactions possible at metal-organic semiconductor interfaces are diverse and direct orbital coupling is not always guaranteed even when chemical intuition favors it. In this talk I will report on an unusual observation of indirect orbital coupling at a metal-organic interface even when direct coupling is geometrically plausible. We have observed that adsorption of the organic semiconductor perylene tetracarboxylic acid dianhydride onto Cr(001) decreases the metal *d*-derived surface state lifetime without causing a shift in its energy. This suggests an indirect electronic interaction that contrasts sharply with expectations of *p-d* electronic coupling based on direct chemisorption. Lifetime changes are measured with scanning tunneling spectroscopy as a function of temperature and quantified as arising from a molecule-induced increase in electron-electron scattering rate into bulk bands. Adsorbate-induced effects extend far beyond the adsorption site of the molecule, decaying exponentially away with a characteristic length scale of ~2.4 nm, similar to the carrier mean free path in Cr.

5:00pm **MI+SA-TuA9 Transitioning into the Ga-rich Regime of Ferromagnetic Manganese Gallium Films Grown on Gallium Nitride: Structure and Magnetism**, *Andrada-Oana Mandru*, J.P. Corbett, A.L. Richard*, Ohio University, *J.M. Lucy*, Ohio State University, *D.C. Ingram*, Ohio University, *F. Yang*, Ohio State University, *A.R. Smith*, Ohio University

Depositions of magnetic atoms such as Mn onto wide-gap semiconducting GaN surfaces give rise to various MnGa alloyed nanostructures, some having promising magnetic properties. Co-depositions of Mn and Ga result in ferromagnetic alloys that grow with high epitaxial quality on GaN. Such sharp interfaces undoubtedly make MnGa/GaN a very attractive spintronic system. Growth under slightly Mn-rich conditions (Mn:Ga composition ratio ~1.09) causes Mn atoms to incorporate at different rates; surfaces become highly Mn-rich, while the bulk retains a 1:1 stoichiometry. In addition, their magnetic properties could potentially be tailored by altering elemental composition and/or film thickness. Motivated by these intriguing observations and possibilities, we explore what happens when crossing the Mn:Ga 1:1 stoichiometric limit into the less studied Ga-rich side. We combine various techniques to investigate in detail the growth, structure and magnetism of MnGa alloys with different thicknesses and compositions, when coupled with GaN substrates.

Samples are prepared using molecular beam epitaxy with GaN/Sapphire used as starting substrate. Subsequent depositions involve a fresh film of GaN followed by thin (~30-50 nm) or ultra-thin (~3.3 nm) MnGa films. Manganese and gallium are co-evaporated from Knudsen cells while keeping the substrate temperature at ~250 °C. The growth is monitored in real time using a 20 keV reflection high energy electron diffraction system. *In-situ* room temperature scanning tunneling microscopy investigations reveal highly epitaxial films with smooth surfaces that exhibit a rich variety of reconstructions. The Mn:Ga composition ratios range from ~1 (stoichiometric) to ~0.42 (very Ga-rich), as determined by Rutherford backscattering spectrometry. For stoichiometric films, x-ray diffraction characterizations show primarily MnGa peaks; upon transitioning into the Ga-rich regime, we find a co-existence of Mn₃Ga₅ and Mn₂Ga₅ phases, with Mn₂Ga₅ becoming predominant for the highly Ga-rich samples. Magnetic investigations reveal that all films exhibit ferromagnetism, including the very Ga-rich ones. Vibrating sample magnetometry measurements performed on the thin samples show stepped hysteresis loops, along with a decrease in coercivity and magnetic moment values as the Ga concentration increases. Additional superconducting quantum interference device measurements performed on the ultra-thin samples show that large magnetic anisotropies are induced by decreasing the thickness of our films. Most recently, similar investigations applied to FeGa magnetostrictive alloys reveal very interesting surfaces and magnetic properties.

5:20pm **MI+SA-TuA10 A Depth-Dependent Model for Atomic Valence in Magnetoelectric Systems**, *Mikel Holcomb, R. Trappen, J. Zhou*, West Virginia University, *Y-H. Chu*, National Chiao Tung University, *S. Dong*, Southeast University

Interfacial magnetoelectricity across a multilayer system is known to sometimes result in much larger coupling between electric and magnetism than in single phase systems. The cause has been controversial, but the atomic valence of the magnetic element in these systems is known to change with an applied voltage. We wanted to understand how the interfacial atomic valence was effected as a function of film thickness in thin films of La_{0.7}Sr_{0.3}MnO₃ on PbZr_{0.2}Ti_{0.8}O₃. To separate the Mn valence at the interfacial layer with PZT from the bulk region of LSMO, we took advantage of the drastically different attenuation length of two techniques: x-ray absorption in *L*-edge total electron yield mode and *K*-edge fluorescence yield mode. By globally fitting both sets of experimental

* Falicov Student Award Finalist

results, we were able to develop a depth-dependent model to estimate the layer by layer valences in our materials as a function of thickness. This empirical model was developed under the guidance of theoretical work from a two-orbital double exchange model, which also explored the effects of substrate termination and ferroelectric polarization direction. Estimates based on the data and models for surface, interface and bulk valence as well as surface and interface length scales will be discussed.

5:40pm **MI+SA-TuA11 Atomic-Scale Magnetism on a Complex Insulating Surface**, *Barbara Jones*, IBM Research - Almaden, *O.R. Albertini*, Georgetown University, *S. Gangopadhyay*, IBM Research - Almaden, *A.Y. Liu*, Georgetown University

We will describe and analyze the unusual magnetic properties of transition metal atoms on complex, hybrid surfaces. In collaboration with IBM Almaden's Scanning Tunneling Microscopy team, we use DFT+U to calculate the properties of transition metal atoms on one or two atomic layers of insulator on top of a metal such as silver. We show the transition of the interface from bulk insulator or metal to a nanolayer that is nominally insulating, but that hybridizes strongly with the addition of a magnetic adatom to produce a long spin-polarized tail into the vacuum, akin to a metal. We report the results of detailed calculations of a range of magnetic atoms (Mn, Fe, Co, Ni) on MgO/Ag. MgO is a common spintronic insulator, but in a nanolayer on metallic Ag, its behavior is not that of the bulk. We find that each magnetic atom has its own surface signature, with very different local spin and charge interactions with this surface, and compare it to that of other related systems. Using an onsite Hubbard U parameter which we determine from first principles, we are able to study the variability of the magnetic moment and nature of bonding. The magnetic adatoms affect the surrounding interface layer in unexpected ways. We are able to obtain interesting insights which help us understand how magnetism propagates along surfaces as well as between interfaces. These systems have potential for future spintronics or quantum computing applications.

6:00pm **MI+SA-TuA12 Substrate Induced Spin-state Locking of [Fe(H₂B(pz)₂)(bipy)] on Au(111)**, *Sumit Beniwal**, *X. Zhang*, *S. Mu*, University of Nebraska - Lincoln, *A. Naim*, *P. Rosa*, *G. Chastanet*, CNRS Universite de Bordeaux, France, *J. Liu*, Northeastern University, *G. Sterbinsky*, *D. Arena*, Brookhaven National Laboratory, *P.A. Dowben*, *A. Enders*, University of Nebraska - Lincoln

Spin-crossover (SCO) complexes hold promise for spintronics applications as room-temperature single molecular magnets. Their signature functionality arises from a central transition metal atom, which is in a d⁴-d⁷ configuration in a (pseudo)octahedral N₆ environment and can be switched between a diamagnetic low-spin (S=0) and a paramagnetic high-spin (S=2) state by external stimuli such as temperature, pressure, light and electric field. The switching of the molecular spin-state is accompanied by change of other physical and electronic properties of these complexes, such as color, magnetic susceptibility and electrical conductivity. Application in devices requires that the molecules are in contact with metal electrodes, which can significantly alter their electronic and magnetic properties. This study makes use of a comprehensive suite of surface-sensitive spectroscopy and microscopy tools to investigate the electronic properties of SCO complex [Fe(H₂B(pz)₂)(bipy)] on Au(111) to identify characteristic signatures of spin-state of the molecules across thermal spin transition temperature. Variable temperature scanning tunneling microscopy, performed as a function of film thickness, revealed that ordering in the molecular layers is established as the films are cooled well below their spin transition temperature, and this ordering is maintained when the films are brought back to room temperature. Temperature and thickness dependent studies of electronic structure using X-ray photoemission (XPS), X-ray absorption spectroscopy (XAS) and inverse photoemission (IPES) on surface supported networks, reveal substrate effects on the spin state. Satellite features in core level XPS Fe 2p_{3/2} peaks are characteristic of the spin transition, whereas angle-resolved XPS (ARXPS) helps to separately determine the electronic structure of interfacial molecules and of molecules away from the interface. Fe L-edge X-ray absorption XAS spectra taken on ultrathin films suggest that the substrate inhibits thermally induced transitions of the molecular spin state, so that both high-spin and low-spin states are preserved far beyond the spin transition temperature of free molecules. These results demonstrate that thin films of the spin crossover complexes studied have distinctively different phase transition behavior as compared to bulk-like samples, which is evidence that interface interactions can considerably affect the molecules' structural conformation, spin state as well as electronic properties. Understanding such interface effects can help establish conditions to control the spin state of molecules and to engineer spin state transitions.

* **Falicov Student Award Finalist**

Tuesday Evening Poster Sessions

Magnetic Interfaces and Nanostructures

Room: Hall 3 - Session MI-TuP

Magnetic Interfaces Poster Session

MI-TuP1 Optical and Magneto-Optical Properties of $Zn_{1-x}Mn_xO$ / ZnO Hollow Nanospheres, *Da-Ren Liu, C.J. Weng*, National Applied Research Laboratories, Taiwan, Republic of China

Recently, diluted magnetic semiconductors (DMS) have generated widespread interest due to their potential applications for spintronic devices. Mn-doped ZnO is one of the most promising diluted magnetic semiconductors materials due to its room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanosphere with different diameter (100nm~800nm) by atomic layer deposition (ALD). Then the $Zn_{1-x}Mn_xO$ ($0 < x < 0.1$) coatings were grown on ZnO hollow nanospheres by pulsed laser deposition (PLD). According to the results of high-resolution x-ray diffraction, Mn-doping does not change the wurtzite structure of ZnO and the $Zn_{1-x}Mn_xO$ hollow nanospheres are polycrystalline. Photoluminescence spectra and transmittance show an increase of the band gap with the increasing Mn ion concentration. The magneto-optical properties of the $Zn_{1-x}Mn_xO$ / ZnO hollow nanospheres were measured by micro-MOKE spectroscopy and strongly depend on the Mn composition fraction.

