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

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

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

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

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

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

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

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

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

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

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

References

1. A. Hoffmann and H. Schultheiß, Curr. Opin. Solid State Mater. Sci. 19, 253 (2015)
2. A. Hoffmann and S. D. Bader, Phys. Rev. Appl. 4, 047001 (2015).
3. W. Jiang, et al., AIP Adv. 6, 055602 (2016).
4. W. Jiang, et al., Science 349, 283 (2015).
5. O. Heinonen, et al., Phys. Rev. B 93, 094407 (2016).
6. A. Hoffmann, IEEE Trans. Magn. 49, 5172 (2013).
7. W. Jiang, et al., arXiv:1603.07393.

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

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

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

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

[1] S.V.Grigoriev, Yu.O. Chetverikov, D.Lott, A. Schreyer, Phys. Rev. Lett. 100, 197203. (2008)

[2] S.V.Grigoriev, D. Lott,2 Yu. O. Chetverikov,1 A. T. D. Grünwald, R. C. C. Ward, and A. Schreyer, Phys. Rev. B 82, 195432 (2010)

[3] V. V. Tarnavich, D. Lott, S. Mattauch, A. Oleshkevych, V. Kapaklis, and S. V. Grigoriev, Phys. Rev. B 89, 054406 (2014)

[4] K. Chen, D. Lott, F. Radu, F. Choueikani, E. Otero, P. Ohresser, Scientific Reports 5, 18377 (2015)

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

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

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

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

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

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

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

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

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

Moderator: Valeria Lauter, Oak Ridge National Laboratory

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[4] B. Engelkamp *et al.*, Phys. Rev B **92**, 085401 (2015).

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

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

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

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

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

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

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Applied Surface Science
Room 101B - Session AS+AC-TuM

Practical Surface Analysis II: Microanalysis, Nanoanalysis, Atom Probe, and All Things 'Small'

Moderators: Arun Devaraj, Pacific Northwest National Laboratory, Daniel Gaspar, Pacific Northwest National Laboratory

8:00am **AS+AC-TuM1 Progress Toward Atomic-Scale Tomography*,* *Thomas Kelly,*** CAMECA Instruments Inc. **INVITED**

There have been efforts of late to produce three-dimensional images at the atomic scale where every atom is accounted for and the position information is quite precise. All atoms in a two-dimensional thin film of boron nitride were imaged and identified by Krivanek et al. [1]. Scott et al. were able to produce three-dimensional images using electron tomography that show every atom in a gold nanoparticle containing over 7000 gold atoms [2]. Using atom probe tomography (APT), Moody et al. have shown three-dimensional images of several million atoms in an aluminum alloy where each atom is positioned correctly in a face-centered cubic lattice and 60% of the atoms are detected [3]. These are all impressive and important developments. They suggest what atomic-scale microscopy might ultimately achieve: recording with high precision the position and identity of every atom in a technologically relevant structure. This capability can fairly be termed atomic-scale tomography (AST).

If AST is to be achieved, it appears that APT and electron microscopy should be used synergistically to capture the strengths of one technique to overcome the limitations of the other. This question has been explored in detail [4] and the conclusion is that there are some ways that AST can be achieved. The instrumental developments needed to reach AST with APT and (S)TEM as a basis include: trajectory corrections for precise atom placement and detecting 100% of the atoms without ambiguity in identity. The former may be achieved by imaging the specimen apex to enable precise ion trajectory simulation toward the detector. An electron column integrated into an atom probe can, in principle, record the specimen apex shape throughout an entire atom probe experiment. Detectors for recording all atoms might be based on superconducting materials [5]. If these detectors also record an ion's kinetic energy, then most time of flight-based ambiguities in peak identification can be eliminated [6].

Once these instruments are combined, the full analytical capabilities of each can be used synergistically. This presentation will outline approaches that should be pursued to reach this end and review the current plans to build an atomic-scale tomograph.

[1] O. L. Krivanek, et al., *Nat. Lett*, vol. 464, p. 571, 2010.

[2] M. C. Scott et al., *Nature*, vol. 483, pp. 444–447, 2012.

[3] M. P. Moody et al., *Micros Microanal*, vol. 17, pp. 722–723, 2011.

[4] T. F. Kelly et al., *Microsc. Microanal.*, vol. 19, pp. 652–664, 2013.

[5] R. F. McDermott, J. R. Suttle, and T. F. Kelly, "Unpublished research," 2015.

[6] T. F. Kelly, *Micros Microanal*, vol. 17, pp. 1–14, 2011.

9:20am **AS+AC-TuM5 Atom Probe Tomography and Electron Microscopy Investigation of Composition and Structure of Functionalized Carbon*,* *Chilan Ngo*,** *D.R. Diercks, M.B. Strand, S. Pylypenko,* Colorado School of Mines

Carbon is one of the most studied materials due to its broad range of properties, versatility, and low cost. Functionalization or doping of carbon with heteroatoms is an effective way to tailor the properties of carbon and further modify the material for various applications. While significant efforts have been placed on understanding the composition, structure and properties of doped carbon supports, there is a lack of understanding regarding the 3-D distribution of dopant within high surface area materials. In this work, we expand the understanding of nitrogen-functionalized carbon materials by focusing on analysis of nitrogen distribution through atom probe tomography (APT), transmission electron microscopy (TEM), and complementary characterization techniques. Specifically, APT analysis has been applied to provide unique, high-resolution insight into the composition/structure of high-surface area carbon – demonstrating feasibility of the technique towards such materials. Nitrogen-doped carbon nanospheres were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different nitrogen concentration and varied relative distribution of nitrogen functionalities. Sample preparation was performed via focused-ion beam (FIB), in order to isolate C spheres into a workable APT tip. The work presented herein provides a foundation not only for further understanding of N-doped carbon materials and N-containing nonprecious catalysts (NPMCs) employed in a variety of important catalytic reactions, but also to prepare model high-surface area materials, compatible for study via *in situ* liquid and electrochemistry TEM techniques.

