Monday Morning, October 28, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+MI+SA+TF-MoM

Actinides and Rare Earths: Experiment and Electron Correlation
Moderator: T. Durakiewicz, Los Alamos National Laboratory

8:20am AC+MI+SA+TF-MoM1 Our Understanding of the Condensed-Matter Physics of Actinides: What have we Learned in 50 Years?, *G. Lander*, ITU, Karlsruhe, Germany **INVITED**
By 1950 the Manhattan Project and the early nuclear industry had a large legacy of new materials that were poorly understood from a physics perspective. The physics of uranium and plutonium are good examples.

By the mid-1960s progress had been made in applying many physical techniques (many of which, such as sensitive transducers to measure elastic constants, had also been a development of WW II) on the actinide elements and many of their compounds, particularly the simple dioxides. Most theoretical treatments considered the elements and their metallic compounds within the framework of d transition-metals, as many properties seemed to follow these metals, rather than those of the $4f$ lanthanide series.

By the mid-1970s the group at Argonne National Laboratory had shown, *inter alia*, that a large orbital moment existed in the actinides even if many properties followed itinerant-electron behavior, and the first band-structure calculations showed how difficult it was to resolve this dichotomy.

The discovery of so-called heavy-fermion superconductors, such as UBe_{13}, at Los Alamos National Laboratory in the early 1980s brought considerable prominence to the field and was a precursor, although not recognized at the time, to the discovery of high-T_c materials in 1986. The further discovery (in 2001) of superconductivity at 18 K in $PuCoGa_5$, also at Los Alamos, shows the key importance of the electronic ground state of the $5f$ electrons and how this drastically affects the physical properties.

Theory has always been "behind" experiments in the actinides; however, the experimental results have proved a sensitive test to the most advanced electronic-structure calculations, such as dynamical mean-field theory (DMFT) within the local-density approximation, so that in some respects the actinides have become a "test bed" for the newest theoretical models.

60 years after some of the pioneering condensed-matter experiments on these materials, we have a far better picture of the actinides, the importance of the orbital moments, the relevance of intermediate coupling, and the criterion that determine whether the $5f$ states behave as localized or itinerant. However, we do not have *predictive* theories – they are all *reactive*. This implies that we still need to maintain an experimental capability, as these materials will be with us a very long time, even if we abandon nuclear energy.

The challenge today is how to maintain and nurture that experimental capability in a climate where even depleted uranium is regarded with suspicion and its handling demands kilograms of paperwork? Without experiments will theory follow?

9:00am AC+MI+SA+TF-MoM3 5f Electron Localization, *J.L. Smith*, Los Alamos National Laboratory **INVITED**
The light actinide elements show a large number of crystal structures and low-melting points. At the element americium, this $5f$-electron series finally settles down and looks like the rare-earth series. This occurs because the $5f$ electrons have ceased to form energy bands and have localized. The superconductivity of americium proved this. I will review how the tug of war between itinerant and localized behavior leads to all of the interesting properties and touch on such things as quantum critical points. This has impact on the understanding of the other long rows in the periodic table.

9:40am AC+MI+SA+TF-MoM5 Historical Aspects and Perspectives of X-Ray Spectroscopy in Lanthanide and Actinide Materials, *G. Kaindl*, Freie Universität Berlin, Germany **INVITED**
The talk addresses some aspects in the use of tunable x-rays in studies of electronic and magnetic properties of lanthanide and actinide materials by x-ray absorption fine-structure (XANES) and resonant elastic x-ray scattering (REXS), emphasizing related features of these 4f and 5f materials.

Based on early applications of L- and M-edge XANES to lanthanide valence studies, the method was applied to U and Th compounds, exploring XANES at various thresholds (L, M, N, O) [1], and then to the more radioactive actinides Np, Pu, and Am as well as to high-pressure studies. Subsequently, the method has been improved both experimentally (e.g. high-resolution XANES [2]) and theoretically [3], and even compounds of Pa, Cm, and Cf in solid and aqueous environments have been investigated by now.

Resonant magnetic x-ray scattering was first applied to Ho metal, where the magnetic scattering cross-section is enhanced by a factor of 50, when the x-ray energy is tuned across the L_{III} absorption edge of Ho [4]. Subsequently, much larger enhancements up to 5 magnitudes were observed at the M_V edges of U in UAs [5] and of Eu in the antiferromagnetic (AFM) semiconductor EuTe [6]. In the latter, an epitaxial thin EuTe(111) film was studied, and virtually background-free magnetic Bragg-peaks with pronounced Laue oscillations were found. From these, the AFM order in the EuTe(111) film could be derived with atomic-layer resolution. The magnetization of the outermost layer was found to decrease significantly stronger with temperature than that of the bulk layer [6]. In a further pioneering experiment that employed a synchrotron slicing source for the production of tunable soft x-rays with pulse widths as short as 100 fs (probe pulses) and synchronized pump pulses of 400 nm wavelength, the dynamics of the AFM order could be studied by fs soft x-ray diffraction [7].

References

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11:00am AC+MI+SA+TF-MoM9 High Energy Resolution X-ray Spectroscopy of f-electron Systems, *K.O. Kvashnina*, European Synchrotron Radiation Facility (ESRF), France, *J.G. Tobin*, Lawrence Livermore National Laboratory
This contribution will provide an overview of the possible spectroscopic techniques and experiments that become available for f-electron systems using high energy resolution X-ray emission spectrometer[1]. As an example we will show the studies of the electronic structure of cerium (Ce) and uranium (U) nanostructured materials by means of high energy resolution fluorescence detection (HERFD) and resonant inelastic X-ray scattering (RIXS) via transitions between core levels and between core and valence levels[2–5]. The experimental spectral features will be characterized using a variety of theoretical codes including the LDA+U approximation within DFT[6], atomic multiplet theory[7] and full multiple scattering FEFF[8].

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11:20am AC+MI+SA+TF-MoM10 Signatures of the γ - α Volume Collapse in Cerium, *M.J. Lipp*, Lawrence Livermore National Laboratory **INVITED**

High-pressure x-ray emission measurements of the $L\gamma_1$ (L_2N_4) emission line were used to decide the longstanding debate over the nature of the famous iso-structural (γ-α) volume collapse at 0.75 GPa in elemental cerium that ends in a critical point at 1.5 GPa and 480 K. The satellite structure of this line offers direct access to the total angular momentum observable $<J^2>$ as shown by extended local atomic model calculations and experiences a 30% step-like decrease across the volume collapse. This validates the Kondo model in conjunction with previous measurements of the equation of state at high temperature that were also well fit by the Kondo volume collapse model plus a quasiharmonic representation of the phonons - but could also be reproduced within the Hubbard-Mott framework. The remaining satellite in the α -phase after the volume collapse does not change significantly over the pressure range studied. Direct comparison is made with previous predictions by dynamical mean field theory.

Magnetic Interfaces and Nanostructures
Room: 202 A - Session MI-MoM

Topological Materials, Rashba Systems, and Heusler Alloys
Moderator: V. Lauter, Oak Ridge National Laboratory

8:20am MI-MoM1 Rotating Spin and Giant Splitting: Unoccupied Surface State at Tl/Si(111), *M. Donath*, S.D. Stolwijk, A.B. Schmdit, Muenster University, Germany, *K. Sakamoto*, Chiba University, Japan, *P. Krueger*, Muenster University, Germany

Tl/Si(111)-(1x1) is an outstanding example for a system with peculiar spin-orbit-induced spin effects in the surface electronic structure. An occupied surface state with classical in-plane Rashba-type spin topology around the center of the surface Brillouin zone was found to exhibit an out-of-plane spin rotation upon approaching the K point [1].

We used spin- and angle-resolved inverse photoemission with sensitivity to the in-plane and the out-of-plane spin-polarization directions to explore the unoccupied states. A recently developed rotatable source for spin-polarized electrons provided access to two spin-polarization directions. We identified an unoccupied surface state with the same spin topology as the occupied state, yet with a much larger spin-dependent splitting in energy of 0.6 eV. Theoretical calculations provide an explanation for this giant splitting. It is attributed to the strong localization of the unoccupied surface state close to the heavy Tl atom in contrast to the occupied state, which is located at the outermost Si atoms.