MI-TuP3 Scanning Tunneling Microscopy Study of Magnetic Layers Grown on MgO(001) by Molecular Beam Epitaxy, *Jeongihm Pak, A.-O. Mandru, J.P. Corbett, A.R. Smith*, Ohio University

Magnetic coupling between ferromagnetic (FM) and antiferromagnetic (aFM) layers is of high importance to exchange bias and related magnetic technologies. It is essential to achieve atomically smooth and flat magnetic films onto which we can deposit transition metals (e.g. Fe, Mn and Cr) to create magnetic bi-layer systems that will allow us to probe possible magnetic coupling. In this study, we grow FM Fe and aFM Mn and Cr films on MgO(001) using molecular beam epitaxy (MBE) and investigate the surfaces using scanning tunneling microscopy (STM).

The growth experiments take place in an ultra-high vacuum (UHV)-MBE chamber, equipped with Fe, Mn and Cr effusion cells, a 20 keV reflection high energy electron diffraction (RHEED), and a quartz crystal sensor (for flux calibrations). Fe, Mn and Cr films are grown on MgO(001) over a range of sample temperatures. The prepared samples are transferred *in-situ* to the adjacent UHV room temperature STM analysis chamber for surface studies. The streaky RHEED patterns indicate single crystal films grown with smooth surfaces and STM topography images reveal atomically smooth and flat surfaces on each film. X-ray diffraction (XRD) confirms the (001) growth face for Fe and Cr. Magnetic force microscopy (MFM) is performed on each film to explore the magnetic domain structure. Ultimately, we aim to extend the present study to include spin-polarized STM measurements that will probe the magnetic coupling between FM and aFM layers, e.g. sub-monolayer Fe on Mn (or Cr) substrates (and vice versa).

Wednesday Morning, October 21, 2015

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-WeM

Magnetism, Complexity and Superconductivity in the Actinides and Rare Earths

Moderator: Tomasz Durakiewicz, Los Alamos National Laboratory

8:00am **AC+AS+MI-WeM1 The Valence-Fluctuating Ground-State of δ -Pu**, *Marc Janoschek*, Los Alamos National Laboratory **INVITED**

Plutonium (Pu) is arguably the most complex elemental metal known because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. This complex electronic structure leads to emergent behavior—all a direct consequence of its 5f electrons—including six allotropic phases, large volumetric changes associated with these transitions of up to 25%, and mechanical properties ranging from brittle α -Pu to ductile δ -Pu. Pu also exhibits a Pauli-like magnetic susceptibility, electrical resistivity and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. Finally, while experiments find no sign for static magnetism in Pu, most theories that use the correct volume predict a magnetically ordered state. This discrepancy might be reconciled by recent Dynamical Mean Field Theory (DMFT) calculations that suggest that the electronic ground state of δ -Pu is a quantum-mechanical admixture of localized and itinerant valence configurations. The question whether the ground state of δ -Pu is indeed a true quantum-mechanical superposition may only be answered via observation of the associated virtual valence (charge) fluctuations among the distinct $5f^6$, $5f^7$, and $5f^8$ configurations. The characteristic energy scale for the associated spin fluctuations is expected to $T_K \approx 800$ K ($E_{sf} \approx 70$ meV) that will result in a dynamical spectral response centered at this energy for $T < T_K$. We have performed high-energy inelastic neutron spectroscopy at room temperature using a large polycrystalline sample of δ - ^{242}Pu with a total mass of $m \approx 21$ g at the Lujan Center and at the Spallation Neutron Source. Our measurements demonstrate the existence of high energy magnetic fluctuations centered at $E_{sf} = 84$ meV, in good agreement with the DMFT calculations. In addition, they allow us to extract the magnetic form factor of δ -Pu, yielding critical information about its valence state. These unprecedented results place show that the magnetism in Pu is not "missing" but dynamic, but dynamic, and is driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of δ -Pu and associated Sommerfeld coefficient. Furthermore, because the various valence configurations imply distinct sizes of the Pu ion, the valence-fluctuating ground state of Pu also provides a natural explanation for its complex structural properties and in particular the large sensitivity of its volume to small changes in temperature, pressure or doping.

8:40am **AC+AS+MI-WeM3 Exchange Bias in Heterostructures Based on UO_2** , *Evgeniya Tereshina*, Institute of Physics ASCR, Czech Republic, *Z. Bao*, PANalytical B.V., Netherlands, *L. Havela*, Charles University in Prague, Czech Republic, *R. Springell*, University of Bristol, UK, *S. Danis*, Charles University in Prague, Czech Republic, *A. Mackova*, Nuclear Physics Institute ASCR, Czech Republic, *T. Gouder*, *R. Caciuffo*, Institute for Transuranium Elements (ITU), Germany **INVITED**

Interfacial exchange interaction in bilayers consisting of two dissimilarly ordered magnetic materials (e.g. an antiferromagnet (AF) and a ferro- or ferrimagnet (F)) may give rise to a phenomenon called the magnetic exchange bias (EB) effect [1]. The EB manifests itself as a shift of a magnetic hysteresis loop along the field direction when the bilayer is field-cooled below the Néel temperature (T_N) of the AF. This property is of great value for magnetic recording applications. Despite the conceptual simplicity, a generally accepted theory that predicts the EB behavior for an apt pair of materials is still missing. The reason for that might be in poorly defined interface structure in both magnetic and crystallographic aspects.

Critical dependence of EB on magnetic anisotropy brings us the possibility to use actinides with strong spin-orbit interaction as the key ingredient. Here we report exchange bias studies in magnetic bilayers consisting of a stoichiometric UO_2 film grown epitaxially on different substrates and covered with polycrystalline metallic ($\text{Ni}_{180}\text{Fe}_{20}$ and Fe) and highly textured oxide (Fe_3O_4) layers of variable thickness. Large longitudinal exchange bias ~ 2.6 kOe is found in $\text{UO}_2/\text{Fe}_3\text{O}_4$ bilayers [3] while UO_2 combined with metallic ferromagnets displays perpendicular exchange coupling with an order of magnitude smaller EB. Interestingly, unusual effects in $\text{UO}_2/\text{Fe}_3\text{O}_4$ were observed, namely, exchange bias did not vanish at T_N of UO_2 . Apart from the fact that single layers of magnetite were showing some EB (not

more than 25 % of the total effect in $\text{UO}_2/\text{Fe}_3\text{O}_4$), the EB in $\text{UO}_2/\text{Fe}_3\text{O}_4$ bilayers exceeded notably that of the single Fe_3O_4 's to approx. 70 K that was attributed to possible proximity effects of Fe_3O_4 on T_N of UO_2 and/or to the magnetic anisotropy of UO_2 preserved locally above T_N . The effects were observed for the samples of quality controlled by different methods such as X-ray Photoelectron Spectroscopy, conventional X-ray Diffraction, Transmission Electron Microscopy and Rutherford Backscattering Spectroscopy. The work has been supported by the Czech Science Foundation, grant No. 13-25866P.

[1] W. H. Meiklejohn and C. P. Bean, "New magnetic anisotropy", Phys. Rev. B 102, 1413 (1956).

[2] V. Sechovsky, L. Havela, in: Magnetic Materials, K.H.J. Buschow (Ed.), Elsevier, Amsterdam, 1998, Vol. 11, p. 1.

[3] E. A. Tereshina et al., Appl. Phys. Lett. 105, 122405 (2014).

9:20am **AC+AS+MI-WeM5 Transport and Magnetism of 4f and 5f Systems: What we can Learn from Thermoelectric Power**, *Krzysztof Gofryk*, Idaho National Laboratory **INVITED**

The interplay between different electronic ground states, especially magnetism and superconductivity, has evolved in a climate of discovery in which many of the fundamental rules of condensed matter physics are questioned by materials with unexpected properties. These "emergent properties," such as complex magnetism, heavy-fermion superconductivity, the coexistence of magnetism and superconductivity, and/or Kondo physics emerge from complex materials in which quasiparticles develop different states of organization and correlation. The majorities of these bizarre electronic ground states are encountered in f -electron systems and are linked to the hybridization between the f -states and ligand electrons. How these properties evolve with the progressive filling of the f -shells remains an open question, but it is a key ingredient for their understanding. The 4f and 5f strongly correlated electron systems at the border of magnetism are of active current interest, particularly because the accompanying quantum criticality provides a route towards both strange-metal, non-Fermi-liquid behavior, and unconventional superconductivity. In spite of large theoretical and experimental efforts the nature of the electronic behaviors is still unclear. One way to address the electronic properties of these fascinating materials is to perform extensive transport studies such as Hall, Nernst, or Seebeck effects. In particular, the latter one has gained importance in recent years in thermoelectric materials as potential solutions for applications, such as spot cooling of electronic components, waste heat recovery system and/or remote power generation in space stations and satellites. In addition, the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level, it can therefore be used as a tool to characterize the electronic structure of materials, especially in the vicinity of the narrow gap or pseudo-gap. During the talk I will provide a general introduction to the magnetic and transport characteristics of 4f and 5f electron systems. Then, I will present thermoelectric properties of selected 4f and 5f materials and give an overview on how the thermoelectric power studies can be used to probe electronic properties in this class of materials. I will discuss implications of the results, and their limitations.

11:00am **AC+AS+MI-WeM10 Magnetic Properties of 2-2-1 Rare-earth and Uranium Compounds and their Interaction with Hydrogen**, *Silvie Maskova*, Charles University, Prague, Czech Republic, *R.V. Denys*, Institute for Energy Technology, Kjeller, Norway, *I. Halevy*, Nuclear Research Center Negev, Beer-Sheva, Israel, *K. Miliyanchuk*, *L. Akselrud*, Ivan Franko National University of Lviv, Lviv, Ukraine, *A. Kolomiets*, Lviv Polytechnic National University, Lviv, Ukraine, *V. Yartys*, Institute for Energy Technology, Kjeller, Norway, *M. Giovannini*, University of Genova, Genova, Italy, *L. Havela*, Charles University, Czech Republic

We have been studying some members of large family of $\text{A}_2\text{T}_2\text{X}$ (A = Rare-Earth (RE) or actinide, T = transition metal, X = p -metal) compounds crystallizing in the Mo_2FeB_2 structure type (space group $P4/mbm$). $\text{U}_2\text{T}_2\text{X}$ interact with H_2 only at high pressure (≈ 100 bar) reaching 2 H/f.u. The H absorption produces a lattice expansion, while the tetragonal structure is preserved. The H atoms presumably enter the 8k position inside the U_3T tetrahedra occupied randomly up to 50%. On the other hand, it was found that some $\text{RE}_2\text{T}_2\text{X}$ compounds can absorb more hydrogen compared to their U-counterparts in much lower H pressures. The amorphization of the structure upon hydrogenation (4 H/f.u.) was found for $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$ with light RE (La, Nd). $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$ with heavy RE behave similar way as $\text{U}_2\text{T}_2\text{X}$ compounds (2 H/f.u., crystal structure type not changed). For the isostructural indide $\text{Nd}_2\text{Ni}_2\text{In}$ the hydrogen absorption of 7 H/f.u. leads to the orthorhombic distortion of the crystal structure.