9:40am **AS+AC-TuM6 Advanced XPS Imaging and Spectromicroscopy: a Review of Current Capabilities*,* *Olivier Renault,*** CEA-University Grenoble Alps, France

At the practical level, XPS imaging is still poorly used today. This is due to on the one hand to instrumental issues with for instance the difficulty to produce nice secondary electron images to help quick navigation at the surface; on the other hand, lower counting statistics of core-level images necessitate high transmission imaging spectrometer and in some cases post-processing of image data sets using, e.g, PCA. XPS imaging and spectromicroscopy is nevertheless complementary to ToF-SIMS and Auger as it provides quantification and chemical speciation, besides accessing the mesoscopic scale. It should therefore deserve a much broader use to better understand laterally heterogeneous systems. On some instruments, electronic band structure imaging, equivalent to ARUPS microscopy, is becoming possible in routine use, widening significantly the capabilities of photoelectron microscopy with laboratory sources for important applications, e.g., novel 2D materials. In this contribution, we will review through various examples from graphene doping [1] to oxide-based resistive memories and single layer MoS2, the current capabilities of XPS imaging and spectromicroscopy as implemented with a PEEM-based commercial instrument enabling core-level images with sub-µm scale lateral resolution. The benefits of band structure imaging for 2D semiconducting materials will be addressed [2]. Finally, perspectives regarding photoelectron microscopy with hard x-rays will be drawn [3].

This work was performed on the Nanocharacterization platform of CEA-MINATEC.

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

[2] M. Frégnaux, O. Renault et al., Surf. Interface Anal. 2016 (in press).

[3] M. Patt et al., Rev. Sci. Instrum. 85 (11) (2014) ; C. Zborowski, O. Renault et al., Appl. Phys. Lett. 2016 (accepted).

11:00am **AS+AC-TuM10 Challenges and Solutions for Confined Volume Characterization in Semiconductor Systems*,* *Wilfried Vandervorst,*** IMEC & KULeuven, Belgium **INVITED**

Pushing the limits in IC-technology towards the nanometer scale, novel materials and in particular interfacial interactions in 3D-devcies play a crucial role leading to a demand for concepts suited to probe very small volumes and enable atomic scale observations.

Atom probe tomography (APT) can provide 3D-composition analysis within very small volumes (a few nm^3) with high sensitivity and accuracy. Nevertheless the presence of many materials with different evaporation fields and inhomogeneous laser-tip interactions creates tip distortions and trajectory aberrations inducing severe artefacts in reconstructed profile. Limits in mass resolving power, the presence of multiple charge states, cluster emission and variable detection efficiencies and strong laser power effects do hamper accurate and precise quantification and/or deviation from the correct composition.

Complementary to the resolving power of APT, is the application of scanning probes which enable to grasp the electrical activity of dopants or identify conduction paths within such volumes. As SPM is inherently a 2D-method, concepts for expanding into the depth dimension are explored (cfr Scalpel SPM, ion beam sputtering icw SPM) with applications in logic device engineering, failure analysis and memory cell development.

As APT and SPM suffer from a poor productivity and a lack of statistical averaging over large areas as required in more production oriented metrology. A solution can be found through ensemble measurements whereby spatial resolution is provided by the device under investigation and not by the probing beam. We will illustrate this concept through applications of "self focusing SIMS" which allows to determine the composition from trenches as small as 20 nm without having an ion beam with nm-resolution. Moreover within the area of selective area deposition SF-Sims may provide a unique analysis capability sampling defectivity of self-assembled monolayers and limited selectivity.

Similarly crystallinity in narrow trenches (< 50 nm) can be obtained through channeling RBS whereby again we use a large beam but nevertheless probe the information from an array of very fine features. In all these cases, the averaging over a large array provides excellent statistics and in some cases dramatically improved productivity through the enhanced signal versus the case of a very focused probe beam. The latter is ultimately exemplified in Raman experiments on narrow SiGe-trenches where we demonstrate that very narrow features (20 nm) provide a significantly enhanced (50-100x) compared to its blanket counterpart enabling to probe composition and structural properties from a small volume.

11:40am **AS+AC-TuM12 Characterization of Protein G B1 Immobilized Gold Nanoparticles using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy***, Y.-C. Wang,* ***David Castner****,* University of Washington

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto nanoparticle surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have significant impact on the clinical outcomes of these carriers by impacting its biostability and efficacy.

In this work, Protein G B1, a protein that will selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs using either carbonyldiimidazole (CDI) chemistry or through a maleimide-cysteine bond. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the protein G B1 immobilization. Unlike conventional NP characterization techniques such as dynamic light scattering (DLS) and UV/Vis, XPS and ToF-SIMS can provide additional information on the surface elemental composition, protein coverage and orientation.

XPS analysis confirmed the AuNP functionalization with both the maleimide and OEG-SAMs. After incubation with protein, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of both SAMs. Loosely bound protein on the AuNPs was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization, CDI activation, and protein immobilization by identifying signature secondary ions from each step of the protein immobilization process. Further, by utilizing high surface sensitivity and small sampling depth (2nm) of ToF-SIMS, the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite end of the protein. As expected, the non-site specific CDI chemistry did not lead to a well-defined orientation on the AuNPs. In contrast, we were able to control the orientation of the immobilized protein using maleimide functionalized AuNPs and cysteine mutants of Protein G B1. The systematic characterization of this study provided detailed information about protein-nanoparticle interactions that advances our understanding of the complex protein-NP interface.

12:00pm **AS+AC-TuM13 What's New in Wetting? Inorganic Nanotubes at a Water Interface - A Molecular View***,* ***Sidney Cohen****, O. Goldbart, I. Kaplan-Ashiri,* Weizmann Institute of Science, Israel*; P. Glazyrina,* Ural Federal University, Russia*; H.D. Wagner,* Weizmann Institute of Science, Israel*; A. Enyashin,* Ub Ras, Russia*; R. Tenne,* Weizmann Institute of Science, Israel