Since the lower-lying spin component approaches the Fermi level, this leads to almost completely out-of-plane polarized valleys in the vicinity of the Fermi level. As the valley polarization is oppositely oriented at the K and K' points, backscattering should be strongly suppressed in this system.

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8:40am MI-MoM2 Searching Majorana Fermion in Topological Insulator/Superconductor Heterojunction, *J. Jia*, Shanghai Jiao Tong University, China

Topological superconductors (TSCs) have attracted a great deal of attention recently because of the Majorana modes they host, which can be used in fault-tolerant quantum computation relying on their non-Abelian braiding statistics. While TSCs are very rare in nature, it has been proposed that an alternative way to realize them is by inducing superconductivity in the surface states of a topological insulator (TI) through the proximity effect (PE). Here we report the first experimental evidence for PE induced TSC in $Bi_2Te_3/NbSe_2$ heterojunction and the observation of Abrikosov vortices and core states. In particular, we found unusual splitting behavior in the zero-bias peak of the core states that may be attributed to the formation of Majorana fermions. Our work demonstrates the promise of using proximity effect induced TSC for realizing Majorana fermions and topological quantum computing.

9:00am MI-MoM3 Visualizing Topological States of Matter, *A. Yazdani*, Princeton University **INVITED**

Soon after the discovery of quantum mechanics it was realized why some solids are insulating (like diamond) and others are highly conducting (like graphite),even though they could be comprised of the same element. Now, 80 years later, the concept of insulators and metals is again being fundamentally revised. During the last few years, it has become apparent that there can be a distinct type of insulator, which can occur because of the topology of electronic wavefunctions in materials comprised of heavier elements. Strong interaction between the spin and the orbital angular momentum of electrons in these compounds alters the sequence in energy of their electronic states. The key consequence of this topological characteristic (and the way to distinguish a topological insulator from an ordinary one) is the presence of metallic electrons with helical spin texture at their surfaces. I will describe experiments that directly visualize these novel quantum states of matter and demonstrate their unusual properties through spectroscopic mapping with thescanning tunneling microscope (STM). These experiments show that the spin texture of these states protects them against backscattering and localization. These states appear to penetrate through barriers that stop other electronic states. I will describe these experiments and our most recent attempts to create and visualize other topological states such as creation of Majorana fermions, which are another instance of boundary state associated with topological order.

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9:40am MI-MoM5 Probing Spin Textures of Topological Surface States in Ternary Chalcogenides, *A. Kimura*, Hiroshima University, Japan **INVITED**

Three-dimensional topological insulators (3D TIs) with a gapless topological surface state (TSS) in a bulk energy gap induced by a strong spin-orbit coupling have attracted much attention as key materials to revolutionize current electronic devices. A spin helical texture of a TSS, where the electron spin is locked to its momentum, is a manifestation of a 3D TI.

A number of well-known thermoelectric and phase-change materials have so far been predicted to be 3D TIs. In order to experimentally confirm their topological natures, spin- and angle- resolved photoemission spectroscopy (SARPES) is one of the most powerful tools and it has actually been playing major roles in finding some real 3D TIs [1, 2]. Among the established 3D TIs, Bi_2Se_3 has been most extensively studied because of its relatively large energy gap and the simplest TSS. However, the topological surface state is energetically obscured by bulk continuum near and below the Dirac point, which is disadvantageous for spintoronic applications.

SARPES experiments were performed at the ESPRESSO end station attached to the APPLE-II type variable polarization undulator beam line (BL-9B) at Hiroshima Synchrotron Radiation Center (HSRC) [3]. The VLEED-type spin detector utilized in the ESPRESSO machine achieves a 100 times higher efficiency compared to that of conventional Mott-type spin detectors [2]. Photoelectron spin polarizations are measured by switching the direction of in-plane target magnetizations, thereby simultaneously eliminating the instrumental asymmetry, which is a great advantage for a quantitative spin analysis of nonmagnetic systems such as 3D TIs.

In this talk, some of the ternary 3D TIs such as $TlBiSe_2$ [4], $GeBi_2Te_4$ [5], Bi_2Te_2Se, and Bi_2Se_2Te [6] are shown to possess TSSs with marked spin polarizations. It has been revealed that a disorder in the crystal has a minor effect on the surface-state spin polarization, which is ~70% near the Dirac point in the bulk energy gap region (~180 meV). Highly spin-polarized features are also found for Bi_2Te_2Se and Bi_2Se_2Te, which are persistent across the Dirac point. The availability of both upper and lower TSSs promises to extend the variety of spintoronic application, for instance, to dual gate TI devices and topological p-n junctions.

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10:40am MI-MoM8 (Un)expected Spin Topology in Unoccupied Bands of Bi/Ag(111), *S.N.P. Wissing, A.B. Schmidt,* Westfälische Wilhelms-Universität Münster, Germany, *Chr.R. Ast,* Max-Planck-Institut für Festkörperforschung Stuttgart, Germany, *H. Mirhosseini,* Max-Planck-Institut für Mikrostrukturphysik Halle, Germany, *J. Henk,* Martin-Luther-Universität Halle-Wittenberg, Germany, *M. Donath,* Westfälische Wilhelms-Universität Münster, Germany

The spin topology of electronic bands, caused by spin-orbit interaction in Rashba systems and topological insulators, is subject of current debate. In some cases, the experiments findings are in conflict with theoretical predictions. In this contribution, we will discuss this issue with respect to the spin-resolved unoccupied electronic structure of the surface alloy Bi/Ag(111) ($\sqrt{3}\times\sqrt{3}$)R30°.

Surface alloys of heavy elements on noble metal fcc(111) surfaces exhibit surface states with giant Rashba-type spin splittings. Therefore, they have been investigated thoroughly in recent years, in particular their occupied band structure by spin- and angle-resolved photoemission. Above the Fermi level, however, there is basically a blank area on the $E(k_\parallel)$ map.

We present a study on the unoccupied electronic structure of Bi/Ag(111) with spin- and angle-resolved inverse photoemission. Above the Fermi level, we identified several states with distinct spin dependence. We determined their nature concerning symmetry, bulk vs. surface character, energy vs. momentum dispersion, and spin dependence. In particular, we focused our attention to the spin character of the m_j=1/2 surface state. While theoretical calculations [1] predict a complex spin topology, where the spin polarization changes sign at the band maximum, our experimental findings indicate a spin splitting compatible with the classical Rashba model. To shed more light on this issue, we investigated the spin topology with the help of first-principles electronic-structure calculations. We will discuss the difficulty of assigning a pure spin character to a particular Rashba band, especially in view of the experimental geometry, which itself influences the measured spin character.

[1] G. Bihlmayer *et al.*, Phys. Rev. B **75**, 195414 (2007)

11:00am MI-MoM9 Growth and Properties of Skyrmionic MnSi Thin Film, *J.Y. Yi, S.W. Tang,* University of Tennessee, *G.X. Cao,* Oak Ridge National Laboratory, *D.G. Mandrus,* University of Tennessee, *Z. Gai,* Oak Ridge National Laboratory

MnSi is well-known for its magnetic chiral structure due to lack of inversion symmetry of B20 crystal structure at 29.5K to 43K. The helical magnetic structure results from Dzyaloshinsky-Moriya (DM) spin-orbit interactions. Inspired by its magnetic structure, which is left-handed spiral oriented along <111> axes, and low mismatch between Si(111) and MnSi(111) as well, we successfully grew the MnSi(111) thin film by co-evaporating Mn and Si on Si(111) in UHV. The structural, electric properties and magnetic properties of MnSi(111) thin film are examined using in-situ low temperature STM, STS and ex-situ SQUID magnetometer.