Recently, we have been studying several isostructural $\text{RE}_2\text{T}_2\text{Mg}$ (T = Ni, Pd). The H absorption in these compounds depends on the type of transition

metal. The compounds with Ni tend to absorb up to 8 H/f.u. The crystal structure is changed to monoclinic (space group $P21/c$). If the transition metal is Pd, the hydrogen absorption is lower, reaching approx. 6 H/f.u. and the crystal structure is modified in different way. The Tb_2Pd_2Mg -hydride crystallizes in a new ternary structure type ($Fmmm$). In the case of Mg-compounds, the hydrogen absorption is not reversible. Upon desorption of H the initial crystal structure is not restored.

We have found that in U-compounds the ordering temperatures increase upon hydrogenation contrary to the RE-compounds where the ordering temperatures are dramatically reduced. Magnetic properties of U-compounds strongly depend on the inter-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a band narrowing. As a consequence doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of RE_2T_2X compounds. For RE compounds, hydrogenation affects mainly the $4f$ -magnetic moments and their ordering. The exchange coupling is reduced presumably by reducing the concentration of conduction electrons.

11:20am **AC+AS+MI-WeM11 Structural, Electronic, and Magnetic Characteristics of Np_2Co_{17} and Analogue Compounds Under Pressure.** *Itzhak Halevy*, Nuclear Research Center Negev, Israel, *A. Hen*, Institute for Transuranium Elements (ITU), Germany, *I. Orion*, Ben Gurion University, Israel, *E. Colineau*, *R. Eloirdi*, *J.C. Griveau*, ITU, Germany, *F. Wilhelm*, *A. Rogalev*, ESRF, France, *N. Magnani*, *A.B. Shick*, *R. Caciuffo*, ITU, Germany

A previously unknown neptunium-transition-metal binary compound Np_2Co_{17} has been synthesized and

characterized by means of powder x-ray diffraction, ^{237}Np Mössbauer spectroscopy, superconducting-quantum-interference-device magnetometry, and x-ray magnetic circular dichroism. The compound crystallizes

in a Th_2Ni_{17} -type hexagonal structure with room-temperature lattice parameters $a=8.3107\text{\AA}$ and $c=$

8.1058\AA . Magnetization curves indicate the occurrence of ferromagnetic order below $T_C>350$ K. Mössbauer

spectra suggest a Np^{3+} oxidation state and give an ordered moment of $\mu_{Np}=1.57\mu_B$ and $\mu_{Co}=1.63\mu_B$

for the Np atoms located, respectively, at the $2b$ and $2d$ crystallographic positions of the $P6_3/mmc$ space group.

Combining these values with a sum-rule analysis of the XMCD spectra measured at the neptunium $M_{4,5}$ absorption

edges, one obtains the spin and orbital contributions to the site-averaged Np moment [$\mu_S=-1.88\mu_B$,

$\mu_L=3.48\mu_B$]. The ratio between the expectation value of the magnetic-dipole moment and the spin magnetic

moment ($m_{md}/\mu_S=1.36$) is positive as predicted for localized $5f$ electrons and lies between the values

calculated in intermediate-coupling (IC) and jj approximations. The expectation value of the angular part of

the spin-orbit-interaction operator is in excellent agreement with the IC estimate. The ordered moment averaged

over the four inequivalent Co sites, as obtained from the saturation value of the magnetization, is $\mu_{Co}\sim 1.6\mu_B$.

The experimental results are discussed against the predictions of first-principles electronic-structure calculations

based on the spin-polarized local-spin-density approximation plus the Hubbard interaction. The structural behavior of Np_2Co_{17} is investigated by means of high pressure diamond-anvil compression measurements and is compared with that of the isostructural compounds Lu_2Co_{17} and Lu_2Ni_{17} . The Th_2Ni_{17} -type hexagonal crystal structure is preserved with no measurable discontinuous volume collapses up to the highest achieved pressure, $p=43$ GPa. For Np_2Co_{17} , fits to the Birch-Murnaghan and Vinet equations of state give values of the isothermal bulk modulus and

its pressure derivative of $B_0=286$ GPa and $B_0=3$, revealing that this Np compound is a highly incompressible solid with stiffness comparable to that of superhard covalently bonded materials. The isothermal equation of state for the studied compounds are in excellent agreement with the results of *ab initio* fully-relativistic, full potential local spin-density functional calculations. Theoretical estimates of the bulk modulus are given also for Np_2Ni_{17} , for which B_0 is predicted to assume values intermediate between those measured for Lu_2Ni_{17} and Np_2Co_{17} .

11:40am **AC+AS+MI-WeM12 Alloying UH_3 as a Probe into the $5f$ Magnetism.** *Ladislav Havela*, *M. Paukov*, *I. Tkach*, *M. Cieslar*, *Z. Matej*, *D. Kriegner*, *D. Drozdenko*, *I. Turek*, *M. Divis*, Charles University, Czech Republic, *N.-T.H. Kim-Ngan*, Pedagogical University, Poland

Several routes of preparation of alloyed U trihydrides, UH_3 , were discovered. Starting from the U_6T compounds, hydrogenation leads to T atoms embedded in the β - UH_3 structure, with transition-metal atoms T occupying one of the U sites. We have been hydrogenating γ -U alloys, using various transition metals helping (together with ultrafast cooling) to retain the bcc U structure down to low temperatures. As such alloys are much more resistant to hydrogen attack, high pressures of H_2 gas had to be applied. The H absorption corresponds to approx. 3H/atoms per 1 U atom. In none of the cases the alloying metals segregate and two different structures were obtained. The hydrides $(UH_3)_{1-x}Zr_x$ form the α - UH_3 structure, i.e. the bcc structure expands and fills by H. Hence basic electronic properties of α - UH_3 could be established. Starting from $U_{1-x}Mo_x$, we obtained $(UH_3)_{1-x}Mo_x$, which tends to be β - UH_3 like, but has the grain size is 1 nm only, i.e. practically amorphous. This amorphous phase also easily accepts additional dopants, as Zr, Fe, Ti, V...however magnetic properties remain only weakly affected. It is quite remarkable that all such materials are ferromagnets with the Curie temperature in the range 160-205 K, even if the active U sublattice is diluted by more than 30% of other metals. In this respect the hydrides are different than conventional band ferromagnets, sensitive to inter-atomic spacings and alloying. Albeit all are metallic, the U-H interaction, which can have a partly ionic character, plays clearly important role. Electronic structure calculations (performed for the α - UH_3 structure and in ferromagnetic or Disordered Local Moment state, with possible random Zr occupancy) suggest a transfer of U-6d and 7s electrons into H-1s states, reducing the hybridization of 5f and non-f states, supporting thus magnetism even if the U-U spacing is below the Hill limit [1].

[1] I. Tkach et al. Phys.Rev. B 91, 115116 (2015).

Wednesday Afternoon, October 21, 2015

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-WeA

Chemistry and Physics of the Actinides and Rare Earths

Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

2:20pm **AC+AS+MI-WeA1 High Resolution X-ray Absorption Spectroscopy as an Advanced Tool for Structural Investigations of Actinides, Tonya Vitova, Karlsruhe Institute of Technology, Germany**
INVITED

Advanced spectroscopy methods, which provide precise speciation, redox state, and electronic structure information, are needed to benchmark and drive improvement of geochemical/thermodynamic modeling and quantum chemical computational methods. The high energy resolution X-ray absorption near edge structure (HR-XANES) spectra contain additional information compared to the conventional XANES spectra, as they are rich in resolved resonant spectral features for specific An oxidation states.^[1] The An $M_{4,5}$ edge HR-XANES probes directly the An valence unoccupied 5f states ($3d \rightarrow 5f$) and thus yields insight to the role these frontier orbitals play in hybridization with ligands and bond formation.

The characterization capabilities of the An $M_{4,5}$ and L_3 edge HR-XANES technique will be highlighted by recent results obtained for both model and complex U, Np and Pu materials. In one example, a single crystal of dicesium uranyl tetrachloride ($Cs_2UO_2Cl_4$) as a model UO_2^{2+} (uranyl ion) compound was investigated using U M_4 ($3d_{3/2} \rightarrow 5f$) and L_3 ($2p_{3/2} \rightarrow 5f/6d$) edge polarization dependent HR-XANES (PD-HR-XANES) with remarkable energy resolution. Comparison of experimentally determined relative energies of U $5f\delta$, $5f\phi$, $5f\pi$, and $5f\sigma$ orbitals, as well as 5f and 6d orbitals obtained from the spectra, to predictions from quantum chemical Amsterdam density functional theory (ADF) and FEFF codes and show excellent results.^[2] A number of examples for determination of An redox states in liquids and solid systems will be discussed. Comparison of U/Pu/Np M_4/M_5 HR-XANES spectra of UO_2^{2+} , NO_2^{2+} and PuO_2^{2+} as well as Pu M_5 HR-XANES and L_3 XANES of various Pu oxidation states in aqueous solution will be presented. In addition, recent results unambiguously demonstrate that U(V) can exist alongside U(IV) and U(VI) in magnetite nanoparticles under anoxic conditions; this underpins the utility of HR-XANES for understanding U retention mechanisms on corrosion products.

[1] At. Vitova, M. A. Denecke, J. Göttlicher, K. Jorissen, J. J. Kas, K. Kvashnina, T. Prüßmann, J. J. Rehr, J. Rothe, Journal of Physics: Conference Series, 430, Bk. O. Kvashnina, S. M. Butorin, P. Martin, P. Glatzel, Phys Rev Lett, 111; Ct. Vitova, K. O. Kvashnina, G. Nocton, G. Sukharina, M. A. Denecke, S. M. Butorin, M. Mazzanti, R. Caciuffo, A. Soldatov, T. Behrends, H. Geckeis, Phys Rev B, 82.

[2] T. Vitova, J. C. Green, R. G. Denning, M. Löble, K. Kvashnina, J. J. Kas, K. Jorissen, J. J. Rehr, T. Malcherek, M. A. Denecke, Inorganic Chemistry, 54, 174-182.

3:00pm **AC+AS+MI-WeA3 Soft X-ray Spectromicroscopy of Actinide Materials, David Shuh, Lawrence Berkeley National Laboratory**
INVITED
Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption spectroscopy (XAS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale.

An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state. The highlights of recent investigations of metallocenes at the carbon K-edge and uranyl complexes at the nitrogen K-edge will be

highlighted in this respect. The spectromicroscopy attributes of the STXM have enabled the investigation of contaminant speciation in a range of model and real environmental systems. The results of the most recent environmentally-related studies, cesium in clay materials relevant to clean up efforts in Japan, will be presented.

Acknowledgement: Supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. DOE at LBNL under Contract No. DE-AC02-05CH11231.

4:20pm **AC+AS+MI-WeA7 Resonant Ultrasound Spectroscopy Detects 100 Part-per-billion Effects in Plutonium, Albert Migliori, Los Alamos National Laboratory**
INVITED

The speeds of sound, or, equivalently, the elastic moduli are some of the most fundamental attributes of a solid, connecting to fundamental physics, metallurgy, non-destructive testing, and more. With modern advances in electronics and analysis, changes in elastic moduli are detectable at 100 parts per billion, providing new and important insight into grand challenges in plutonium science. Applied to ^{239}Pu , the effects of aging are measured in real time as a function of temperature, and the temperature dependence of the elastic moduli of gallium stabilized delta plutonium leads to important questions about the validity of electronic structure theory, and points towards inescapable constraints on any theory of this metal.