Wetting of solid surfaces is a complex and subtle phenomenon which has been studied carefully over the past 200 years. A good understanding of wetting can explain many key physical interactions at interfaces, notable examples being in lubrication, composite materials, and capillarity. Wetting phenomena continue to intrigue the scientific community due to the complexity of this seemingly simple process. In recent years, specific nano-scale aspects of wetting have been revealed, highlighting the importance of a molecular-level understanding of wetting. The study of nanotube wetting encompasses the old/new, as well as nanoscale aspect of these endeavors. Proven importance of nanotubes as fillers in ultra-strength nanocomposites, where the interfacial interactions in the nanocomposite are controlled by wetting, lends a technological push to the field. Inorganic nanotubes (INT) formed from tungsten and molybdenum disulfides disperse very well in a variety of polymers, enabling preparation of nanocomposites with enhanced mechanical properties, thermal stability and improved rheological behavior. Nonetheless, the nature of the interaction between a nanotube and polymer liquid has received little attention and is poorly understood.Here we present a combined experimental and theoretical study on the microscopic interaction of WS_2 nanotubes (INT-WS_2) with water. The unique experimental approach is based on manipulation and pull-out of individual nanotubes from water films while monitoring the forces generated with a cantilever in an atomic force microscope (AFM). This method draws on concepts of the classic Wilhemy Balance Technique, while exploiting the exquisite force control of the AFM. The AFM experiments were contrasted with parallel experiments in an environmental scanning electron microscope (ESEM). Detailed theoretical calculations based on density functional theory (DFT) predicted well the interaction energy for large, closed cap nanotubes, but vastly underestimated the interaction energy with small, open-ended nanotubes. For those small diameter tubes, force-field molecular dynamics (MD) simulations together with a thermodynamic analysis qualitatively explain the observed behavior, strongly implicating a dominant capillary effect. Visualization of the pullout in the ESEM together with AFM force traces allow precise modelling of the meniscus formation during pullout, reflecting the energetics of the interface at, and inside the nanotube wall.**Acknowledgment:** Supported by the Israel National Nano-Initiative, the Israel Science Foundation, H. Perlman Foundation. and Act 211 Government of the Russian Federation, contract № 02.A03.21.0006.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces***, T.C. Rödel,* Université Paris-Sud - SOLEIL, France*;* ***Patrick Le Fèvre****,* Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the $LaAlO_3/SrTiO_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of $SrTiO_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO_x layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of $SrTiO_3$, anatase-TiO_2, or $BaTiO_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

[1] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).

[2] A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, Nature **469**, 189 (2011).

[3] T. C. Rödel, F. Fortuna, F. Bertran, M. Gabay, M. J. Rozenberg, A. F. Santander-Syro, and P. Le Fèvre, Phys. Rev. B **92**, 041106 (2015).

[4] T. C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P. Le Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecœur, and A. F. Santander-Syro, Adv. Mater. **28**, 1976 (2016).

8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli**, A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

[1] A. Sala, G. Zamborlini, T.O. Menteş, A. Locatelli; Small **11**(44), 5927–5931(2016).

[2] G. Zamborlini, M. Imam , L.L. Patera , T.O. Menteş , N. Stojić , C.Africh , A. Sala , N. Binggeli , G. Comelli and A.Locatelli; Nano Lett. **15**(9), 6162–6169 (2015).

9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen**, R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to $W(CO)_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se_n. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se_n is gated: the absence of Se, but the presence of $W(CO)_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC***, **Victor Aristov**,* ISSP RAS, Chernogolovka, Russia, Russian Federation*; H.-C. Wu,* BIT, Beijing, China*; O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany*; A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces***, **Nicholas Barrett**,* CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)

[2] J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, Physical Review Letters 111, 127602 (2013)

11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy***, Martina* ***Mueller,*** Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to $SrTiO_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

[3] M. Müller *et al*, J. Electron Spectrosc. Relat. Phenom. 208, 24 (2016)

Actinides and Rare Earths Focus Topic
Room Hall D - Session AC-TuP

Chemistry and Physics of the Actinides and Rare Earths Poster Session

AC-TuP1 Spatially Resolved Uranium Speciation in Nuclear Materials by Scanning Transmission X-ray Microscopy*, **Joseph Pacold**,* Lawrence Berkeley National Laboratory*; M.J. Kristo, K.B. Knight, K.S. Holliday,* Lawrence Livermore National Laboratory*; W.W. Lukens, C.H. Booth, S.G. Minasian, T. Tyliszczak, D.K. Shuh,* Lawrence Berkeley National Laboratory

The production and manipulation of nuclear material can leave distinct physical and chemical signatures, which can later be characterized to provide evidence of the origin and process history of an unidentified specimen, a field known as 'nuclear forensics'. A broad variety of analytical chemistry techniques can provide information about interdicted and post-detonation materials. Here, we present the results of several research studies of uranium-bearing forensic specimens by soft X-ray scanning transmission X-ray microscopy (STXM). STXM yields X-ray absorption spectroscopy data with 25-nm or better spatial resolution, making it possible to quantitatively evaluate variations in oxidation state and other chemical properties across a heterogeneous specimen. Operating in the soft X-ray regime provides access to the $N_{IV,V}$ edges of the actinides and the oxygen *K* edge, which is highly sensitive to variations in U-O bonding, and consequently carries unique fingerprints of uranium oxides and their hydrates. Thus, this approach makes it possible to evaluate the oxidation state and the heterogeneity of nuclear forensic samples, yielding information on formation or process history, and/or past storage conditions. In studies of U-bearing glassy materials, the *L* edges of some transition metals (particularly iron, which influences the redox behavior of uranium) can provide additional insights. Technical developments in STXM operations relevant to forensics are also summarized. In particular, we report on improvements in sample preparation and rapid data analysis methods implemented in STXM experiments at Beamline 11.0.2 of the Advanced Light Source.

AC-TuP2 XPS Investigation on the Reduction of Aged UO_2 Powders during Exposure to Vacuum*, **Scott Donald**, M. Davisson, Z. Dai, A.J. Nelson,* Lawrence Livermore National Laboratory

The evolution in vacuum of UO_2 powder samples, previously aged under a controlled environment composed of 20% O_2 and relative humidity varying from 34% to 98%, was studied using core level x-ray photoelectron spectroscopy. Upon exposure to ultra-high vacuum, the U 4f peak position was found to shift to a lower binding energy with time, consistent with a decrease in the overall oxidation state of the uranium. No samples were found to reduce fully to stoichiometric UO_2 under vacuum; those exhibiting the greatest decay with time asymptotically approached a mean uranium valence of +4.5, analogous to U_4O_9, within 14 days. The reaction rate was found to be variable with the initial mean uranium valence, with more oxidized samples reducing more quickly. Scanning electron microscopy images of the aged powders showed corresponding structural variation and enhanced surface cracking, both of which may serve to facilitate the reduction process.