11:20am MI-MoM10 Skyrmionic MnSi Nanowires on Si: SiO$_2$ Layer as a Catalyst Assistant for the CVD Growth, *S.W. Tang,* University of Tennessee, *I. Kravchenko,* Oak Ridge National Laboratory, *J.Y. Yi, G.X. Cao,* University of Tennessee, *J. Howe,* Oak Ridge National Laboratory, *D.G. Mandrus,* University of Tennessee, *Z. Gai,* Oak Ridge National Laboratory

Magnetic skyrmion, a vortex-like spin-swirling object recently observed in chiral-lattice magnets, are of great interest to future spin-electronic related data storage and other information technology applications. We report that single crystal helimagnetic MnSi nanowires could be synthesized in large amounts via SiO2 thin film assisted chemical vapor deposition comparing to previous reports, SiO2 plays an important role in controlling amount of diffusing Si to achieve relative low supersaturation ratio. Growth process is controlled so as to find the optimized parameters. Based on that, a temperature-time-distance growth phase diagram is plotted. The ac and DC magnetic properties of MnSi nanowires reveal the persistent of the helimagnetic and skyrmion magnetic ordering in the one-dimensional wires. Devices are fabricated via photolithography and e-beam lithography. Transport properties of this single wire device are measured.

11:40am MI-MoM11 Epitaxial Growth, Transport, and Electronic Structure of Half Heusler Compounds: CoTiSb, NiTiSn, and Ni$_2$TiSn/NiTiSn Nanocomposite Films, *J.K. Kawasaki,* UCSB, *L.M. Johansson,* Lund University, Sweden, *J. Shabani, A. Rice,* UCSB, *M. Hjort, R. Timm,* Lund University, Sweden, *B.D. Schultz,* UCSB, *T. Balasubramanian, A. Mikkelsen,* Lund University, Sweden, *C.J. Palmstrom,* UCSB

The Half Heuslers are an attractive family of compounds for high temperature thermoelectrics, and recently there has been renewed interest in these compounds since some are proposed to be topological insulators. We report the epitaxial growth, transport, and angle resolved photoemission

spectroscopy (ARPES) measurements of epitaxial films of the Half Heusler compounds CoTiSb and NiTiSn. Both belong to the subset of Half Heuslers with 18 valence electrons per formula unit that are predicted to be trivial insulators despite being composed entirely of metallic components. Here the CoTiSb and NiTiSn films were grown by molecular beam epitaxy on lattice matched InAlAs/InP (001) and (111), or on MgO (001), respectively. The films are epitaxial and single crystalline, as measured by reflection high-energy electron diffraction, low energy electron diffraction, and X-ray diffraction. Both CoTiSb and NiTiSn films also show surface reconstructions that vary with anneal temperature.

For the CoTiSb, scanning tunnelling spectroscopy and temperature-dependent transport measurements reveal that the films are insulating, with unintentionally doped carrier concentrations and mobilities comparable to that of highly doped conventional compound semiconductors (n = 10^{18} cm^{-3} and μ = 500 cm^2/Vs at 300 K). The CoTiSb films also show a peak in the low temperature (1.8-10 K) magnetoresistance that may result from localization or some other mechanism. ARPES measurements reveal that CoTiSb is a bulk insulator but has surface states within the band gap.

Stoichiometric NiTiSn films also show semiconducting-like transport. Additionally, composites of Full Heusler Ni$_2$TiSn inclusions within a Half Heusler NiTiSn matrix have been grown by codeposition with excess Ni. Despite the large lattice mismatch (2.9%) between the Ni$_2$TiSn and NiTiSn, the Ni$_{1+\delta}$TiSn films remain epitaxial for compositions in excess of $\delta > 50\%$. These Half Heusler / Full Heusler nanocomposites show promise for phonon scattering in thermoelectric applications.

Monday Afternoon, October 28, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+MI+SA+TF-MoA

Actinides and Rare Earths: Theory and Electron Correlation
Moderator: L. Havela, Charles University, Czech Republic

2:00pm **AC+MI+SA+TF-MoA1 Structural and Electronic Relationships Between the Lanthanide and Actinide Elements**, *B. Johansson*, Uppsala University, Sweden **INVITED**
The similarity and difference between the solid state properties of the 4f and 5f transition

metals are pointed out. The heavier 5f elements show properties which have direct

correspondence to the early 4f transition metals, suggesting a localized behaviour of the

5f electrons for those metals. On the other hand, the fact that Pu metal has a 30% lower

volume than its neighbour heavier element, Am, suggests a tremendous difference in the

properties of the 5f electrons for this element relative to the heavier actinides. This change

in behaviour between Pu and Am can be viewed as a Mott transition within the 5f shell

as a function of the atomic number Z. On the metallic 5f side of the Mott transition (i.e.,

early actinides), the elements show most unusual crystal structures, the common feature

being their low symmetry. An analogous behaviour for the lanthanides is found in cerium

metal under compression, where structures typical for the light actinides have been observed

experimentally. A generalized phase diagram for the actinides is shown to contain features

comparable to the individual phase diagram of Ce metal. The crystal structure behaviour of

the lanthanides and heavier actinides is determined by the number of 5d (or 6d) electrons

in the metallic state, since for these elements the f electrons are localized and nonbonding.

For the earlier actinide metals electronic structure calculations – where the 5f orbitals

are treated as part of the valence bands – account very well for the observed ground state

crystal structures. The distorted structures can be understood as Peierls distortions away

from the symmetric bcc structure and originate from strongly bonding 5f electrons occupying

relatively narrow 5f states.

2:40pm **AC+MI+SA+TF-MoA3 Signature of Strong Correlations in Actinides and its Compounds: A Dynamical Mean Field Theory Perspective**, *G. Kotliar*, Rutgers University **INVITED**
Plutonium is a unique element, poised at the edge of a localization delocalization transition. Its compounds exhibit

remarkable phenomena, ranging from insulating behavior with a topologically non trivial band structure in PuB6 [1]

to high temperature superconductivity PuCoGa5 [2].

In the last decade a new paradigm for understanding, modeling and predicting physical properties of these materials

has emerged based on realistic implementations of dynamical mean eld theory (DMFT) concepts [3][8] [9]. This theory

treats the wave (band-like) and the (particle-like) multicon gurational multiplet aspects of the f-electrons on the same

footing. This theory accounts for the volume of δ Pu in a paramagnetic con guration [6] and predicted its phonon

spectra [7].

In DMFT, an underlying self consistent impurity model can be used to reconstruct local observables of a material.

An illustrative example is the valence histogram, describing the weight of each atomic con guration in the ground

state of the solid. This important concept, and the resulting prediction for Pu can now be probed experimentally

using resonant XES [5] and neutron form factor measurements [11].

There are now many applications by many groups which have extended the reach of this approach to many actinide

based compounds. We will review the basis of the DMFT approach and compare some results with selected experiments

on 5f electron system. We will conclude with some new directions to face the challenge for material design in this

eld [10].

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3:40pm **AC+MI+SA+TF-MoA6 Towards a Better Understanding of Low-Energy Excitations in Heavy-Fermion Systems**, *G. Zwicknagl*, Technische Universität Braunschweig, Germany **INVITED**
Metals containing lanthanide or actinide ions have been at the focus of interest in condensed matter physics during the past decades. The presence of the partially filled f-shells leads to unexpected "anomalous" behavior such as heavy fermions, unconventional superconductivity, unusual magnetism as well as their co-existence.

The f-electron systems lie at the intersection of a large number of long-standing problems in the physics of metals. In metals containing ions with partially filled inner shells, we immediately face the fundamental question which picture provides the better starting point for theoretical models, a delocalized description in terms of energy bands or a localized representation which accounts for the atomic properties. The answer to the question which of the above-mentioned pictures is the appropriate starting point seems to depend on the physical quantities under consideration. This fact is a consequence of electronic correlations which prevent to describe the influence of the f-states over the entire temperature and energy range in terms of a unique simple model. While the high-temperature (high-energy) properties of lanthanide compounds can be understood in terms of localized f-moments it is generally accepted by now that the f-electrons should also be described in within a band picture as delocalized states as far as the low-energy excitations are concerned.

Concerning the underlying microscopic picture, it is generally accepted that the formation of strongly renormalized 4f-bands in lanthanides is a consequence of the Kondo effect where the degrees of freedom of the 4f-shell form a collective singlet ground state with the conduction electrons. The Kondo model, however, does not apply to actinide compounds where the situation is more complex. In some compounds, experiments suggest the co-existence of both localized atomic-like 5f-degrees of freedom with itinerant 5f-band states at low temperatures/ low energies. Microscopic model calculations suggest that partial localization of 5f-electrons may result from the intra-atomic Hund's rule-type correlations.