This work was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001089.

5:00pm **AC+AS+MI-WeA9 Spectroscopic Studies of the Oxide Layer formed on Plutonium under Ambient Conditions, Alison Pugmire, Los Alamos National Laboratory, C.H. Booth, Lawrence Berkeley National Laboratory, J. Venhaus, L. Pugmire, Los Alamos National Laboratory**

One of the fundamental challenges of modern science lies in understanding the chemistry and physics of the actinides, and in particular, plutonium. It's unpredictable behavior and reactivity has led to a very poor understanding of its metallurgy and corrosion process. This not only poses a basic scientific challenge, but directly affects the safe, long term storage of this material. In an effort to understand the surface chemistry and corrosion of plutonium, knowledge of the surface oxide composition is paramount. The currently accepted description of the oxide layer formed under ambient temperatures and pressures consists of a thick PuO_2 surface layer over a thin Pu_2O_3 layer at the metal interface. However, recent studies by our group indicate this description is inadequate, and the oxide layer formed in the initial stages, in particular, is much more complex. We have recently focused on studying the oxide layer formed on gallium stabilized δ -plutonium in ambient conditions (pressure, temperature). We have characterized this layer using multiple spectroscopic techniques, including spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS). This diverse and complimentary suite of experimental techniques will address many long-standing issues regarding the nature of the oxide layer and the corrosion mechanism.

5:20pm **AC+AS+MI-WeA10 Covalent Mixing In Actinide and Lanthanide Compounds: Reliable Assignment of Cation Charges, Paul Bagus, University of North Texas, C.J. Nelin, Consultant**

The importance of covalent and ionic interaction and bonding in heavy metal oxides, for example for the actinide dioxides, AnO_2 , is controversial with some claiming that the interactions are nearly purely ionic and with others arguing that there is important covalent character. Similar questions also exist for halides and for lanthanide compounds. One way to view this is to consider how close the actual charge state of the cation is to the nominal oxidation state. Our analysis is based on using wavefunctions for embedded clusters which model the bulk oxides. With these wavefunctions, we show that considerable departures of the cation charge from the nominal value are a common occurrence. We also show how the departure from the nominal charge state depends on several factors including: (1) nominal oxidation state, (2) ligand, and (3) position in the row of the periodic table. It is also necessary to determine which metal orbitals are involved in the covalent mixing. For actinides, the natural choice is the open cation 5f shell but the normally empty 6d shell may also contribute to the covalent mixing and, in fact, may even have a larger contribution than the 5f. In order to characterize the extent and importance of the covalent mixing, two factors need to be taken into account: (1) the estimate of the actual charge state of the cations and (2), perhaps even more important, the contribution of the covalent mixing of the cation and anion frontier orbitals to the total energy of the compound. Our approach to address both of these aspects is to limit the variational freedom when we self-consistently optimize the orbitals of

the models used to represent the compounds studied. By restricting the variational space, the importance of the mixing of ligand and metal frontier orbitals can be explicitly measured by determining the difference between a wavefunction where these frontier orbitals are excluded from the variational process and a wavefunction where they are allowed to mix with other orbitals. With this approach, it is possible to make quantitative estimates of energies associated with the covalent mixing as well as the effective charges that can be associated with the cations and ligands. Furthermore, it is possible to visualize the changes in the charge distribution for different degrees of variational freedom with suitable contour plots. We acknowledge support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE.

5:40pm AC+AS+MI-WeA11 **An XPS and ToF SIMS Investigation of Cerium Oxidation**, *Paul Roussel*, AWE, United Kingdom of Great Britain and Northern Ireland

In this study fcc γ -cerium has been used as a non radioactive surrogate material for fcc δ -plutonium. The common cerium oxides are the trivalent sesquioxide and the tetravalent dioxide both of which are iso-structural with the oxides formed on plutonium metal. Similarly, cerium (1) like plutonium (2) displays parabolic oxidation kinetics at low temperatures and linear kinetics elevated temperatures. This makes cerium an ideal surrogate material to study the kinetics and mechanism of plutonium oxidation. The initial oxidation of cerium at 274 K was studied using X-ray Photoelectron Spectroscopy. On exposure to Langmuir quantities of oxygen cerium rapidly oxidizes to the trivalent oxide followed by the slower growth of the tetravalent oxide. The growth modes of both oxides have been determined. It was found the surface formed tetravalent oxide was unstable in ultra high vacuum and reduced to the trivalent oxide by an apparent solid state diffusion reaction with cerium metal. This reduction reaction can be explained by the thermodynamic instability of the tetravalent dioxide with respect to cerium metal. The complexity of this reduction reaction appears to be enhanced by the formation of surface hydroxyl species as a function of time. Time of Flight Secondary Ion Mass Spectrometry was used to support characterization of the surface hydroxyl species.

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Thursday Morning, October 22, 2015

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-ThM

Nuclear Power and Waste Remediation

Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+MI-ThM1 Applications of Synchrotron Methods to f-Element Research in the Nuclear Fuel Cycle, Melissa Denecke**, The University of Manchester, UK **INVITED**

Celebrating 60 years of civil nuclear power generation offers an excellent opportunity to review synchrotron radiation (SR)-based techniques to characterize nuclear materials and elucidate processes relevant to the nuclear fuel cycle. The penetration capability of intense SR X-ray sources allows in situ investigations, including samples within radiological containments or specialized environments. The presentation will concentrate on application of X-ray spectroscopic techniques in studies related to the nuclear fuel cycle (fuel, cladding, recycle, waste disposal).

8:40am **AC+AS+MI-ThM3 Ab Initio Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors, Alexander I. Landa**, Lawrence Livermore National Laboratory **INVITED**

The U-TRU-Zr and U-TRU-Mo alloys proved to be very promising fuels for TRU-burning liquid metal fast breeder reactors. The optimal composition of these alloys is determined from the condition that the fuel could remain stable in the bcc phase (γ -U) in the temperature range of stability of α -U phase. In other words, both Zr and Mo play a role of ' γ -stabilizers' helping to keep U in the metastable bcc phase upon cooling. The main advantage of U-Pu-Mo fuels over U-Pu-Zr fuels lies in much lower constituent redistribution due to the existence of a single γ -phase with bcc structure over typical fuel operation temperatures. The nucleation time for the decomposition of the metastable alloys, which controls the constituent redistribution process, is directly connected with the excess enthalpy of solution of these alloys. In the present study we perform KKR-ASA-CPA and EMTO-CPA calculations of the ground state properties of γ -U-Zr and γ -U-Mo alloys and compare their heats of formation with CALPHAD assessments. We discuss how the heat of formation in both alloys correlates with the charge transfer between the alloy components, and how the specific behavior of the density of states in the vicinity of the Fermi level promotes the stabilization of the U_2Mo compound. Our calculations prove that, due to the existence of a single γ -phase over the typical fuel operation temperatures, γ -U-Mo alloys should indeed have much lower constituent redistribution than γ -U-Zr alloys where a high degree of constituent redistribution takes place. The binodal decomposition curves for γ -based U-Zr and U-Mo solid solutions are derived from Ising-type Monte Carlo simulations incorporating effective cluster interactions obtained from the Screened Generalized Perturbation and Connolly-Williams methods. We also explore the idea of stabilization of the $\delta-UZr_2$ compound against the α -Zr (hcp) structure due to increase of Zr d-band occupancy by the addition of U to Zr. Analogy with stabilization of the ω phase in Zr under compression is made. Though the U-Pu-Zr and U-Pu-Mo alloys can be used as nuclear fuels, a fast reactor operation on a closed fuel cycle will, due to the nuclear reactions, contain significant amount of MA (Np, Am, Cm). Calculated heats of formation of bcc Pu-U, Pu-Np, Pu-Am, Pu-Cm, Pu-Zr, Pu-Mo, Np-Zr, Np-Mo, U-Am, Np-Am, Am-Zr and Am-Mo alloys are also presented and compared with CALPHAD assessments. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 12-SI-008.

9:20am **AC+AS+MI-ThM5 Shedding Light on Uranium Corrosion in Nuclear Waste Packages, Charilaos Paraskevoulakos**, University of Bristol, UK

Intermediate level waste (ILW) is encapsulated in grout and stored in stainless steel drums. A proportion of these have become a concern for the UK nuclear community, as significant distortion around the circumference of these drums has been observed. Distortion is ascribed to the generation of voluminous and potentially flammable corrosion products forming on uranium metal, e.g. uranium hydride. Thus potential oxygen influx caused by fracturing of canisters will threaten their suitability for waste disposal, potentially causing release of the encapsulated radioactive material or even ignition of the hydride. The association of the uranium corrosion mechanisms with the mechanical degradation of the encapsulants (stainless steel and grout), is the focus of the current project. Finite Element (FE)

Modelling, accelerated uranium corrosion tests as well as diffraction and tomography using synchrotron X-Rays/gamma rays could be employed to investigate the durability of the ILW packages.

9:40am **AC+AS+MI-ThM6 The Optical Properties of Uranium Carbide Measured by Spectroscopic Ellipsometry, Wigbert Siekhaus, A.J. Nelson, C.K. Saw**, Lawrence Livermore National Laboratory

Uranium carbide inclusions are common in metallic uranium, and uranium carbide itself is being used or being considered as a fuel in both gas-cooled, liquid metal cooled, and supercritical water-cooled reactors. To the best of our knowledge the only study of optical properties deals with high temperature radiance. [1] Here we first characterized a uranium carbide cube (supplied by Oak Ridge National Laboratory) with sides of approximately 3 mm length by X-ray diffraction and X-ray photo-electron spectroscopy and then measured its optical properties with an ellipsometer at angles of incidence between 65 and 75 degrees, and over an energy range from 1.26 to 3.2eV. The signal strength was low over that energy range, and too low to be useful above 3.2eV. The measured Δ and Ψ were converted to the dielectric constants ϵ_1 and ϵ_2 shown in the table below using a general oscillator model [2].

E, eV	ϵ_1	ϵ_2	E, eV	ϵ_1	ϵ_2	E, eV	ϵ_1	ϵ_2
1.26	-1.96	5.07	1.95	-0.30	2.73	2.61	2.61	1.32
1.33	-1.69	4.77	2.02	-0.21	2.55	2.68	2.68	1.21
1.40	-1.47	4.45	2.10	-0.12	2.34	2.75	2.75	1.07
1.47	-1.25	4.14	2.18	-0.03	2.18	2.83	2.83	0.94
1.54	-1.06	3.87	2.25	0.04	2.02	2.91	2.91	0.85
1.61	-0.89	3.63	2.32	0.12	1.87	2.98	2.98	0.76
1.69	-0.73	3.44	2.40	0.20	1.73	3.05	3.05	0.67
1.76	-0.60	3.23	2.47	0.28	1.59	3.12	3.12	0.58
1.84	-0.48	2.95	2.54	0.35	1.43	3.20	3.20	0.51

Prepared by LLNL under Contract DE-AC52-07NA27344, LLNL-ABS-670149

[1] D. Manara, F. De Bruycker, K. Boboridis, O. Tougait, R. Eloiardi, M. Malki, High temperature radiance spectroscopy measurements of solid and liquid uranium and plutonium carbides, J Nucl Mater, 426 (2012) 126-138.