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

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

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

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

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

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

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

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

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

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

[1] J.A. Mydosh and P.M. Oppeneer, *Rev. Mod. Phys.***83**, 1301 (2011)

[2] H.C. Walker, *et al*., *Phys. Rev. B***83**, 193102 (2011)

[3] R. Okazaki, *et al*., *Science***331**, 439 (2011).

[4] S. Kambe, *et al*., *Phys. Rev. Lett.***110**, 246406 (2013).

[5] S. Tonegawa et al., *Nat. Comms.* **5**, 4188 (2014)

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

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

[1] S. Maskova, L. Havela, E. Santava, and K. Miliyanchuk, J. of Physics: Conf. Ser.200 (2010) 032040.

[2] S. Maskova, S. Danis, K. Miliyanchuk, O. Stelmakhovych, B. Vondrackova, A.V. Kolomiets, L. Havela, J. Alloys Comp. 646 (2015) 885-892.

[3] L. Havela, K. Miliyanchuk, A. Kolomiyets: Int.J.Mat.Res. 100 (2009) 1182-1186.

[4] H. Maletta, V. Sechovsky, P.A. Veenhuizen, F.R. de Boer, L. Havela, and G. Hilscher, Z.Phys. B – Cond. Matter 72 (1988) 455-460.

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

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

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

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

The Pressure as function of V/V_0 was fitted by Vinet equation to yield the B_{-0} and B_0' of the EOS. B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0 at zero pressure. For our pure Al B_0=68.6GPa while B_0' was kept at 3.6 .

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

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

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

References

[1] Hu, J.: High pressure X-ray beam line X17C. www.bnl.gov/x17c. Updated 07/01/2007

[2] Rietveld, H.M.: J. Appl. Crystallogr. 2, 65 (1969)

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

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

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

1. P. S. Bagus*, et al.*, Surf. Sci. **643**, 142 (2016).

2. P. S. Bagus, M. J. Sassi, and K. M. Rosso, J. Electron Spectrosc. Relat. Phenom. **200**, 174 (2015).

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

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

[1] L. Petit, D. Paudyal, Y. Mudryk, K. A. Gschneidner, Jr., V. K. Pecharsky, M. Lueders, Z. Szotek, R. Banerjee, and J. B. Staunton, Phys. Rev. Lett **115**, 207201 (2015)

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

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

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[*] **Gaede Langmuir Award Winner**

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

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

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

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

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

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

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

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

3. calculation of the pNMR shifts in the An(Et-DPC) $_3^{3-}$ series and comparison with the lanthanide series. The variation in temperature of this shift will be discussed.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Actinides and Rare Earths Focus Topic
Room 103C - Session AC+AS+SA-ThM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Art Nelson, Lawrence Livermore National Laboratory

8:00am **AC+AS+SA-ThM1 Covalency in Oxidized Uranium*, James G. Tobin,*** University of Wisconsin-Oshkosh **INVITED**

Actinides, the 5*f* elements and their compounds, alloys, and mixtures, are a crucially important part of modern technological societies. Moreover, uranium dioxide is the most widely used nuclear fuel for the generation of electricity. Yet, because of the complexity of the 5*f*/6*d* electronic structure in the actinides, a fundamental understanding of their physical behavior, in actinides in general and uranium dioxide in particular, has not been achieved.

Theoretically, it has been proposed that covalency is an important part of the electronic structure of actinide dioxide, although some disagree. Experimentally, spectroscopic studies have been reported which support the hypothesis of 5*f* covalency. However, a crucially important and absolutely essential component has been missing: a systematic study where the nature of the oxidant is changed, so the specifics of the 5*f* and 6*d* covalencies could be varied and monitored. The turning-on and turning-off of an effect is the essence of a true benchmarking. The work reported here clearly and irrevocably establishes experimentally the strong presence of U 5*f* –O 2*p* covalency in the unoccupied density of states of UO2, the most important of our nuclear fuels.

This comparative study will feature the isoelectronic systems uranium dioxide (UO2) and uranium tetrafluoride (UF4). While isoelectronic, both being U^{+4} 5*f* ^{2} in the formal limit, they exhibit substantially different structures. UO2 is a fluorite (cubic) material, while UF4 is monoclinic. However, both exhibit very similar U *L*3 extended x-ray absorption fine structure (EXAFS) behavior, indicative of quantitatively similar interatomic distances. The result of this comparative study is that UF4 exhibits continued 6*d* covalency but the almost complete loss of 5*f* covalency, while UO2 clearly displays both strong 5*f* and 6*d* covalencies. Here we have direct experimental demonstration that 5*f* covalency is important in actinide oxides but can be lost with a more powerful oxidizing agent such as fluorine.

To summarize: Using x-ray emission spectroscopy and absorption spectroscopy, it has been possible to directly access the states in the unoccupied conduction bands that are involved with 5*f* and 6*d* covalency in oxidized uranium. By varying the oxidizing agent, the degree of 5*f* covalency can be manipulated and monitored, clearly and irrevocably establishing the importance of 5*f* covalency in the electronic structure of the key nuclear fuel, uranium dioxide.

Collaborators on this work include: S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng. [*See PHYSICAL REVIEW B **92**, 045130 (2015)]

8:40am **AC+AS+SA-ThM3 An In Situ X-ray Diffraction Study of Plutonium Oxidation*, Paul Roussel,*** *W. Lake,* AWE, UK

X-ray diffraction was used to follow the oxidation of α-phase plutonium in oxygen at a pressure of 500 mbar. The composition of the growing oxide scale consisted of the trivalent cubic sesquioxide α-Pu_2O_3 and tetravalent fluorite dioxide PuO_2. The hexagonal β-sesquioxide phase was not detected. The quantity and lattice parameters of the oxide phases were determined from Rietveld analysis of the diffraction patterns. The lattice parameters of both oxides were found to decrease with increasing oxide quantity. Decreasing lattice parameters occur from increasing oxygen anion concentration in each oxide phase. The rate of oxidation for the total oxide composition at various temperatures below 100 °C was found to be linear, indicative of possible moisture enhanced oxidation. A detailed analysis of the contributions of the individual oxide compositions will be presented. Post oxidation optical microscopy of the coherent oxide scale showed areas of thicker scale typical of island growth. When the oxidation reaction was allowed to proceed to form olive green spalled oxide, X-ray diffraction analysis of the powder showed it to consist as a mixture of both cubic oxide phases.