In the present talk, I shall give an overview over our present understanding of the "Dual Nature" of f-electrons. I present recent results on the suppression of the Kondo state in $YbRh_2Si_2$ [1]. I discuss microscopic

calculations for electron spectroscopies in actinide compounds emphasizing the consequences of strong intra-atomic correlations of the 5f -shell [2,3].

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[3] Gertrud Zwicknagl, Phys. Stat. Sol. B 250, 634 (2013)

4:20pm AC+MI+SA+TF-MoA8 Electronic Structure of EuO under Pressure, *L. Petit*, *D. Szotek, M. Lueders, W.M. Temmerman,* Daresbury Laboratory, UK, *A. Svane*, Aarhus University, Denmark
We present results of an ab-initio study of EuO under pressure. The calculations are based on a first-principles methodology that adequately describes the dual character of electrons, itinerant versus localized by correcting for the unphysical self-interaction that underpins the local spin density approximation. We find that EuO, which at ambient conditions crystallizes in the NaCl structure, undergoes an isostructural insulator to metal transition around 35 GPa. The transition is associated with a change in the ground state valency configuration from $Eu^{2+}(f^7)$ to $Eu^{3+}(f^6)$. At even higher pressure we observe a transition to the CsCl structure. The ground state valency configuration remains Eu^{3+}, i.e. this latter transition is isovalent. We compare our results to a recent experimental investigation that postulates a reentrant valence transition to a nearly divalent Eu^{2+} configuration at high pressures.

Magnetic Interfaces and Nanostructures
Room: 202 A - Session MI+EM+MG-MoA

Frontiers of Complex Oxides
Moderator: G.J. Szulczewski, The University of Alabama, Z. Gai, Oak Ridge National Laboratory

2:00pm MI+EM+MG-MoA1 Deposition of AgFeO$_2$ Thin Films with the Delafossite Structure by Combinatorial Sputtering, *F. Mao*, *T. Nyberg, T. Thersleff, U. Jansson,* Uppsala University, Sweden
Delafossites AMO$_2$ (A= Cu,Ag, Pd, Pt; M=Fe, Co, Ni, Cr, Al, Mn, etc) have received considerable attention due to their potential applications as transparent conducting oxides, photocatalysts, luminescent materials, batteries and thermoelectric materials. Recently, high temperature superconductivity was also suggested for doped members of this type of oxide compounds. Many of the interesting properties of delafossites are related to the crystal structure where linear O-A-O bonds connect layers of slightly distorted edge-sharing MO$_6$ octahedra. Consequently, the delafossites can be described as natural nanolaminates of MO$_2$ layers separated by A atoms.

Copper-based delafossite materials have been studied intensely through synthesis of solid-state reaction, hydrothermal synthesis method, sol-gel methods and, in a few cases, reactive sputtering with high temperature post-annealing ($\geq 700^oC$). To our knowledge, however, no studies have previously been published on silver-based delafossite films deposited directly by sputtering. The main challenge is that the silver based delafossites tend to decompose at high temperature (>400^oC). Furthermore, the synthesis of Ag-based delafossites by reactive sputtering is usually restricted to small window of stoichiometric composition and also the sputtering condition.

The combinatorial materials science enables rapid discovery and optimization of new or known materials for creating ''library'' of composition-structure-property relationship. Compared with the ''one-at-a-time'' sputtering, the combinatorial sputtering with large composition gradient is powerful tool for time-saving and economical development of silver-based delafossite films.

In this work, we demonstrate the combinatorial deposition of delafossite AgFeO$_2$ thin films using co-sputtering of silver and iron targets in a reactive Ar-O$_2$ mixture atmosphere. Rapid screenings of XRD, XPS, XRF were employed to determine the chemical composition and phase structure. The most interesting parts of the materials were studied by TEM. Optical and electrical properties have also been investigated. Our results show that the AgFeO$_2$ films have been successfully deposited by the combinatorial reactive sputtering without post-annealing but the process window is very narrow and strongly dependent on deposition temperature, sputtering power ratio, pulse frequency, O$_2$ flow rate, working pressure, etc. The XRD and TEM showed that the AgFeO$_2$ films grew epitaxially with the direction of (*00l*) in the optimal sputtering condition.

2:20pm MI+EM+MG-MoA2 MBE Growth and Properties of SrCrO$_3$ Thin Films, *Y. Du*, *H. Zhang, R.J. Colby, V. Shutthanandan, S.A. Chambers*, Pacific Northwest National Laboratory
Complex oxides with the perovskite structure exhibit a range of interesting electronic, magnetic, and optical properties. Material synthesis of those structures in thin-film form is of fundamental importance to realize their full potential. SrCrO$_3$ was first reported to be a paramagnetic metallic oxide with a cubic structure, but the property measurements thereafter have been controversial. Almost all SrCrO$_3$ structures have been synthesized through higher pressure and high temperature conditions and no epitaxial thin-film form has been reported to our knowledge. In this talk, we will present on the growth of epitaxial, near-stoichiometric SrCrO$_3$ films on LaAlO$_3$(001) substrates by molecular beam epitaxy using O$_2$ as the oxidant. Coherently strained films are shown to grow in a layer-by-layer fashion. The cation stoichiometry was determined by XPS and RBS. *In-situ* XPS Cr 2p core-level spectra show that majority of the Cr cations in SrCrO$_3$ films are in the 4+ oxidation state, although there is a small amount of Cr^{3+} and higher oxidation states, which could be a result of charge disproportionation. The films are appreciable oxygen deficient, as judged by XPS, RBS, and STEM. The structure and properties of SrCrO$_3$ films will be compared to that of LaCrO$_3$ films grown with similar conditions in the same chamber.

2:40pm MI+EM+MG-MoA3 Oxygen Stoichiometry and Topotactic Phase Reversal in SrCoO$_x$ Epitaxial Films, *H.N. Lee*, Oak Ridge National Laboratory **INVITED**
Strontium cobaltites (SrCoO$_x$) exhibit a wide spectrum of magnetic and electronic phases, ranging from antiferromagnetic insulator to ferromagnetic metal, depending on the oxygen stoichiometry (*x*). The Co valence state change due to the modification of *x* in SCO mainly governs the physical properties. In particular, the redox reactions and subsequent changes in the physical properties are essential ingredient in applications such as solid oxide fuel cells, gas sensors, and many other devices that exploit the redox reactions. In this work, we examined the topotactic transformation between two structurally distinct perovskite (SrCoO$_{3-d}$) and brownmillerite (SrCoO$_{2.5}$) phases. Temperature dependent, ambient controlled real-time x-ray diffraction and ellipsometry conspicuously showed that the topotactic phase transitions accompany a rapid, drastic change in the crystallographic and electronic structures. Interestingly, the topotatic phases were found to be reversible through oxygen (de)intercalation at greatly reduced temperatures. Therefore, we envision that the phase stability of strontium cobaltites may lead to discovery of new oxygen membranes and cathode materials for high performance energy storage.

*The work was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

3:40pm MI+EM+MG-MoA6 Medard W. Welch Award Lecture - Complex Oxide Interfaces: Conquering the (Polar) Catastrophe, *C.G. Van de Walle**, University of California, Santa Barbara **INVITED**
The formation of a two-dimensional electron gas (2DEG) at the interface between two insulators, SrTiO$_3$ (STO) and LaAlO$_3$ (LAO), has sparked huge interest in oxide electronics. In spite of almost a decade of research, the mechanisms that determine the density of this 2DEG have remained controversial. The electronic behavior of these polar/nonpolar interfaces is often modeled using electrostatics based on an ionic representation of the solids. This leads to a "polar catastrophe" in which the potential in the overlayer diverges—similar to the case of (001) interfaces between heterovalent semiconductors (e.g., Ge/GaAs) that were studied 35 years ago [1].

In fact, if the electrons resulting from the polar discontinuity can be confined at the interface, the "catastrophe" can be entirely avoided, and a 2DEG with an electron density of 3.3×10^{14} cm^{-2} (0.5 electrons per unit cell) can be generated. However, experimentally observed densities at the STO/LAO interface are more than an order of magnitude lower.