[2] R. Synowicki, J.A. Woollam CO. Inc. 645 M Street, Suite 102, Lincoln, NE 68508-2243, USA

11:00am **AC+AS+MI-ThM10 Uranium Wet Oxidation in the Presence of Hydrogen Overpressure, Antonios Banos**, University of Bristol, UK

The radioactive intermediate level (IL) and high level (HL) waste have been accumulated in the UK's legacy ponds and silos for over 60 years. There is a great need for these wastes to be retrieved to follow long term storage. Uranium hydride (UH_3) has been identified as a reaction product of the corrosion process. Hydride formation occurs due to the increasing concentration of hydrogen gas, generated from the reaction of uranium, Magnox (MagnoxAl80) and other metals. The highly pyrophoric and unstable nature of UH_3 in air poses considerable environmental risks, due to potential radionuclide release. In this work we will try to simulate the corroding conditions by immersing an initially polished uranium sample in water under vacuum and introducing hydrogen gas overpressure to the system. The ternary system will be investigated in different temperatures and pressures with two main questions awaiting to be answered: 1. Is UH_3 identified? For this reason post-examination of the reacted surface will be conducted using Secondary Ion Mass Spectrometry (SIMS), Focus Ion Beam (FIB) milling. 2. If UH_3 is identified, on which part of the reaction is it produced and how this affects the overall reaction? The kinetics will be monitored using a specifically designed set-up comprised from a stainless steel pot and a pressure controller attached on one end and logged to a computer in order for the whole reaction to be recorded and the rate of corrosion through gas generation to be evaluated.

11:40am **AC+AS+MI-ThM12 Resolving the Issues of 5f Covalency and Ionicity in UO_2 and UF_4 , James Tobin**, Lawrence Livermore National Laboratory

Building upon our recent work, a concerted effort to isolate and understand covalency and ionicity in uranium compounds has been pursued. Specifically, the isoelectronic formal charge systems, uranium dioxide and uranium tetrafluoride, have been investigated with a novel mixture of both soft and hard-x-ray spectroscopies. The results to be discussed will include the following: (1) the use of soft X-ray O1s/F1s X-ray absorption spectroscopy (XAS) and U4d X-ray emission spectroscopy (XES) to follow

the 2p/5f bonding via the unoccupied density of states; (2) the utilization of hard X-ray U L3 extended X-ray absorption fine structure (EXAFS) to trivially distinguish the ordering in each; and (3) the use of hard X-ray L3 resonant X-ray emission spectroscopy (RXES) to distinguish 5f occupation/covalency effects in UO₂ and UF₄. Collaborators include CH Booth, DK Shuh, T. Tyliczszak, G. van der Laan, D. Sokaras, T.-C. Weng, D. Nordlund, S.-W. Yu, W. Siekhaus and P.S. Bagus.

Friday Morning, October 23, 2015

Scanning Probe Microscopy Focus Topic

Room: 212A - Session SP+AS+MI+NS+SS-FrM

Probe-Sample Interactions

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

8:20am **SP+AS+MI+NS+SS-FrM1 Direct Visualization of Magnetolectric Domains in Hexagonal Manganites, Weida Wu, Rutgers University** **INVITED**

Multiferroics are materials with coexisting magnetic and ferroelectric orders, where the cross-coupling between two ferroic orders can result in strong magnetoelectric effects [1-4]. Therefore, it is of both fundamental and technological interest to visualize cross-coupled magnetoelectric domains and domain walls in multiferroics. Recently, intriguing topological defects with six interlocked structural antiphase and ferroelectric domains merging into a vortex core were revealed in multiferroic hexagonal $RMnO_3$ (R =rare earths) [5, 6]. Many emergent phenomena, such as enhanced conduction and unusual piezoelectric response, were observed in charged ferroelectric domain walls protected by these topological defects [7-9]. More interestingly, alternating uncompensated magnetic moments were discovered at coupled structural antiphase and ferroelectric domain walls in hexagonal manganites using cryogenic magnetic force microscopy (MFM) [10], which demonstrates the cross-coupling between ferroelectric and magnetic orders. Here we present the application of a magnetoelectric force microscopy (MeFM) technique that combines MFM with *in situ* modulating high electric fields. This new microscopy technique allows us to image the magnetoelectric response of the domain patterns in hexagonal manganites directly [11, 12]. We find that this response changes sign at each structural domain wall, a result that is corroborated by symmetry analysis and phenomenological modelling, and provides compelling evidence for a lattice-mediated magnetoelectric coupling. The direct visualization of magnetoelectric domains at mesoscopic scales opens up explorations of emergent phenomena in multifunctional materials with multiple coupled orders.

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- [12] Y. Geng et al., *Nat. Mater.* 13, 163 (2014).

9:00am **SP+AS+MI+NS+SS-FrM3 Kelvin Probe Force Microscopy Studies of Magnetic Atoms on Ultrathin Insulating MgO Film, Taeyoung Choi, W. Paul, S. Baumann, C.P. Lutz, A. Heinrich, IBM Almaden Research Center**

The interplay of single atoms and their local environment on surfaces influences the atoms' spin excitations and dynamics, which can be utilized in progress toward atomic-scale memory and quantum information processing. We find that spin-excitation energy of Fe atoms on an insulating MgO film shifts depending on the tip-to-atom separation. This may be attributed to the electric field across the tunneling junction, as well as to local charge and structural changes around the atom. The Kelvin Probe Force Microscopy (KPFM) has been very useful tool to measure changes of local contact potential differences between a tip and a sample at the atomic level [1]. In this talk, we employ tuning fork KPFM/STM and show preliminary results on the charge character and spin excitations of Fe atoms. This work is supported by grants from IBM.

- [1] Leo Gross et al., *Phys. Rev. B* 90, 155455 (2014).

9:20am **SP+AS+MI+NS+SS-FrM4 Nanoscale Schottky Barrier Height Mapping Utilizing Ballistic Electron Emission Microscopy, C. Durcan, W. Nolting, College of Nanoscale Science and Engineering, Vincent LaBella, SUNY Polytechnic Institute**

The Schottky barrier is the electrostatic barrier between a metal and a semiconductor that results in rectification and is found in many types of devices such as source drain contacts to sub 20-nm-node transistors. Naturally, the Schottky barrier height can fluctuate across the interface due to variations in bonding, compositional fluctuations in the materials, and the presence of defects. However measuring and mapping these electrostatic fluctuations is impossible with bulk IV or CV techniques. This presentation will demonstrate how the Schottky barrier height can be mapped to nanoscale dimensions using an STM based technique called ballistic electron emission microscopy (BEEM). The STM tip is positioned on a regularly spaced grid and BEEM spectra are acquired from which the barrier height can be extracted. A map and histogram is then generated by measuring and fitting thousands of these spectra. These maps provide detailed insight into the electrostatic fluctuations occurring at the buried interface with nanoscale resolution that cannot be accomplished with other bulk measurements.

9:40am **SP+AS+MI+NS+SS-FrM5 Electron Transport Studies of Metal Films Utilizing Ballistic Electron Emission Microscopy, Christopher Durcan, SUNY College of Nanoscale Science and Engineering, V. LaBella, SUNY Polytechnic Institute**

Understanding scattering of electrons in nanometer thick metal films is of fundamental and technological importance. One method to study electron scattering is with ballistic electron emission microscopy (BEEM), which is a three terminal STM based technique that measures both scattering through a metal film and the Schottky barrier height for metal-semiconductor junctions with both nanometer spatial resolution and meV energy resolution. This presentation will describe our work at understanding the relationship between the metal resistivity and the electron scattering lengths measured with BEEM by exploring metals with a range of resistivities from Ag (1.7 $\mu\Omega$ -cm) to Cr (12.6 $\mu\Omega$ -cm). In addition, nanoscale mapping of the Schottky barrier height of these metals to silicon will also be presented to understand the spatial uniformity of the transport.

10:00am **SP+AS+MI+NS+SS-FrM6 Utilizing Ballistic Electron Emission Microscopy to Study Sidewall Scattering of Electrons, Westly Nolting, C. Durcan, R. Balsano, College of Nanoscale Science and Engineering, University of Albany, V. LaBella, College of Nanoscale Science and Engineering, SUNY Polytechnic Institute**

Sidewall scattering of electrons within aggressively scaled metallic interconnects increases the resistance since the mean free path (~40 nm) is larger than the dimensions of the material. One method to study hot-electron scattering in nm-thick metallic films is Ballistic Electron Emission Microscopy (BEEM), which is an STM based technique. In this work, we perform BEEM scattering measurements on lithographically patterned fin structures with a Schottky diode interface to determine its ability to measure sidewall scattering. This is accomplished by acquiring BEEM spectra on a regularly spaced grid and fitting the results to determine both the Schottky barrier height and the slope of the spectra. The slope of the spectra is related to the scattering in the film and interface. The position of fin structures are then determined by mapping both the Schottky height and slope over a square micron to observe scattering at the interface caused by the patterned structures. The poster will discuss the fabrication of the patterned 50-nm-pitched sidewall structures that are used for mapping the sidewall scattering. In addition, it will present the preliminary BEEM measurements on these structures.

10:20am **SP+AS+MI+NS+SS-FrM7 Progress in Nanoscale Magnetic Resonance Imaging, Daniel Rugar, IBM Research Division** **INVITED**

Nuclear magnetic resonance (NMR) is the basis of powerful spectroscopic and imaging techniques, but extension to nanoscale samples has been a longstanding challenge due to the insensitivity of conventional detection methods. We are exploring the use of individual, near-surface nitrogen-vacancy (NV) centers in diamond as atomic-size magnetometers to detect proton NMR in organic material located external to the diamond. Using a combination of electron spin echoes and proton spin manipulation, the NV center senses the nanotesla field fluctuations from the protons, enabling both time-domain and spectroscopic NMR measurements on the nanometer scale. By scanning a small polymer test object past a near-surface NV center, we have recently demonstrated proton magnetic resonance imaging (MRI) with spatial resolution on the order of 10 nm.

One key issue in NV-NMR experiments is the loss of spin coherence when the NV center is located near the diamond surface. Although this loss of coherence is frequently attributed to the effect of magnetic noise emanating from unpaired spins on the diamond surface, we will show evidence that electric field noise from fluctuating surface charge may be the dominant factor.