Our initial XRD work presented at this meeting in 2012 suggested the initial oxide film grown on δ-plutonium might be amorphous. This work has been repeated using the XRD in-situ environmental reaction cell and the results will be presented.

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9:00am **AC+AS+SA-ThM4 Advanced Applications of Synchrotron Sources to Describe Water Soluble Plutonium Colloids*, Thomas Dumas,*** CEA, France*; E. Dalodière, M. Virot,* ICSM Marcoule*; V. Morosini,* CEA Marcoule*; T. Chave,* ICSM Marcoule*; C. Hennig,* Helmholtz Zentrum Dresden-Rossendorf*; T. Wiss,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements*; D.K. Shuh, T. Tyliszcaak,* Lawrence Berkeley National Laboratory*; P. Moisy,* CEA Marcoule*; I. Nikitenko,* ICSM Marcoule

Colloidal species of Pu(IV) were shown to play a central role in the speciation of plutonium in various aqueous wastes and in biosphere [1-3]. However, a comprehensive understanding of the behavior and structure of Pu colloids remains elusive and hinders progress on the development of reliable processes of their management. Preparation of plutonium colloidal species with controlled composition and properties is still a challenge. Herein, we report the preparation of stable Pu(IV) colloids by the action of ultrasonic waves on PuO_2 in salt-free water conditions. Sonochemical colloid was compared with hydrolytic colloid using HRTEM, Pu LIII-edge EXFAS and STXM/NEXAFS techniques.

HRTEM revealed nanostructured morphology for both colloids composed of particles of PuO_2 (*fcc*, space group) measuring about 7 nm and 3 nm, respectively. The EXAFS spectra of colloidal PuO_2 nanoparticles were fitted on the basis of PuO_2 cristal structure. Combined HRTEM and EXAFS results revealed the correlation between the coordination numbers (i.e. Pu-O and Pu-Pu) and atomic surface-to-volume ratio of studied PuO_2 nanoparticles.

The STXM/NEXAFS technics implemented at ALS BL 11-0-2 was used for the first time to study plutonium colloids. It offers a new topographic angle to describe colloids combined to spectroscopic measurements at oxygen K edge. It first revealed that the oxygen state of hydrolytic Pu colloid is influenced by hydrolyzed Pu(IV) species in much more extend than the sonochemical colloids. Moreover the topographic analysis highlight discrepancies in plutonium and oxygen distribution for hydrolytic Pu colloid on the contrary to sonolitic one.

Complementarily to previous studies, this work confirmed that plutonium colloids (hydrolytic and sonochemical) can be described as core-shell nanoparticles composed of quasi stoichiometric PuO_2 core and hydrolyzed Pu(IV) moieties at the surface shell. Nevertheless, the application of soft X-ray technics highlight the strong influence of the synthetic route on colloid chemical composition and hence its expectable reactivity.

1. A. B. KERSTING, Plutonium Transport in the Environment, *Inorg. Chem.,***52**, 3533 (2013).

2. A. I. ABDEL-FATTAH, D. ZHOU, H. BOUKHALFA, S. TERIMALA, S. D. WARE, A. A. KELLER, Dispersion Stability and Electrokinetic Properties of Intrinsic Plutonium Colloids: Implications for Subsurface Transport, *Env. Sci. Technol.*, **47**, 5626 (2013).

3. C. WALTER, M. A. DENECKE, Actinide Colloids and Particles of Environmental Concern, *Chem. Rev.,* **113**, 995 (2013).

9:20am **AC+AS+SA-ThM5 *In Pristinum* Observation of Plutonium Hydride*, Martin Brierley,*** *J.P. Knowles,* AWE

The reaction of plutonium with hydrogen creates plutonium hydride in an energetic process which often liberates the reaction product as a powder. Plutonium hydride is pyrophoric; therefore study of the reaction product usually requires that it is passivated by careful exposure to oxygen prior to removal from the reaction chamber. The passivation process is highly energetic with the potential to significantly affect the microstructure of the reaction product and surrounding metal. In this study we used a scanning electron microscope with an adjoining reaction chamber to maintain vacuum between reaction and analysis to grow plutonium hydride and subsequently analyse the reaction products as formed.

Initial work on electro refined Pu gave a slow reaction to hydrogen, requiring an *in situ* heat treatment to form hydride. Analysis of the reaction product was made *in vacuo* following reaction, preventing oxygen from accessing the sample. Subsequent cross sectional analysis of the reaction product morphology was performed, showing a coating of a hydride product layer with an open structure under the original surface oxide [1].

A sample of mixed α/δ phases was successively exposed to hydrogen for increasing durations of 60, 7200 and 70320 s. No evidence of reaction was evident following the 60 s and 7200 s exposures, unlike that observed in experiments on gadolinium [2] and uranium [3]. Following the 70320 s exposure, 96 % of the available hydrogen was consumed and several large anisotropic reaction sites had formed. The hydride sites on this mixed phase sample exhibited anisotropic growth similar to δ-stabilised plutonium samples investigated previously [4]. Deformation of the δ-phases surrounding hydride sites occurred via slip processes. Cracks formed in the overlying oxide layer above the deformed material allowing facile access for hydrogen to reach fresh Pu at the metal/oxide interface. Subsequent cross sectional analysis revealed anisotropic growth of hydride reaction sites, strongly supporting our previously proposed mechanism for anisotropic growth [4]. The α-phase domains resisted deformation and instead transferred the stresses from the hydride reaction front further into the surrounding metal. Post experimental cross sections through reaction sites suggest that hydride regions associated with α-domains had not undergone complete reaction.