We have used a combination of first-principles calculations and Schrödinger-Poisson simulations to investigate this problem [2]. The termination of the wider-band-gap overlayer is key: surface states that act as a sink for electrons limit the 2DEG density. I will discuss the effects of LAO surface reconstructions, including hydrogenation. These results apply to oxide interfaces in general, and explain why the SrTiO$_3$/GdTiO$_3$(GTO) interface has been found to exhibit the full density of 0.5 electrons per unit cell [3].

An interesting question can be raised now: why is it that oxide interface can sustain this huge 2DEG density, while semiconductor interfaces are commonly accepted to undergo atomic reconstructions to eliminate the polar catastrophe? I will suggest that the insights gained from oxide

* Medard W. Welch Award Winner

interfaces may be used to design semiconductor interfaces that could sustain similar 2DEGs.

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4:20pm MI+EM+MG-MoA8 Magnetic Reconstructions in Ultrathin Oxide Heterostructures, *H. Hwang*, Stanford University **INVITED**
Complex oxides are fascinating systems which host a vast array of unique phenomena, such as high temperature (and unconventional) superconductivity, 'colossal' magnetoresistance, all forms of magnetism and ferroelectricity, as well as (quantum) phase transitions and couplings between these states. In recent years, there has been a mini-revolution in the ability to grow thin film heterostructures of these materials with atomic precision. With this level of control, the boundary conditions at oxide surfaces and interfaces have been used to form new electronic phases. Here we focus on the magnetic reconstructions found in perovskites heterostructures, particularly for manganite thin films and rectifying junctions. In the later case, a direct correlation is found between the junction properties and the reconstructions at the interface.

5:00pm MI+EM+MG-MoA10 A New Tool to Manipulate the Transition Metal Crystal Field: Creating Local Dipoles via Cation Ordering, *B. Nelson-Cheeseman*, University of St. Thomas*, H. Zhou, J. Hoffman,* Argonne National Laboratory*, P. Balchandran, A. Cammarata, J.M. Rondinelli,* Drexel University*, A. Bhattacharya*, Argonne National Laboratory
In complex oxides, the intriguing electronic, magnetic and orbital properties often result from how the oxygen anions surround the transition metal cation. Altering this bonding geometry, and thus the transition metal crystal field, can stabilize new and exciting ground states. Here, we present a novel method to tune the positions of the oxygen anions--and, thus, the crystal field--by creating polar interfaces *within* a single thin film material. By using the atomic monolayer control of molecular beam epitaxy (MBE), we are able to introduce "artificial" interfaces into a thin film of LaSrNiO4--a material in which the La and Sr dopant cations are usually randomly arranged over the A-sites. Using MBE, we interleave full layers of SrO (+0) and LaO(+1) in a series of chemically equivalent LaSrNiO4 films, varying the pattern of SrO and LaO layers relative to the NiO2 layers. This technique allows us, in one material, to capitalize on the polar interface phenomena found in more traditional multi-component systems (e.g. LAO/STO). Through synchrotron surface x-ray diffraction and Coherant Bragg Rod Analysis (COBRA) performed at the Advanced Photon Source, we directly investigate the La and Sr cation order and the resulting atomic displacements throughout the film thickness for each ordering pattern. We correlate these results with theoretical calculations and transport measurements of the layered nickelate films. For a particular interface pattern, we find that the nickel-oxygen bond lengths change by as much as 10% compared to the random alloy control films. The ability to modify the bond lengths by such a significant amount, while still maintaining the overall chemical equivalency of the material, could have broad implications for re-envisioning the electronic, magnetic and orbital properties of well-known oxide materials.

5:20pm MI+EM+MG-MoA11 Hybridized L1' Ordered Phase Induced by Strain in Epitaxial $Fe_{38.5}Pd_{61.5}$ Thin Films, *M.A. Steiner, R.B. Comes, J.A. Floro, W.A. Soffa, J.M. Fitz-Gerald*, University of Virginia
Thin films of 3d-4d/5d magnetic alloys such as Fe-Pt, Co-Pt, and Fe-Pd are of technological interest due to their ordered $L1_0$ tetragonal intermetallic phase which exhibits a high magnetocrystalline anisotropy of K ~ 10^7 to 10^8 ergs/cm^3, comparable to that of 3d-4f rare earth magnets. Strong hard-magnet properties, combined with the ductility and chemical inertness from their ennobled metallic nature, make these alloys ideal for applications in ultra-high-density magnetic storage or micro-electro-mechanical systems where the thermally induced KV/k_BT superparamagnetic limit is an important constraint. The Co-Pt system has been shown to decompose under bulk conditions into a novel, strain-induced chessboard microstructure at the eutectoid composition between its ordered $L1_0$ and $L1_2$ intermetallic phases, and related 3d-4d/5d material systems may also be expected to produce strain-induced microstructural behavior. Within this class of materials, Fe-Pd alloys possess comparatively moderate magnetocrystalline anisotropies relative to Co-Pt and Fe-Pt. The Fe-Pd

phase diagram, however, exhibits a considerably lower order-disorder transition temperature range that renders the material well-suited for nanostructured magnetic applications by enabling lower processing temperatures.

Epitaxial films of $Fe_{38.5}Pd_{61.5}$ at the $L1_0$-$L1_2$ eutectoid composition have been grown on MgO (001) oriented substrates by pulsed laser deposition. It is found that ordered thin films of $Fe_{38.5}Pd_{61.5}$ are deposited as a single phase, initially surmised to be $L1_2$ due magnetic data and the location and orientation of the X-Ray Diffraction (XRD) peaks. Careful analysis of peak intensities, however, results in an anomalously large long-range ordering parameter. Quantitative XRD analysis of the films shows that this is due to a perturbation in the Pd-site occupancy of the non-stoichiometric Fe atoms in the films; resulting in a hybridization of the $L1_0$ and $L1_2$ ordered structures. This L1'hybridized ordered structure, first postulated by thermodynamic principles to exist for the Au-Cu system[†], is believed to be induced by the accommodation of epitaxial strain from the substrate. In addition to its verification, the thermodynamic behavior of this new strain-induced phase is addressed in relation to the equilibrium phase diagram.

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Tuesday Morning, October 29, 2013

Graphene and Other 2D Materials Focus Topic
Room: 104 B - Session GR+AS+EM+MI+MN-TuM

Optical, Magnetic, Mechanical and Thermal Properties of 2D Materials

Moderator: A.A. Balandin, University of California, Riverside, D. Gunlycke, Naval Research Laboratory

8:00am GR+AS+EM+MI+MN-TuM1 Long-range Magnetic Order in a Purely Organic 2D Layer Adsorbed on Epitaxial Graphene, *M. Garnica, D. Stradi, S. Barja, F. Calleja, C. Diaz, M. Alcami, N. Martin, A.L. Vazquez-de-Parga, F. Martin, R. Miranda*, Universidad Autónoma de Madrid, Spain

Collective magnetic properties are usually associated to d or f electrons which carry the individual magnetic moments. Band magnetism in organic materials based on π electrons has remained an experimental challenge, in spite of rigorous predictions of a fully spin polarized ground state in half-filled flat band organic systems. Cryogenic Scanning Tunneling Microscopy (STM) and Spectroscopy in UHV and accurate Density Functional Theory (DFT) simulations show that isolated TCNQ molecules deposited on a monolayer of graphene epitaxially grown on Ru(0001) acquire charge from the substrate and develop a sizeable magnetic moment, which is revealed by a prominent Kondo resonance. The magnetic moment is preserved upon dimer and monolayer formation. The self-assembled 2D monolayer of magnetic molecules develops spatially extended spin-split electronic bands visualized in the real space by STM, where only the majority band is filled, thus becoming a 2D, purely-organic magnet whose predicted spin alignment in the ground state is visualized by spin-polarized STM at 4.6 K [1]. Since the added charge occupies spatially extended intermolecular bands with well-defined spin character, one might speculate that the TCNQ monolayer could act as a spin filter or 2D spin polarizer, adding magnetic functionalities to graphene by altering the spin polarization of a current flowing in graphene.