Work performed in collaboration with M. Kim, H. J. Mamin, M. H. Sherwood, C. T. Rettner, K. Ohno, and D. D. Awschalom

11:00am **SP+AS+MI+NS+SS-FrM9 Reactive Intermediates Created and Analyzed by Scanning Probe Microscopy**, *Bruno Schuler*, IBM Research - Zurich, Switzerland, *N. Pavliček*, IBM Research - Zurich, *S. Collazos*, CIQUS, Universidade de Santiago de Compostela, *N. Moll*, *S. Fatayer*, IBM Research - Zurich, *D. Pérez*, *E. Guitán*, CIQUS, Universidade de Santiago de Compostela, *G. Meyer*, IBM Research - Zurich, *D. Peña*, CIQUS, Universidade de Santiago de Compostela, *L. Gross*, IBM Research - Zurich

Reactive intermediates are involved in most chemical transformations. However, their characterization is a great challenge because of their short lifetime and high reactivity.

Here we report on the creation of single radicals and diradicals on a thin insulating surface by means of atomic manipulation. Importantly, the thin insulating film facilitates the stabilization of these reactive intermediates at cryogenic temperatures. The molecules were characterized by atomic-resolution atomic force microscopy (AFM) imaging with a CO functionalized tip [1] and scanning tunneling microscopy (STM) orbital imaging [2]. We show that the molecules' reactivity is preserved even at low temperatures by performing different on-surface reactions by atomic manipulation. As an example, the generation of arynes is discussed, a very reactive intermediate caught for the first time [3].

References:

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- [2] J. Repp et al. *Phys. Rev. Lett.* **94**, 026803 (2005)
- [3] N. Pavliček et al. On-surface generation and imaging of arynes by atomic force microscopy. (submitted)

11:20am **SP+AS+MI+NS+SS-FrM10 The Negative Stiffness and Positive Damping of Squeezed Air in Dynamic Atomic Force Microscopy**, *x. Yu*, *M. Tao*, *Nancy Burnham*, Worcester Polytechnic Institute

By oscillating a micro-sized cantilever beam at a certain frequency and observing its interaction with the sample surface, dynamic mode atomic force microscopy (AFM) has gained attention for characterizing mechanical properties of a variety of materials at the micro and nano scales. The thin air film, confined between the oscillating cantilever beam and the stationary sample surface, causes the so-called "squeeze-film effect" when the gap between the two boundaries is less than a hundred microns. Although studies have shown that the squeeze film can act as a spring and a damper in accelerometers and microelectromechanical systems [1], the influence of the squeeze-film effect on the dynamics of an AFM cantilever has not been previously explored, to the authors' knowledge. In this project, the stiffness and damping properties of the squeeze film between an oscillating AFM cantilever and a glass slide were calculated from the cantilevers' amplitude and phase responses as recorded by the AFM digital system. The smaller the cantilever-sample gap, the larger the absolute values of the stiffness and the damping of the squeeze film. Results from different cantilevers (consequently having different spring constants and resonant frequencies) indicated that the air film exhibited **negative stiffness and positive damping**, with normalized changes from free values of up to 40%. Theoretical analysis was conducted using an equivalent-circuit model [2] along with the phasor diagram, and the derived stiffness and damping values were in excellent agreement with the experimental ones. Interestingly, a rotation angle between 20° and 30° in the fit of the data to the model reveals a phase *lead* of the squeeze-film damping before the usual air damping when the cantilever is far from a surface: the maximum squeeze-film damping occurs before the maximum velocity of the cantilever because air becomes less dense as it rushes out of the tip-sample gap. The surprising sign of the stiffness is thus explained by the phase lead. Future work includes incorporating the squeeze-film effect into more accurate measurements of a material's stiffness and damping properties using dynamic AFM.

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Thin Film

Room: 111 - Session TF+MI-FrM

Thin Films for Light Trapping, Plasmonic, and Magnetic Applications

Moderator: Angel Yanguas

8:20am **TF+MI-FrM1 Designing and Deposition of Multilayer Selective Surface for Tuning Absorption and Reflection of Solar Spectra**, *Z. Ren*, *Feng Cao*, University of Houston **INVITED**

Spectrally-selective solar absorbers are widely used in solar hot water and concentrating solar power (CSP) systems. However, the performance at high temperatures (>500 °C) can be further improved. Recent progress on cermet-based solar absorbers has shown promising high temperature thermal stability and wavelength selectivity. Here we explore W-Ni-Al₂O₃, W-Ni-YSZ (yttria-stabilized-zirconia), and W-Ni-SiO₂ cermet based spectrally selective surfaces for high-temperature solar absorber applications. The developed multilayer selective surfaces are deposited by magnetron sputtering on different substrates depending on applications. The absorber consists of two solar absorbing cermet layers with different W-Ni volume fraction inside the dielectric matrix, one or two anti-reflection coatings (ARCs), and one tungsten IR reflection layer for reduced IR emittance and improved thermal stability. All these absorbers show an absorbance of > 90% for temperature up to 500 °C and emittance of ~5% at about room temperature and 10-15% at 500 °C.

Recently we are developing a new kind of absorber that reflects a certain range of wavelength and absorbs the rest of the whole solar spectra. The absorbed part is used for electrical power generation by steam engine and the reflected part is used for solar photovoltaic conversion. The thermal energy can be easily stored for later conversion to provide electrical power around the clock without worrying the Sun's night time.

9:00am **TF+MI-FrM3 Femtomagnetism in FePt Nanoparticles for Heat Assisted Magnetic Recording**, *J.-Y. Bigot*, *J. Kim*, *M. Vomir*, Institut de Physique et Chimie des Matériaux de Strasbourg; Université de Strasbourg and CNRS, France, *O. Mosendz*, *S. Jain*, *Dieter Weller*, HGST a Western Digital company **INVITED**

Implementing larger and faster recording capacities, like in Heat Assisted Magnetic Recording (HAMR) devices, requires investigating the magnetization dynamics of nanostructures at the sub-picosecond time scale. The case of L₁₀ FePt "nanocrystals" is of particular interest as HAMR media can be designed with grain diameter below today's D ~ 8 nm. The magnetic anisotropy is sufficiently high and results in coercive fields larger than 5 Tesla at room temperature [1, 2].

Femtosecond magneto-optics allows investigating the dynamical properties of such films [3] and nanoparticles [4] with a temporal resolution well adapted to the actual needs of performant materials that can be addressed in the time scale of a few picoseconds or faster. In the case of materials for HAMR, the pre-heating with femtosecond laser pulses allows reaching very high electron temperatures beyond the Curie point without over heating the lattice. It is therefore a relevant approach to use femtosecond pulses as it allows improving the conditions for obtaining an efficient switching due to the laser pre-heating. In that context, the variation of the coercive field H_c and magnetization at saturation M_s are important quantities to be characterized. We have investigated such dynamics in L₁₀ FePt nanoparticles and accurately characterized the nonlinear variation of M_s and H_c upon varying the laser density of energy. We demonstrate that the Curie temperature can be reached during a few hundreds of femtoseconds, showing that the speed for addressing bits of information can be further improved in ultrafast HAMR applications.

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10:00am **TF+MI-FrM6 Application of High Refractive Index Layers to Perfect Absorbers for Solar and Thermal Radiations**, *Motofumi Suzuki, K. Nishiura, S. Masunaka, K. Namura*, Kyoto University, Japan

In this presentation, we demonstrate that high refractive index materials such as β -FeSi₂ are key to achieve anti-reflective interference coatings on an opaque substrate. β -FeSi₂ is known as an eco-friendly semiconductor and its bulk refractive (n) and extinction (k) indices are higher than 5 and zero, respectively, in infrared (IR) region ($\lambda > 1.55 \mu\text{m}$). We have reported that the high refractive index of β -FeSi₂ is quite useful to reduce the reflectance of metal substrates and that β -FeSi₂ thin films/stainless steel substrate systems show nice spectrally selective absorption properties in IR region. For sputtered polycrystalline β -FeSi₂ thin films, we recently found that $k \approx 0.3$ in IR region, which is different from the bulk value. Thus, we redesigned antireflective-layered structures on an opaque substrate and prepared them. As the results, a system of β -FeSi₂/W shows perfect absorption properties, where absorbance reaches higher than 99% at desired wavelength regions, while that in other regions is lower than a few %. On the other hand, another interesting optical property of β -FeSi₂ is that both n and k are considerably high in visible to NIR region ($\lambda < 1.55 \mu\text{m}$). This enables us to design multilayered broadband absorbers for VIS to $\lambda < 2.0 \mu\text{m}$. The designed multilayers consist of SiO₂/ β -FeSi₂/SiO₂/ β -FeSi₂/W, where the upper β -FeSi₂ layer absorbs VIS and NIR ($\lambda < 1.0 \mu\text{m}$) and the bottom β -FeSi₂ layer/W absorbs IR ($1.0 \mu\text{m} < \lambda < 2.0 \mu\text{m}$). The optimized multilayers absorb more than 95% of solar energy and the emittance at 450 °C is lower than 6%. No significant change in absorptive properties in both single and multilayered absorbers has been recognized after they are annealed in air at least up to 500 °C. The perfect absorbers with high refractive index layers are useful for applications to solar selective absorbers for solar thermal power generation and spectrally selective thermal emitters for thermophotovoltaic power generation, IR heaters, radiation cooling.

10:20am **TF+MI-FrM7 Antireflection Coatings for Tandem Solar Cells**, *Bo Yuan*, University of Delaware, *B. Thibeault*, University of California at Santa Barbara, *K. Dobson*, University of Delaware, *A. Barnett*, University of New South Wales, Australia, *R.L. Opila*, University of Delaware

Because of the ability to exploit multiple absorption bands, Multi-junction Solar Cells (MJSCs) are the most efficient solar cells ever developed. As on single junction solar cells, Antireflection Coatings (ARCs) are utilized to achieve broadband absorption. Due to the fact that the total current of MJSCs is limited by the subcell that has the lowest generated current, ARCs on MJSCs must have the ability to minimize light loss at the range of limiting cell, but optimally all across the visible spectrum.

Unlike conventional Double Layer Antireflection Coatings (DLARCs) that can only reduce light reflection at certain wavelengths, moth eye structures are able to mitigate light loss over broadband wavelength due to their smooth change of refractive index. We report the fabrication of such a Subwavelength Structure (SWS) by using wet etching and dry etching of dielectric materials. Silicon wafers are used here as the substrate to test the quality of ARCs. ZnO has been chosen as one dielectric material because of its excellent transmittance and durability. It also has a close index match to the underlying GaInP window layer in this tandem cell. Wet etching using oxalic acid has been utilized here to texture the ZnO surface because it is a simple and cost-effective method. A low reflection (less than 10%) over a broad range of wavelength (400-970nm) has been achieved. However, it turns out that wet etching is not very controllable and cannot fabricate the high aspect ratio periodic structure necessary for optimal absorption. A Zn(C₂O₄) · 2H₂O bulk phase was found on the ZnO surface.