References

1. M. Brierley et al., Journal of Nuclear Materials 469 (2016) 39-42

2. G.M. Benamar, et al., Journal of Alloys and Compounds 520 (2012) 98–104.

3. R.M. Harker, A.H. Chohollo, MRS Online Proceedings Library Archive, 1444 (2012) 189

4. M. Brierley, et al., Journal of Nuclear Materials 469 (2016) 145-152

9:40am **AC+AS+SA-ThM6 Evidence for f- and d-orbital Mixing in Lanthanide and Actinide Dialuminides, MAl$_2$ (M = Ce, Sm, Eu, Yb, Lu, U, Pu)**, ***Stefan Minasian***, Lawrence Berkeley National Laboratory (LBNL); *A.B. Altman, J. Arnold,* University of California at Berkeley; *E.D. Bauer,* Los Alamos National Laboratory; *C.H. Booth, J.I. Pacold, C.D. Pemmaraju, D.G. Prendergast, D.K. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory (LBNL)

For most scientific and technical applications, aluminum is well-regarded as a trivalent, electropositive and Lewis-acidic metal. However, this textbook model fails to adequately explain the unusual chemical and physical properties of many f-element molecules, materials, and alloys incorporating aluminum and other group 13 elements. In order to develop a more nuanced model of aluminum electronic structure, we have turned to metal K-edge X-ray Absorption Spectroscopy (XAS), which is an established technique for evaluating electronic structure in bioinorganic and inorganic compounds. Pre-edge peaks in K-edge XAS correspond to bound state transitions between core and unoccupied orbitals. Therefore, by comparing pre-edge features to established references, information can be gathered on the electronic structure of a system and the orbitals involved in bonding. However, there is very little precedent for the measurement and interpretation of aluminum K-edge XAS for molecules and materials.

This presentation will describe our recent efforts to develop Al K-edge XAS as a probe of chemical bonding and electronic structure in Al molecules and materials with lanthanide and actinide metals. Work began by examining a series of molecular aluminum compounds and by systematically varying supporting ligands and oxidation states. Features in the Al K-edge spectra were fully assigned through a comprehensive polarization study and comparison with the results of XCH and DFT calculations. Results were interpreted within a molecular orbital framework, providing unique insight that could not be obtained from analysis of NMR or metrics from single-crystal X-ray diffraction. These results have laid a foundation for ongoing efforts with lanthanide and actinide aluminum alloys, MAl$_2$ (M = Ce, Sm, Eu, Yb, Lu, U, and Pu). Comparisons between the Al K-edge spectra and earlier resonant X-ray emission spectra for the MAl$_2$ compounds provide unique insight into how electronic structure influences the desirable physical properties of these materials. For EuAl$_2$ and YbAl$_2$, the increasing occupancy of the 4f orbitals enhances screening of the 5d orbitals, resulting in enhanced Al 3p and Ln 5d orbital mixing for Eu and Yb that is not observed for Ce, Sm, or Lu. For UAl$_2$ and PuAl$_2$, the Al K-edge XAS and theory results also provides convincing evidence of Al 3p and 6d orbital mixing. Because of the enhance radial extension of the 6d orbitals, 6d orbital involvement in bonding for PuAl$_2$ is more likely to have an impact on the stability of the Pu–Al bonds. Current efforts are focused on evaluating f-element interactions with aluminum in other stoichiometric and non-stoichiometric alloys.

11:00am **AC+AS+SA-ThM10 Comparative Analysis of Uranium Oxide Films**, ***Miguel Santiago Cordoba***, Los Alamos National Laboratory

Depleted Uranium (DU) Oxide thin films are considered to be employed as surrogates and reference compounds for systematic studies on the elucidation of fundamental properties of actinide materials. The goal of this work is to compare surface morphologies of DU oxide thin films fabricated by two techniques, polymer assisted deposition (PAD) and electron beam evaporation (EBE). In this contribution, we utilized a MultiMode atomic force microscope (AFM) operating in tapping mode in order to compare and establish a contrast among the three dimensional surface structures of polycrystalline U$_3$O$_8$ and UO$_2$ films fabricated by PAD, and UO$_2$ thin films deposited by EBE. Differences in surface morphology are analyzed, and the information provided by AFM is compared against other complementary techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Reported results revealed that films fabricated by both techniques had granular structure, with morphologies strongly depending on the fabrication methods and conditions.

*Approved for public release LA-UR-16-22993

11:20am **AC+AS+SA-ThM11 Soft X-ray Spectroscopy of Actinide Materials**, ***David Shuh***, *S.G. Minasian, C. Pemmaraju, A. Canning, D.G. Prendergast,* Lawrence Berkeley National Laboratory; *T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley; *A. Modin, S. Butorin, J. Nordgren, L. Werme, P. Oppeneer,* Uppsala University, Sweden

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 fine structure spectroscopy (NEXAFS), 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.

Electronic Materials and Photonics
Room 102A - Session EM+AC+SS+TF-ThM

Radiation Detection Materials and Devices

Moderators: Sean King, Intel Corporation, Michelle Paquette, University of Missouri-Kansas City

8:00am **EM+AC+SS+TF-ThM1 Novel High Energy Resolution Scintillator Detectors**, ***Arnold Burger***, *E. Rowe, L. Matei, P. Bhattacharya, M. Groza,* Fisk University; *K. Stassun,* Vanderbilt University; *A. Stowe,* Consolidated Nuclear Security Y-12; *N. Cherepy, S. Payne,* Lawrence Livermore National Laboratory **INVITED**

This presentation will review the status of bright scintillators for gamma and thermal neutrons applications. The scintillators are based on single crystals of halides or selenides that are activated by rare earth ions or are self activated. The main features that make them attractive for biological, medical, space and national security applications are: (i) high stopping power of radiation, (ii) high energy resolution, (iii) fast decay time, (iv) crystal growability at low cost, (v) good gamma/neutron discrimination via pulse shape analysis, and (vi) good spectral matching with silicon photodetectors for compact and low power devices and instrumentation.