[1] M. Garnica et al, Nature Physics http://dx.doi.org/10.1038/NPHYS2610 (2013)

8:20am GR+AS+EM+MI+MN-TuM2 Graphene Thermal Properties and Applications for Thermal Management of Li-Ion Batteries, *P. Goli, S. Legedza, A.A. Balandin*, University of California, Riverside

Graphene's superior intrinsic thermal conductivity, flat geometry, flexibility and demonstrated capability for integration with other materials make graphene very promising for thermal management applications [1-2]. The thermal conductivity of graphene flakes incorporated within different materials can degrade due to coupling to the adjacent layers and phonon scattering on defects and edges [2]. At the same time, the thermal conductivity of graphene and FLG in different composite materials can remain relatively high compared to conventional thin films [3]. A possibility of using a mixture of graphene and FLG as fillers in thermal interface materials (TIM) has also been demonstrated [4-5]. In this talk we report on a possibility of using graphene as a filler material in phase-change materials (PCMs) for thermal management of Lithium-ion batteries. Lithium-ion batteries are superior to other types of batteries owing to their high-energy storage density. However, their applications are limited due to strong self-heating effects coupled with the adverse effect of temperature on the battery life-time. Prior work on thermal issues in Li-ion battery packs has demonstrated that a passive thermal management system based on PCMs is a promising approach. The PCM thermal management uses the latent heat stored in the material as its phase changes over a small temperature range. However, PCMs typically have low thermal conductivity (below 1 W/mK at room temperature). They store heat from the batteries rather than transfer it outside. For this reason, the usefulness of PCM passive thermal management for the high-power Li-ion batteries is limited. We found that incorporation of graphene to the hydrocarbon-based PCM allows one to increase its thermal conductivity by more than two orders of magnitude while preserving its latent heat storage ability. A combination of the sensible and latent heat storage together with the improved heat conduction outside of the battery pack leads to a significant decrease in the temperature rise inside a typical Li-ion battery pack. The described combined heat storage – heat conduction approach can lead to a transformative change in thermal management of Li-ion and other types of batteries [6].

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8:40am GR+AS+EM+MI+MN-TuM3 Graphene Nano-Photonics and Carrier Dynamics, *F. Koppens, P.A. Gonzalez*, ICFO - The Institute of Photonic Sciences, Spain **INVITED**

In this talk I will review the new and strongly emerging field of graphene nano-photonics. In particular, I will show how to exploit graphene as a host for guiding, switching and manipulating light and electrons at the nanoscale [1,2]. This is achieved by exploiting surface plasmons: surface waves coupled to the charge carrier excitations of the conducting sheet. Due to the unique characteristics of graphene, light can be squeezed into extremely small volumes and thus facilitate strongly enhanced light-matter interactions.

One particular example of these enhanced light-matter interactions is the non-radiative energy transfer from light emitters to graphene. We experimentally and theoretically quantified this energy transfer process and find that the emitter decay rate follows a universal distance-scaling relation and is enhanced by a factor 90 [3].Additionally, I will discuss novel types of hybrid graphene photodetectors [4] and new exciting results on carrier dynamics and carrier multiplication in graphene. By studying the ultrafast energy relaxation of photo-excited carriers after excitation with light of varying photon energy, we find that electron-electron scattering (and thus carrier multiplication) dominates the energy relaxation cascade rather than electron-phonon interaction [5]. This singles out graphene as a promising material for highly efficient broadband extraction of light energy into electronic degrees of freedom, enabling a new class of high-efficiency optoelectronic and photovoltaic applications.

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9:20am GR+AS+EM+MI+MN-TuM5 Graphene Mechanics and NEMS Applications, *J.C. Hone*, Columbia University **INVITED**

This talk will review collaborative efforts in characterizing the mechanical properties of graphene, and its application to nano-electromechanical devices (NEMS). We use nano-indentation of freely suspended membranes to measure mechanical properties. These measurements, when combined with nonlinear anisotropic continuum modeling, reveal that graphene is both ultrastiff (in-plane Young's modulus equivalent to 1 TPa) and the strongest known material (in-plane breaking strength equivalent to 100 GPa). Our recent work demonstrates that CVD-grown graphene, even in the presence of grain boundaries, can retain almost all of this intrinsic strength, opening the door to large-area high-strength films. For NEMS applications, we have developed techniques that allow fast, highly sensitive electronic readout. We are applying graphene NEMS to studies of fundamental physics in the quantum Hall regime and applications in electro-mechanical signal processing. In particular, I will dsicuss our recent work on graphene voltage controlled oscillators for generation of frequency modulated signals.

10:40am GR+AS+EM+MI+MN-TuM9 Nano-plasmonic Phenomena in Graphene, *D.N. Basov*, University of California San Diego **INVITED**

Infrared nano-spectroscopy and nano-imaging experiments have uncovered rich optical effects associated with the Dirac plasmons of graphene [*Nano Lett. 11, 4701 (2011)*]. We were able to directly image Dirac plasmons propagating over sub-micron distances [*Nature 487, 82 (2012)*]. We have succeeded in altering both the amplitude and wavelength of these plasmons by gate voltage in common graphene/SiO$_2$/Si back-gated structures. Scanning plasmon interferometry has allowed us to visualize grain

boundaries in CVD graphene. These experiments revealed that grain boundaries tend to form electronic barriers that impede both electrical transport and plasmon propagation. Our results attest to the feasibility of using electronic barriers to realize tunable plasmon reflectors: a precondition for implementation of various metamaterials concepts. Finally, we have carried out pump-probe experiments probing ultra-fast dynamics of plasmons in exfoliated graphene with the nano-scale spatial resolution.

11:20am GR+AS+EM+MI+MN-TuM11 Controlled Growth of Large-Area Mono-, Bi-, and Few-Layer Graphene by Chemical Vapor Deposition on Copper Substrate, *C.-Y. Park*, *Y. Kim*, Sungkyunkwan University, Republic of Korea
Direct synthesis of graphene using a chemical vapor deposition (CVD) has been considered a facile way to produce large-area and uniform graphene film, which is an accessible method from an application standpoint. Hence, their fundamental understanding is highly required. Unfortunately, the CVD growth mechanism of graphene on Cu remains elusive and controversial.

Here, we present the effect of graphene growth parameters on the number of graphene layers were systematically studied and growth mechanism on copper substrate was proposed. Parameters that could affect the thickness of graphene growth include the pressure in the system, gas flow rate, growth pressure, growth temperature, and cooling rate. We hypothesis that the partial pressure of both the carbon sources and hydrogen gas in the growth process, which is set by the total pressure and the mole fraction of the feedstock, could be the factor that controls the thickness of the graphene. The graphene on Cu was grown by the diffusion and precipitation mode not by the surface adsorption mode, because similar results were observed in graphene/Ni system. The carbon-diffused Cu layer was also observed after graphene growth under high CH_4 pressure. Our findings may facilitate both the large-area synthesis of well-controlled graphene features and wide range of applications of graphene.

11:40am GR+AS+EM+MI+MN-TuM12 Charged Vacancy Defects in Graphene: Stability and Charge States, *Y. Liu*, *M. Weinert*, *L. Li*, University of Wisconsin Milwaukee
We perform atomic resolution imaging of vacancy defects in graphene using non-contact atomic force microscopy, and directly determine their charges by local contact potential difference measurement. We observe reconstruction, healing, and merging of vacancy defects. Combined with first-principles calculations, we further show that vacancy defects are typically positively charged, while H adsorbates at these sites can produce negatively charged structures, and their charge states are not necessarily integer-valued. These results provide new insights into the stability of charged vacancy defects in graphene, as well as the functionalization of graphene for chemical sensing and catalysis, and underline the tunability of these functions by controlling the size and doping of vacancy defects.