Thus, lithography and plasma etching have been employed because of their better process control capability and less dependence on the crystalline orientation of the material. We then switched to using Ta₂O₅ since it has similar optical properties to ZnO and also a broad bandgap to ensure its transparency. Dry etching of Ta₂O₅ gives us nanocones with aspect ratio (height over base diameter) of 1.26. At an angle of 8 degree from normal incidence, textured Ta₂O₅ achieved the averaged reflection as low as 6% over 320-900nm and it outperforms DLARCs and textured ZnO over a wide range of wavelength. Future work will focus on fabricating this moth eye structure on III-V/SiGe tandem cells and simulating the reflectance spectra using Finite Difference Time Domain methods.

10:40am **TF+MI-FrM8 Preparation and X-ray Characterization of Highly Oriented Magnetic and Magnetoelectric Thin Films**, *Radomir Kuzel*, Charles University in Prague, Czech Republic, *J. Bursik, M. Soroka, K. Knizek*, Academy of Sciences of the Czech Republic

Different kind of thin films with remarkable magnetic and magnetoelectric properties require strong preferred orientation in order to utilize strong anisotropy of their properties.

The main aim of the work is to prepare the films of hexagonal ferrites showing magnetoelectric effects. There are several types of these materials

marked as e.g. M-type [(Ba,Sr)Fe₁₂O₁₉, space group P6₃/mmc], Y-type [(Ba,Sr)₂Me₂Fe₁₂O₂₂, s. g. R-3m], Z-type [(Ba,Sr)₃Me₂Fe₂₄O₄₁, s. g. P6₃/mmc], and others. Our attention was focussed mainly to Y-type where the best properties are expected. All these lattices are long along c -axis and this should be oriented perpendicular to the surface. The films were prepared through the chemical solution method either on SrTiO₃ (111) or sapphire Al₂O₃ (0001) substrates, respectively. We are looking not only for suitable substrates but also we have succeeded in using seed template interlayers, for example M hexaferrite SrFe₁₂O₁₉. A detailed inspection revealed that growth of seed layers starts through the break-up of initially continuous film into isolated grains with expressive shape anisotropy and hexagonal habit. Promising type of such seed layers seem also to be SrAl₁₂O₁₉ films where two kinds of preparation were investigated – deposition of SrAl₁₂O₁₉ onto sapphire substrate and reaction SrO + Al₂O₃.

Other type of magnetic films studied were magnetic spinels Co₃O₄ prepared by decomposition of films of layered cobaltates Na_xCoO₂ deposited by chemical solution deposition method and grown on sapphire substrates.

The films were characterized mainly by AFM and by several XRD techniques. Phase transitions and thermal stability were studied in symmetric Bragg-Brentano geometry, degree of preferred orientation by rocking curves (omega scans) and phi scans of asymmetric reflections, pole figures and also by reciprocal space maps. Residual stresses were also tested but they were usually zero or negligible. All the films were strongly oriented with the planes parallel to the surface but different kind of in-plane orientations was observed often structures with several domains.

11:00am **TF+MI-FrM9 Size Effects on the Order-Disorder Phase Transition Temperature in FeNiPt Nanoparticles**, *G. Sutherland, D. Wood*, Brigham Young University, *A. Warren, K. Coffey*, University of Central Florida, *Richard Vanfleet*, Brigham Young University

Chemically ordering metal alloys such as FePt are hard magnets and good candidates for magnetic data storage in their ordered phase but not in the disordered state. The order-disorder phase transition temperature is impacted by the size of the particle with surface energies becoming significant for nanometer sized particles. Theoretical and computational approaches have predicted lowering of phase transition temperatures as the particle size decreases. Experimental evidence is more limited. Observation of ordering in nanoparticles is a complex interplay between thermodynamic and kinetic factors. Using Fe-Ni pseudo binary alloys with Pt allows isolation of thermodynamic variables. We see a size dependent reduction of order-disorder temperature in this system with particles in the 5 – 12 nm range. At 6 nm the reduction is ~15%

11:20am **TF+MI-FrM10 A Comparison of Heptane Solvent Annealing versus Thermal Annealing Block Copolymers for Bit Patterned Advanced Media**, *Allen Owen, A. Montgomery, H. Su, S. Gupta*, University of Alabama

Hard disk drive storage media is trending towards both smaller physical size and greater storage capacity 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. Statistical designs of experiments were carried out comparing the effect of nanopatterning via ion milling Co/Pd multilayers using two different annealing methods for PS-PFS block copolymers. The design of experiments for each annealing method varied the etch angle, etch time and etch power during ion milling. Wafers that were sputter-deposited with Co/Pd multilayered thin films were spin-coated with PFS block copolymer and solvent annealed under heptane vapor in an oil bath at 35 °C for 6 hours. Identical wafers were thermally annealed in atmosphere at 140 °C for 48 hours. After annealing, the films were ashed in oxygen to remove the PS, leaving the PFS spheres as masks for the subsequent ion milling. The results from each annealing study showed that nanopillars with a nominal size of ~ 30 nm have been fabricated. The thermally annealed Co/Pd multilayers yielded a 407% increase in coercivity to ~6.6 kOe, while the heptane annealed thin film resulted in a 223% increase to ~4.2 kOe. A statistical design of experiments comparing two different etch techniques: (i) inductively coupled plasma reactive ion etching (ICP-RIE) and (ii) ion milling was carried out for these two annealing methods. The results indicate that process optimization can be achieved with a combination of the correct annealing and etching techniques.

Authors Index

Bold page numbers indicate the presenter

— A —

Acremann, Y.: MI-TuM3, 4
Aghaee, M.: TF+EM+MI+MS-TuM4, **6**
Akselrud, L.: AC+AS+MI-WeM10, 12
Albertini, O.R.: MI+SA-TuA11, 10
Arena, D.: MI+SA-TuA12, 10
Arenholz, E.: MI-TuM1, 4

— B —

Back, C.H.: MI+SA-TuA1, 9
Backes, D.: MI-TuM3, 4
Bagus, P.S.: AC+AS+MI-WeA10, **14**
Balsano, R.: SP+AS+MI+NS+SS-FrM6, 18
Banos, A.K.: AC+AS+MI-ThM10, **16**
Bao, Z.: AC+AS+MI-WeM3, 12
Barnett, A.: TF+MI-FrM7, 20
Bartels, L.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA4, 8
Baumann, S.: SP+AS+MI+NS+SS-FrM3, 18
Beach, G.S.D.: MI+SA-TuA3, **9**; MI-
TuM12, 5