8:40am **EM+AC+SS+TF-ThM3 Improved p–n Heterojunction Device Performance Induced by Irradiation in Amorphous Boron Carbide Films**, ***George Peterson***, *Q. Su,* University of Nebraska - Lincoln; *Y. Wang,* Los Alamos National Laboratory; *P.A. Dowben, M. Nastasi,* University of Nebraska - Lincoln

Amorphous hydrogenated boron carbide films (a-B$_{10}$C$_{2+x}$:H$_y$) on Si p–n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These devices were found to be robust when irradiated with 200 keV He$^+$ ions. For low doses of irradiation, contrary to most other electrical devices, the electrical performance improved. On the heterojunction I(V) curve, reverse bias leakage current decreased by 3 orders of magnitude, series resistance across the device decreased by 64%, and saturation current due to generation of electron–hole pairs in the depletion region also decreased by an order of magnitude. It is believed that the improvements in the electrical properties of the devices are due to an initial passivation of defects in the $a\text{-}B_{10}C_{2+x}{:}H_y$ film resulting from electronic energy deposition, breaking bonds and allowing them to reform in a lower energy state, or resolving distorted icosahedron anion states.

9:00am **EM+AC+SS+TF-ThM4 Amorphous Hydrogenated Boron Carbide for Direct-Conversion Solid-State Neutron Detection***, **Gyanendra Bhattarai**, T.D. Nguyen, S. Dhungana, A.N. Caruso, M.M. Paquette,* University of Missouri-Kansas City

The trade-off between conversion layer thickness and penetration depth of primary reaction products inherently limits the efficiency of conversion-layer solid-state neutron detectors, motivating the need for direct-conversion solutions. Direct-conversion devices, in principle, offer nearly unity detection efficiency, a minimum of fabrication steps, large-area scalability, and high efficiency density, all of which are essential for small-sized neutron spectrometers as well as for large-area detectors. However, to date, there is a lack of well-developed semiconductor materials with high thermal neutron absorption that also lead to energetic reaction products amenable to detection. Amorphous hydrogenated boron carbide ($a\text{-}B_xC{:}H_y$), a complex disordered semi-insulating material, is a promising candidate because of its high neutron absorption and high resistivity. Additionally, excellent mechanical, chemical, and thermal stability make it suitable for harsh detection environments. The main challenges, however, in the study of $a\text{-}B_xC{:}H_y$ are its low charge carrier mobility, the difficulties associated with making proper electrical contacts for accurate charge transport measurements, and the inefficacy of traditional experimental techniques and interpretations to address the complex nature of the material (i.e., it is a high-resistivity, disordered, molecular solid). This contribution will present an overview of how $a\text{-}B_xC{:}H_y$ may lead to high-efficiency neutron detectors based on theoretical simulations, the study of its charge transport metrics focusing mainly on charge carrier mobility and lifetime, and the development of proper electrical contacts on PECVD grown thin films of this material.

9:20am **EM+AC+SS+TF-ThM5 Radiation Damage of Low-κ Interlayer Dielectrics Studied with Electrically Detected Magnetic Resonance***, **Michael Mutch**, P.M. Lenahan,* Pennsylvania State University*; S.W. King,* Intel Corporation

Radiation effects of MOS devices have been extensively studied due to the demand for electronic devices in space applications.[1] The scaling of these MOS devices will lead to an eventual need for low-dielectric constant (i.e., low-κ) dielectrics to reduce parasitic capacitances associated with scaling of back-end-of-line interlayer dielectrics (ILDs). However, little is known about radiation effects of low-κ ILDs. We utilize electrically detected magnetic resonance (EDMR) via spin-dependent trap-assisted tunneling (SDTAT) to study point defects in porous low-κ a-SiOC:H systems before and after exposing samples to radiation damage. SDTAT/EDMR has the sensitivity and analytical power to specifically identify only those defects which are involved in electronic transport. Due to the inherent complexity of the a-SiOC:H systems, multiple frequency EDMR is utilized to better understand defect structure when featureless spectra are present.

The a-SiOC:H films are grown via PECVD, and exhibit carbon dangling bonds prior to porogen removal via UV-annealing.[2] After porogen removal via UV treatment, it has been shown, via multiple frequency EDMR, that silicon dangling bonds are the dominating defect center responsible for SDTAT in these films.[2] The porous a-SiOC:H systems were subjected to a 15 Mrad total dose via a cobalt-60 dry cell gamma-ray source while simultaneously applying either positive, negative, or no bias. We find that the post-radiation IV curves are a strong function of the biasing conditions which were applied during radiation. This likely indicates that electron and hole traps will both play a role in radiation damage effects in these systems. We find that the EDMR response amplitude is greatly increased (by a factor of 4 or greater) after irradiation for all biasing conditions. This result indicates a substantial increase in the density of defects involved in electronic transport. Multiple frequency EDMR measurements suggest that the generated defects are primarily silicon dangling bonds.

[1] J. R. Schwank et al., IEEE Trans. Nuc. Sci. **55**, 1833 (2008).

[2] M. J. Mutch et al., J. Appl. Phys. **119**, 094102 (2016).

9:40am **EM+AC+SS+TF-ThM6 Modeling Unit Displacement Damage in Amorphous Silicon Oxycarbides***, **Hepeng Ding**, M. Demkowicz,* MIT

Amorphous silicon oxycarbide (SiOC) is of great technological interest. To study its potential application as a radiation-resistant material, we present *ab initio* modeling investigations of unit displacement damage processes in it using density functional theory. We model 0.1 keV primary knock-on atoms (PKA) in SiO_2, SiOC, and hydrogenated SiOC (SiOCH) with different hydrogen levels. We find that PKAs affect the carbon-clustering tendency in both SiOC and SiOCH. Our results also suggest that SiOCH is irradiation indifferent, i.e., upon PKA, the potential energy does not increase and there is no major structural change.

This work was funded by the DOE Office of Nuclear Energy, Nuclear Energy Enabling Technologies, Reactor Materials program, under contract No. DE-NE0000533. Computational support was provided by DOE-NERSC and DOE-OLCF.