Magnetic Interfaces and Nanostructures
Room: 202 A - Session MI+EM-TuM

Spintronics and Magnetoelectrics
Moderator: P. Fischer, Lawrence Berkeley National Laboratory, M. Donath, Muenster University, Germany

8:00am MI+EM-TuM1 Molecular Beam Epitaxy and Spintronics, *S. Andrieu*, *F. Bonell*, *T. Hauet*, Institut Jean Lamour, CNRS-Université de Lorraine, France, *F. Bertran*, Synchrotron SOLEIL, France **INVITED**
The growth and control of thin magnetic films has enabled the emergence of new branches of physics like nanomagnetism and spintronics, which stimulate an intense and successful research activity both in fundamental and applied directions. The reduced size of films and devices yields to the occurrence of new magnetic behaviors not present in bulk materials. Similarly, a new electronics based on the use of the spin of the electron was born in the 80's. The role of the Molecular Beam Epitaxy (MBE) was of prime importance in the development of these activities. The discovery of new phenomena was often highlighted from the synthesis of perfectly controlled systems by MBE (GMR in Fe/Cr(001), Half-metal magnetic effect in $LaSrMnO_3$, electric-field effect on magnetic anisotropy in FePt,...). Since the knowledge on the electronic properties of such thin films is crucial to understand the magnetic and electronic transport properties in these MBE-grown model systems, synchrotron radiation facilities were also used (XMCD, spin- and symmetry-resolved photoemission, diffraction,...). The strong impact of MBE growth and SR characterization in the understanding of fundamental issues in nanomagnetism and spintronics is then illustrated through the example of fully epitaxial MgO-based Magnetic Tunnel Junctions (MTJs). The physics

of coherent tunneling will be first introduced using the example of Fe/MgO/Fe(001) MTJs [1]. The effect of dislocations in the MgO barrier on transport properties will be illustrated using the example of FeV_x/MgO MTJs [2]. Unexpected transport properties in $FeCo_x$/MgO will be presented and explained with the help of spin and symmetry resolved photoemission [3]. Finally, very recent results will be presented, like manipulation of the magnetic anisotropy at the Fe/MgO interface using an electric field [4], or insertion of the Half-metallic ferromagnetic $(CoFe)_3Ge$ in MgO-based MTJs.

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8:40am MI+EM-TuM3 Engineering Single Spins in Semiconductors for Sensing and Computation, *D. Awschalom*, University of California, Santa Barbara, *W.F. Koehl*, *A.L. Falk*, University of Chicago, *G. Calusine*, University of California, Santa Barbara, *F.J. Heremans*, University of Chicago, *V.V. Dobrovitski*, Ames Laboratory, Iowa State University, *A. Politi*, University of California, Santa Barbara **INVITED**
Semiconductor defects, while generally considered undesirable in traditional electronic devices, can confine isolated electronic spins and are promising candidates for solid-state quantum bits (qubits) [1]. Alongside research efforts focusing on nitrogen vacancy (NV) centers in diamond, an alternative approach seeks to identify and control new spin systems with an expanded set of technological capabilities, a strategy that could ultimately lead to "designer" spins with tailored properties for future quantum information processing. We discuss recent experimental results identifying such spin systems in the 4H, 6H, and 3C crystal polymorphs of silicon carbide (SiC) [2,3]. Using infrared light at near-telecom wavelengths and gigahertz microwaves, we show that these spin states can be coherently addressed at temperatures ranging from 20 K to room temperature. Long spin coherence times allow us to use double electron-electron resonance to measure magnetic dipole interactions between spin ensembles in inequivalent lattice sites of the same crystal. Since the inequivalent spin states have distinct optical and spin transition energies, these interactions could lead to engineered dipole-coupled networks of separately addressable qubits. Together with the availability of industrial scale crystal growth and advanced microfabrication techniques for SiC, these results make this system a promising platform for photonic, spintronic, and quantum information applications that merge quantum degrees of freedom with classical electronic and optical technologies.

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9:20am MI+EM-TuM5 Semiconductor Spintronics -- New Avenues and Perspectives: Graphene as a Spin Tunnel Barrier in MTJs and Silicon, *B.T. Jonker*, *E. Cobas*, *O.M.J. van 't Erve*, *C.H. Li*, *A.L. Friedman*, *J.T. Robinson*, Naval Research Laboratory **INVITED**
Graphene has been widely studied for its high in-plane charge carrier mobility and long spin diffusion lengths. In contrast, the out-of-plane charge and spin transport behavior of this atomically thin material have not been well addressed. Tunnel barriers are the basis for many spintronic devices, and to date have relied upon oxides which often exhibit defects, trap states and interdiffusion which compromise performance and reliability. We show here that while graphene exhibits metallic conductivity in-plane, it serves effectively as an insulator for transport perpendicular to the plane. We fabricate magnetic tunnel junctions, and demonstrate electrical spin injection/detection in silicon using graphene as a tunnel barrier.

The graphene was grown by chemical vapor deposition on copper foil and incorporated as the tunnel barrier by physical transfer and standard lithographic processes to form Co / graphene / NiFe magnetic tunnel junctions (MTJs) 20-40 um in diameter [1]. Non-linear *I-V* curves and weak temperature dependence of the zero-bias resistance provide clear evidence for tunneling. The magnetic field dependence exhibits the classic signature of MTJ behavior, and the structures exhibit tunneling magnetoresistance (TMR) to 425 K, in good agreement with theory [2]. The TMR decreases monotonically with both bias and temperature, typical of MTJ behavior.

Single-layer graphene also successfully circumvents the classic issue of conductivity mismatch between a metal and a semiconductor for electrical spin injection and detection, providing a highly uniform, chemically inert and thermally robust tunnel barrier. Hanle spin precession measurements demonstrate spin injection and provide quantitative values for spin lifetimes. Devices with NiFe / single layer graphene / Si contacts exhibit the classic Lorentzian lineshape due to spin injection and dephasing. We demonstrate electrical generation and detection of spin accumulation in silicon above room temperature, and show that *(a)* the corresponding spin lifetimes correlate with the silicon carrier concentration, and *(b)* the contact resistance–area products are two to three orders of magnitude lower than those achieved with oxide tunnel barriers on silicon substrates with identical doping levels [3]. This reduction of contact resistance enables spin injection and quantitative measurements of spin lifetimes in silicon nanowires, as well.

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10:40am MI+EM-TuM9 Graphene Direct Growth on Magnetic Oxides on Co(0001): Graphene Effects on Oxide Magnetic Behavior, *F. Paquale, Y. Cao, H. Kasi, S. Gaddam,* University of North Texas*, L. Kong, Y. Wang, C. Binek, P.A. Dowben,* University of Nebraska-Lincoln*, J. Kelber*, University of North Texas

The direct growth of graphene on thin (< 50 Å) magnetic oxides on cobalt or other ferromagnetic substrates (Gr/oxide/Co) presents interesting opportunities for development of practical magnetic and magnetoelectric graphene devices. We have grown single and few layer graphene (Gr) directly on $Co_3O_4(111)/Co(0001)$ by MBE, and have very recently grown graphene by e-beam-assisted deposition on $Cr_2O_3(0001)/Co(0001)$. XPS data demonstrate the presence of a sp^2-indicative π --> π* shakeup feature but with C(1s) peak binding energies of 284.9 (±0.2) eV for $Gr/Co_3O_4(0001)$ -- significantly larger than the 284.5 eV value common for graphitic systems. This indicates significant graphene-to-oxide charge transfer. LEED images yield the expected C_{6v} symmetry and 2.5(±0.1) Å lattice spacing for graphene, with a 2.8(±0.1) Å O-O distance at the oxide surface. All are consistent with the literature and indicate incommensurate graphene/oxide interfaces. Domain sizes of ~ 1800 Å are estimated from the LEED data for $Gr/Co_3O_4(111)$, comparable to HOPG. 3 monolayer (ML) $Gr/Co_3O_4(111)/Co(0001)$ exhibits room temperature resistivity 10^2-10^3 times smaller than for graphene transferred to other substrates, and consistent with strong p-type doping, as indicated by XPS. Magneto-optic Kerr effect (MOKE) results demonstrate the presence of antiferromagnetic (AF) ordering for the $Gr/Co_3O_4(111)/Co(0001)$ heterostructures up to at least 420 K, with evidence of exchange interaction effects as well. No antiferromagnetic polarization is observed for Co_3O_4/Co films in the absence of graphene, indicating a role played by graphene in the magnetic ordering of the oxide. These results indicate the potential suitability of such films for non-local spin valves and similar devices operating at realistic device temperatures. This talk will also present results for on-going MOKE and transport measurements on $graphene/Cr_2O_3/Co(0001)$ samples. The ability to apply both magnetic and electric fields to such stacks provides the potential for magnetoelectric spin-transistors and tunneling devices.