Beniwal, S.: MI+SA-TuA12, **10**

Biegalski, M.D.: MI-TuM1, 4

Bigot, J.-Y.: TF+MI-FrM3, 19

Bleuse, J.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA11, 8

Bonetti, S.: MI-TuM3, 4

Booth, C.H.: AC+AS+MI-WeA9, 14

Borisov, P.: MI-TuM5, 4

Burnham, N.A.: SP+AS+MI+NS+SS-
FrM10, **19**

Bursik, J.: TF+MI-FrM8, 20

— C —

Caciuffo, R.: AC+AS+MI-WeM11, 13;
AC+AS+MI-WeM3, 12

Cairney, J.M.: AP+AS+MC+MI+NS-MoM6,
1

Cameron, D.C.: TF+EM+MI+MS-TuM4, 6

Cao, F.: TF+MI-FrM1, **19**

Caretta, L.: MI-TuM12, **5**

Cen, C.: MI-TuM5, 4

Chastanet, G.: MI+SA-TuA12, 10

Chen, Z.: MI-TuM3, 4

Chhowalla, M.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA11, 8

Choi, T.: SP+AS+MI+NS+SS-FrM3, **18**

Chopdekar, R.V.: MI-TuM1, 4; MI-TuM13,
5

Christen, H.M.: MI-TuM1, 4

Chu, Y.-H.: MI+SA-TuA10, 9

Cieslar, M.: AC+AS+MI-WeM12, 13

Coffey, K.: TF+MI-FrM9, 20

Colineau, E.: AC+AS+MI-WeM11, 13

Collazos, S.: SP+AS+MI+NS+SS-FrM9, 19

Corbett, J.P.: MI+SA-TuA9, 9; MI-TuP3, 11

Creatore, M.: TF+EM+MI+MS-TuM4, 6

Cushman, C.V.: MG+2D+MI+NS+TF-
MoA6, 3

— D —

Danis, S.: AC+AS+MI-WeM3, 12

Dauskardt, R.H.: TF+EM+MI+MS-TuM12,
7

Decker, M.: MI+SA-TuA1, 9

Denecke, M.A.: AC+AS+MI-ThM1, **16**

Denys, R.V.: AC+AS+MI-WeM10, 12

Devaraj, A.: AP+AS+MC+MI+NS-MoM5, 1

Ding, Y.: TF+EM+MI+MS-TuM12, 7

Divis, M.: AC+AS+MI-WeM12, 13

Diwan, A.: MG+2D+MI+NS+TF-MoA6, 3

Dobson, K.: TF+MI-FrM7, 20

Donath, M.: MI-TuM10, **4**; MI-TuM11, 4

Dong, S.: MI+SA-TuA10, 9

Dougherty, D.B.: MI+SA-TuA7, **9**

Dowben, P.A.: MI+SA-TuA12, 10

Drozdenko, D.: AC+AS+MI-WeM12, 13

Durcan, C.: SP+AS+MI+NS+SS-FrM4, 18;
SP+AS+MI+NS+SS-FrM5, **18**;
SP+AS+MI+NS+SS-FrM6, 18

Dürr, H.A.: MI-TuM3, 4

— E —

Eder, K.: AP+AS+MC+MI+NS-MoM6, 1

Eklund, A.: MI-TuM3, 4

Eloirdi, R.: AC+AS+MI-WeM11, 13

Enders, A.: MI+SA-TuA12, 10

— F —

Fatayer, S.: SP+AS+MI+NS+SS-FrM9, 19

Felfer, P.J.: AP+AS+MC+MI+NS-MoM6, 1

Folven, E.: MI-TuM13, 5

Frégnaux, M.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA11, 8

Frisch, J.: MI-TuM3, 4

— G —

Gangopadhyay, S.: MI+SA-TuA11, 10

George, S.M.: TF+EM+MI+MS-TuM5, 6

Giovannini, M.: AC+AS+MI-WeM10, 12

Gofryk, K.: AC+AS+MI-WeM5, **12**

Gomez, M.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA4, **8**

Gouder, T.: AC+AS+MI-WeM3, 12

Grepstad, J.: MI-TuM13, 5

Griveau, J.C.: AC+AS+MI-WeM11, 13

Grob, F.: TF+EM+MI+MS-TuM3, 5

Gross, L.: SP+AS+MI+NS+SS-FrM9, 19

Guitán, E.: SP+AS+MI+NS+SS-FrM9, 19

Gupta, S.: TF+MI-FrM10, 20

— H —

Halevy, I.: AC+AS+MI-WeM10, 12;
AC+AS+MI-WeM11, **13**

Havela, L.: AC+AS+MI-WeM10, 12;
AC+AS+MI-WeM12, **13**; AC+AS+MI-
WeM3, 12

Heinrich, A.: SP+AS+MI+NS+SS-FrM3, 18

Hen, A.: AC+AS+MI-WeM11, 13

Hernandez, J.M.: MI-TuM3, 4

Holcomb, M.: MI+SA-TuA10, **9**

Homola, T.: TF+EM+MI+MS-TuM4, 6

Hono, K.: AP+AS+MC+MI+NS-MoM1, 1

— I —

Ikeda, N.: TF+EM+MI+MS-TuM6, 6

Ingram, D.C.: MI+SA-TuA9, 9

Isheim, D.: AP+AS+MC+MI+NS-MoM3, 1

— J —

Jain, S.: TF+MI-FrM3, 19

Janoschek, M.J.: AC+AS+MI-WeM1, **12**

Jasiuk, I.: MG+2D+MI+NS+TF-MoA5, 3

Jia, Y.: MI-TuM13, 5

Johansson, P.: TF+EM+MI+MS-TuM4, 6

Johnson, T.A.: MI-TuM5, 4

Jones, B.A.: MI+SA-TuA11, **10**

— K —

Karim, A.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA7, **8**

Katine, J.: MI-TuM3, 4

KC, A.: MI-TuM5, 4

Kent, A.D.: MI-TuM3, 4

Kim, H.: 2D+EM+MC+MI+NS+SP+SS+TF-
TuA11, 8

Kim, J.: TF+MI-FrM3, 19

Kim-Ngan, N.-T.H.: AC+AS+MI-WeM12,
13

Kitano, M.: TF+EM+MI+MS-TuM6, 6

Knizek, K.: TF+MI-FrM8, 20

Kolomiets, A.: AC+AS+MI-WeM10, 12

Kriegner, D.: AC+AS+MI-WeM12, 13

Krueger, P.: MI-TuM10, 4

Krüger, P.: MI-TuM11, 4

Kukreja, R.: MI-TuM3, 4

Kuusipalo, J.: TF+EM+MI+MS-TuM4, 6

Kuzel, R.: TF+MI-FrM8, **20**

— L —

LaBella, V.: SP+AS+MI+NS+SS-FrM4, **18**;
SP+AS+MI+NS+SS-FrM5, 18;
SP+AS+MI+NS+SS-FrM6, 18

Landa, A.: AC+AS+MI-ThM3, **16**

Langenkämper, Ch.: MI-TuM11, 4

Lederman, D.: MI-TuM5, **4**

Lee, J.-H.: AP+AS+MC+MI+NS-MoM8, 1

Lee, M.: MI-TuM13, 5

Lee, S.I.: TF+EM+MI+MS-TuM1, **5**

Lee, W.K.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA3, **8**

Li, B.: MI-TuM1, 4; MI-TuM13, 5

Linford, M.R.: MG+2D+MI+NS+TF-MoA6,
3

Liu, A.Y.: MI+SA-TuA11, 10

Liu, D.R.: MI-TuP1, **11**

Liu, J.: MI+SA-TuA12, 10

Lucy, J.M.: MI+SA-TuA9, 9

Lutz, C.P.: SP+AS+MI+NS+SS-FrM3, 18

— M —

Macia, F.: MI-TuM3, 4

Mackova, A.: AC+AS+MI-WeM3, 12

Magnani, N.: AC+AS+MI-WeM11, 13

Malm, G.: MI-TuM3, 4

Mandru, A.-O.: MI+SA-TuA9, **9**; MI-TuP3,
11

Mann, M.: MI-TuM12, 5

Martinez, J.:
2D+EM+MC+MI+NS+SP+SS+TF-
TuA4, 8

Maskova, S.: AC+AS+MI-WeM10, **12**

Masanaka, S.: TF+MI-FrM6, 20

Matej, Z.: AC+AS+MI-WeM12, 13

Maydannik, P.S.: TF+EM+MI+MS-TuM4, 6

McIntyre, P.C.: TF+EM+MI+MS-TuM6, 6

Mehta, A.: MI-TuM1, 4

Meng, S.: AP+AS+MC+MI+NS-MoM5, 1

Meyer, G.: SP+AS+MI+NS+SS-FrM9, 19

Migliori, A.: AC+AS+MI-WeA7, **14**

Miliyanchuk, K.: AC+AS+MI-WeM10, 12

Miyamoto, K.: MI-TuM11, 4

Moll, N.: SP+AS+MI+NS+SS-FrM9, 19

Montgomery, A.: TF+MI-FrM10, 20

Mosendz, O.: TF+MI-FrM3, 19

Mu, S.: MI+SA-TuA12, 10

— N —

Nagase, M.: TF+EM+MI+MS-TuM6, 6

Naim, A.: MI+SA-TuA12, 10

Namura, K.: TF+MI-FrM6, 20

Nelin, C.J.: AC+AS+MI-WeA10, 14

Nelson, A.J.: AC+AS+MI-ThM6, 16

Nishiura, K.: TF+MI-FrM6, 20

Nolting, W.: SP+AS+MI+NS+SS-FrM4, 18;
SP+AS+MI+NS+SS-FrM6, **18**

— O —

Obstbaum, M.: MI+SA-TuA1, 9

Ohkubo, T.: AP+AS+MC+MI+NS-MoM1, 1

Ohldag, MI-TuM3, 4

Opila, R.L.: TF+MI-FrM7, 20

Orion, I.: AC+AS+MI-WeM11, 13

Owen, A.: TF+MI-FrM10, **20**

— P —

Pak, J.: MI-TuP3, **11**
Paraskevoulakos, C.: AC+AS+MI-ThM5, **16**
Parikh, P.: AP+AS+MC+MI+NS-MoM5, **1**
Park, C.-G.: AP+AS+MC+MI+NS-MoM8, **1**
Paukov, M.: AC+AS+MI-WeM12, **13**
Paul, W.: SP+AS+MI+NS+SS-FrM3, **18**
Pavliček, N.: SP+AS+MI+NS+SS-FrM9, **19**
Peña, D.: SP+AS+MI+NS+SS-FrM9, **19**
Pérez, D.: SP+AS+MI+NS+SS-FrM9, **19**
Poodt, P.: TF+EM+MI+MS-TuM3, **5**
Pugmire, L.: AC+AS+MI-WeA9, **14**

— R —

Rajagopalan, R.: TF+EM+MI+MS-TuM10, **6**
Ramprasad, R.: MG+2D+MI+NS+TF-MoA3, **3**
Randall, C.: TF+EM+MI+MS-TuM10, **6**
Ren, Z.: TF+MI-FrM1, **19**
Renault, O.J.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **8**
Retterer, S.: MI-TuM13, **5**
Richard, A.L.: MI+SA-TuA9, **9**
Rigutti, L.: AP+AS+MC+MI+NS-MoM10, **2**
Ritter, K.T.: MI-TuM10, **4**
Robinson, J.T.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **8**
Rogalev, A.: AC+AS+MI-WeM11, **13**
Romero, A.H.: MI-TuM5, **4**
Rosa, P.: MI+SA-TuA12, **10**
Roussel, P.: AC+AS+MI-WeA11, **15**
Routkevitic, D.: TF+EM+MI+MS-TuM5, **6**
Rugar, D.: SP+AS+MI+NS+SS-FrM7, **18**
Ruzic, D.N.: MG+2D+MI+NS+TF-MoA5, **3**

— S —

Sasaki, T.: AP+AS+MC+MI+NS-MoM1, **1**
Saw, C.K.: AC+AS+MI-ThM6, **16**
Schmidt, A.B.: MI-TuM10, **4**; MI-TuM11, **4**

Scholl, A.: MI-TuM13, **5**
Schuler, B.: SP+AS+MI+NS+SS-FrM9, **19**
Seol, J.-B.: AP+AS+MC+MI+NS-MoM8, **1**
Sharma, K.: TF+EM+MI+MS-TuM5, **6**
Shchelkanov, I.A.: MG+2D+MI+NS+TF-MoA5, **3**
Sheehan, P.E.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **8**
Shick, A.B.: AC+AS+MI-WeM11, **13**
Shuh, D.K.: AC+AS+MI-WeA3, **14**
Siekhaus, J.: AC+AS+MI-ThM6, **16**
Singh, B.: MG+2D+MI+NS+TF-MoA6, **3**
Smith, A.R.: MI+SA-TuA9, **9**; MI-TuP3, **11**
Soroka, M.: TF+MI-FrM8, **20**
Springell, R.: AC+AS+MI-WeM3, **12**
Sterbinsky, G.: MI+SA-TuA12, **10**
Stöhr, J.: MI-TuM3, **4**
Su, H.: TF+MI-FrM10, **20**
Sutherland, G.: TF+MI-FrM9, **20**
Suzuki, M.: TF+MI-FrM6, **20**

— T —

Takamura, Y.: MI-TuM1, **4**; MI-TuM13, **5**
Tan, A.J.: MI-TuM12, **5**
Tao, M.: SP+AS+MI+NS+SS-FrM10, **19**
Tereshina, E.: AC+AS+MI-WeM3, **12**
Thibeault, B.: TF+MI-FrM7, **20**
Tkach, I.: AC+AS+MI-WeM12, **13**
Tobin, J.G.: AC+AS+MI-ThM12, **16**
Trappen, R.: MI+SA-TuA10, **9**
Turek, I.: AC+AS+MI-WeM12, **13**

— U —

Urazhdin, S.: MI-TuM3, **4**

— V —

Valentin, M.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA4, **8**
van den Bruele, F.: TF+EM+MI+MS-TuM3, **5**
Vanfleet, R.: TF+MI-FrM9, **20**

Varaksa, N.: TF+EM+MI+MS-TuM5, **6**
Venhaus, J.: AC+AS+MI-WeA9, **14**
Vitova, T.: AC+AS+MI-WeA1, **14**
Voiry, D.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **8**
Vomir, M.: TF+MI-FrM3, **19**

— W —

Wang, F.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA9, **8**
Wang, J.: MI+SA-TuA7, **9**
Warren, A.: TF+MI-FrM9, **20**
Wei, D.: MI+SA-TuA1, **9**
Weller, D.: TF+MI-FrM3, **19**
Weng, C.J.: MI-TuP1, **11**
Whitener, K.E.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **8**
Wilhelm, F.: AC+AS+MI-WeM11, **13**
Wissing, S.N.P.: MI-TuM10, **4**
Woltersdorf, G.: MI+SA-TuA1, **9**
Wood, D.: TF+MI-FrM9, **20**
Wu, W.: SP+AS+MI+NS+SS-FrM1, **18**
Wynn, T.: MI-TuM13, **5**

— Y —

Yang, F.: MI+SA-TuA9, **9**
Yartys, V.: AC+AS+MI-WeM10, **12**
Young, A.: MI-TuM13, **5**
Young, A.F.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA1, **8**
Yu, x.: SP+AS+MI+NS+SS-FrM10, **19**
Yuan, B.: TF+MI-FrM7, **20**

— Z —

Zhang, X.: MI+SA-TuA12, **10**
Zhou, J.: MI+SA-TuA10, **9**