11:00am **EM+AC+SS+TF-ThM10 Position-Sensitive 3D CZT Gamma-Ray Detectors with Thickness Up to 50 mm***, **Ralph James**, A.E. Bolotnikov, G.S. Camarda, Y. Cui, G. De Geronimo, J. Fried, A. Hossain, G. Mahler, U. Roy, E. Vernon, G. Yang,* Brookhaven National Laboratory **INVITED**

High-granularity position-sensitive detectors allow for accurate charge-signal corrections to overcome non-uniformities in the devices' responses caused by crystal defects. The operational principle of position-sensitive detectors is analogous to the well-known drift ionization chambers used for tracking charged particles and detecting the interaction events generated by gamma rays. Advantages of the position-sensitive designs were realized in a number CZT detectors, including CAPture™, hemispherical, Frisch-ring, capacitive Frisch-grid and even pixel detectors in which pixel contacts act like shielding electrodes. In our virtual Frisch-grid (VFG) devices, the sensing strips are separated from the crystal surfaces by a thin insulating layer, as it was originally done in other Frisch-grid designs. The amplitudes of the signals readout from the strips are used to measure the coordinates of the interaction points and correct the response non-uniformities. The drift time and the cathode-to-anode ratio were used to independently evaluate the location of the interaction points in Z directions, correct for electron loss, and identify and reject the events for which the charge losses caused by defects are so great that they cannot be corrected accurately. Combining these two techniques allows us to significantly enhance the spectral responses of position-sensitive VFG detectors, and to significantly improve their performance. Such high-granularity position-sensitive detectors open up the opportunity for using thicker, less expensive crystals. We demonstrated that today's CZT material is suitable for detectors with up to 40-50-mm drift distances, provided that the detectors have the ability to correct their response non-uniformities on a scale comparable to the sizes of electron clouds, which is ~100 m m. We employed an ASIC and data-acquisition system developed by BNL's Instrumentation Division for arrays of VFG detectors. For each detector we used 6 ASIC channels to read the negative signals from the cathode and from four position-sensing pads, and the positive signals from the anode. For each interaction event, the anode signal correlates with the *X* and *Y* values converted from the 4 strip signals and Z coordinate evaluated from the cathode signal. This relationship allows us to correct each anode signal in accordance with the location of the interaction point. We selected the voxel sizes to achieve the best performance, typically ~30x30 pixels in *XY*-space and ~100 segments in the Z-direction. The performance of thick position-sensitive VFG detectors fabricated from CZT crystals will be reported for a variety of radioactive sources and testing conditions.

11:40am **EM+AC+SS+TF-ThM12 Understanding the Electrical Properties of U_3O_8 for Direct Conversion Neutron Detectors***, **Brandon Shaver**, S. Lawson, B. Musicó,* The University of Tennessee Knoxville*; S. Dhungana, G. Bhattarai, M.M. Paquette, A.N. Caruso,* University of Missouri-Kansas City*; T. Meek,* The University of Tennessee Knoxville

With a high neutron fission cross section for ^{238}U, U_3O_8 is one of a series of uranium oxide semiconductors that may be suitable for direct-conversion neutron detectors. However, the electrical transport properties of U_3O_8 are not well-characterized: the literature that does exist reports largely inconsistent resistivity values, and similarly contradictory values for work function. One of the reasons for these wide ranges is that slight changes in stoichiometry in urania-based systems, UO_2 for example, can have a tremendous influence on electrical properties; however, the details of these effects are not well-understood. We seek to rigorously characterize the electrical transport properties in U_3O_8 to understand the range of values that can be achieved and—importantly—their relationship to fabrication method as well as composition/microstructure. Samples of U_3O_8 pellets have been made by uniaxial pressing of U_3O_8 powder and subsequent sintering under various conditions. These samples have then been characterized to determined their microstructure, exact stoichiometric composition, and electrical properties. By carefully studying the relationship between sample preparation and electrical properties, we aim to establish the ability to control and optimize the electrical transport metrics of U_3O_8 critical for detection applications.

12:00pm **EM+AC+SS+TF-ThM13 Radiation Damage in 4H SiC nMOSFETs Detected by Electrically Detected Magnetic Resonance***, **Ryan Waskiewicz**, M.A. Anders, P.M. Lenahan,* Pennsylvania State University*; A.J. Lelis,* U.S. Army Research Laboratory

Metal oxide semiconductor field effect transistors (MOSFETs) based upon 4H-SiC have great promise in high power and high temperature applications. An area of substantial interest is in outer space, where the devices will be subjected to ionizing radiation. The effects of ionizing radiation have been well studied in Si-based MOS devices, where E' and Pb centers play dominating roles as oxide and interface traps respectively. Very little is known about the types of defects created in radiation damage in SiC MOSFETs. In order to develop a fundamental understanding of ionizing radiation effects, we have performed a study utilizing electrically detected magnetic resonance (EDMR) via the bipolar amplification effect (BAE) [1]. We observe several changes between the pre- and post-irradiation EDMR results, which strongly indicate change in the structure of the SiC/SiO_2 interface region but relatively little change in the number of observed interface defects.

The devices used in this study had 50 nm thick thermally grown gate oxides in N_2O. After oxidation, the devices were subjected to the standard post-oxidation NO anneal at 1175°C. The n-channel 4H-SiC MOSFETs have been subjected to 6MRads of gamma radiation from a 60Co gamma source while a 10V bias applied to the gates. Standard transistor characteristic measurements made on the devices before and after irradiation indicate a threshold voltage shift of approximately -4V. We observed several significant changes in the EDMR response, the most obvious EDMR differences are in the amplitude of the BAE EDMR measurements as a function of applied gate voltage. The maximum EDMR amplitude increased by a factor of 7 as a result of the irradiation, and the gate bias at which the peak occurred shifted by approximately -4V, consistent with the approximate -4V shift in threshold voltage. BAE measurements measure spin dependent recombination due to deep level defects at and very close to the SiC/SiO_2 interface. We find significant change in the EDMR line shapes, observing significant post-irradiation broadening of the spectra. Surprisingly, we are unable to observe either silicon or carbon dangling bond defects in these preliminary measurements. It is clear from the measurements that both the pre-irradiation and post-irradiation measurements are dominated by silicon vacancies on the SiC side of the interface. EDMR measurements as a function of microwave power show quite significant changes in the saturation behavior of the magnetic resonance. These results suggest significant structural changes in the interface region.

[1] Thomas Aichinger and Patrick M. Lenahan, Appl. Phys. Lett. **101**, (2012)

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