11:00am MI+EM-TuM10 Nanocluster Size Effects in Au-Co Nanocomposite Thin Films: Correlated Non-linear Magneto-Optics and Magneto-Transport Studies, *K. Yang*, The College of William and Mary*, V. Kryutyanskiy, I. Kolmychek, T. Murzina,* Moscow State University, Russian Federation*, R.A. Lukaszew*, The College of William and Mary

Magnetic materials in nanometer scale typically exhibit significant different magnetic and magnetic-optical properties compared to bulk materials. Composite thin films with magnetic metal clusters embedded in a non-magnetic metal matrix offer a tailored self-assembled nanoscale platform to investigate magneto-optical and magneto-transport properties and possible correlations between them in constrained geometries. The magnetic clusters size as well as the overall composite thin film thickness can be tailored via adequate deposition conditions to achieve a viable nanocluster binary system. We have previously shown that Au/Co/Au trilayers as well as Au-Co nanocomposite thin films exhibit strong enhancement of the linear magneto-optical properties under surface plasmon polariton excitation. [1] Based on these previous results on linear optics measurements, we

investigate now the non-linear optical properties such as second harmonic generation (SHG) as well as the magneto-transport properties in Au-Co nanocomposite thin films. Optical SHG is a sensitive probe of surface and buried interfaces due to inversion symmetry breaking at the interfaces of center-symmetric materials which allows probing structural and morphological properties near interfaces. Here we observe a non-monotonous dependence of the SHG magnetic contrast on the cobalt content in Au-Co films, which reveals a sharp increase close to the transition from a granular-like type structure with Co clusters embedded in gold, to an interconnected composite structure when percolation of the cobalt clusters sets in. We also find a SHG enhancement for Co fractional content of 0.35, within the granular structure regime, that can be associated with localized surface plasmon resonance as well as with local field enhancement in an inhomogeneous composite. Furthermore, the magneto-transport measurement (i.e. the magneto-resistance, MR) properties of the Au-Co composite thin films follow similar trend as a function of Co content as the non-linear SHG magnetic contrast before percolation and dramatically deviate once percolation sets in. Thus, our correlated SHG-MR results in Au-Co nanocomposite thin films with varying Co content will be presented and discussed.

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11:20am MI+EM-TuM11 Spin and Heat Transport through Interfaces between Metals and Magnetic Insulators, *G.E.W. Bauer*, Tohoku University, Japan **INVITED**
Spin caloritronics is the science and technology of the physical phenomena (and their control) associated with the coupling of charge, spin, and heat currents in nanoscale structures and devices [1]. Bilayers of magnetic insulators and normal metals have attracted interest in this field because they display the spin Seebeck effect, i.e. the generation of a spin motive force by an applied temperature difference over the interface. In this talk I will address the theory and applications of power and voltage generation by thermally excited magnetization dynamics at the interface of a magnetic insulator such as yttrium iron garnet (YIG) and normal metals such as platinum.

[1] G.E.W. Bauer, E. Saitoh & B. J. van Wees, Nature Materials 11, 391–399 (2012)

Tuesday Afternoon, October 29, 2013

Electronic Materials and Processing
Room: 101 B - Session EM+MI+NS+SS+TF-TuA

High-k Oxides for MOSFETs and Memory Devices II/Oxides and Dielectrics for Novel Devices and Ultra-dense Memory I
Moderator: J. Kim, University of Texas at Dallas, C.L. Hinkle, University of Texas at Dallas

2:00pm EM+MI+NS+SS+TF-TuA1 Metal-Atom Dimer Model of Oxygen Vacancy Behaviour in Oxide RRAM, *J. Robertson*, Cambridge University, UK
Resistive random access memories (RRAM) have great potential as future non-volatile memories with a faster read and write time than Flash memory. RRAM works by the forming of a conductive filament across a resistive film between the electrodes, which is then SET and RESET between its conductive and resistive states [1-2]. Typical films are oxides such as TiO_2, Ta_2O_5 and HfO_2, and the conductive filament is believed to consistent of a percolation path of oxygen vacancies. Recently there have been various models of this oxygen vacancy path, in terms of molecular dynamics [3], or ordered vacancy structures [4]. Here we use an ordered model of vacancies in HfO_2 or TiO_2, as in a local M_2O_3 structure in the MO_2 matrix. In Ti_2O_3, the Ti atoms form an ordered line of Ti-Ti dimers along the c axis, and the bonding state stabilises the Ti^{3+} state along the path. The transition between the ordered and disordered phase of dimers describes the low to high resistivity state of RRAM, as in the metal-insulator transition in Ti_2O_3.

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2:20pm EM+MI+NS+SS+TF-TuA2 Investigation of Sub-Gap Defect States in High-k Dielectric Materials Using Reflection Electron Energy Loss Spectroscopy, *B. French*, S.W. King, Intel Corporation
The electrical reliability of high-k metal gate transistors is a growing concern as the nano-electronics industry moves to sub-12 nm dimensions and new 3D multi gate transistor technologies. In order to understand the various possible reliability failure mechanisms in high-k dielectric devices, knowledge of the band gap and defect states in high-k dielectrics is needed, but experimental identification of both the chemical identity and energy level of the defects contributing to reliability issues in high-k materials has gone largely unreported in many cases. In this regard, we have utilized Reflection Electron Energy Loss Spectroscopy (REELS) to determine the band gap of numerous single crystalline and amorphous high-k dielectric materials. We demonstrate that for standard single crystalline materials such as Quartz, Al_2O_3, and TiO_2 REELS band gap measurements agree with known values. For amorphous high-k thin film materials, we further demonstrate that REELS band gap measurements in most cases agree with optical measurements of the same materials. However, in some cases, we have observed that REELS analysis is complicated by the existence of defect states within the band gap of these materials. While troublesome for band gap measurements, we demonstrate that this sensitivity can be utilized to determine the energy level of various defects in pristine and sputter damaged high-k dielectrics and in some cases the chemical identity of the defect can be determined.

2:40pm EM+MI+NS+SS+TF-TuA3 Atomistic Mechanism of RRAM Operations, *G. Bersuker*, SEMATECH **INVITED**
Non-volatile resistive switching memory (RRAM) technology shows a promise to overcome the scaling limit approached by the conventional electron storage memories. Among a variety of RRAM systems, the HfO2-based technology is especially attractive due to its fab-friendly fabrication process, high endurance and retention, and sub-nanosecond switching-speed assuming that low-current, low-variability operations can be achieved. This study aims to identify critical features of the material structure and operation conditions controlling the inherently stochastic switching process. The forming of the initial conductive filament in hafnia and its subsequent disruption/restoration responsible for the switching between high and low resistive states are modeled considering oxygen vacancies/ions generation and recombination and oxygen ion diffusion in the surrounding oxide driven by the local temperature and electric field. The simulations reveal the main structural characteristics of the dielectric stack affecting variability and allow assessing the effect of different forming conditions on the overall filament geometry/composition, thus, providing general guidelines for optimizing device operations.

4:00pm EM+MI+NS+SS+TF-TuA7 Bipolar Selector Devices for Cross-point ReRAM, *H.S. Hwang*, POSTECH, Republic of Korea **INVITED**
ReRAM has been considered as a promising candidate to overcome scaling limits of the conventional FLASH memory due to its superior performance. To realize the high density memory, 3D cross-point array or Vertical ReRAM are necessary [1]. To integrate cross-point ($4F^2$) ReRAM device array, we need to develop bi-directional selector device to suppress the sneak current path through the unselected devices. Although various candidates with selector properties were recently reported, several problems such as insufficient current density at set/reset operations for nano-scale devices, low selectivity, and poor endurance have been raised. In this talk, two different types of selector device for cross-point ReRAM are introduced.

A. Threshold switching device

Various reports on threshold switching device with oxides of V, Nb, and Ti have been reported. This threshold switching is attributed to formation of a metallic phase as a result of local Joule heating induced metal-insulator transition (MIT) of the corresponding suboxides such as VO_2, NbO_2, and Ti_2O_3. Among them, we investigated threshold switching characteristics of NbO_2 [2]. Ultrathin NbO_2 layer (< 10nm) exhibits excellent threshold switching characteristics. Especially, thermal stability of threshold switching was obtained at a high temperature. Threshold switching property remains stable up to 433K, which is much higher than VO_2 material (only a 340K). Furthermore, we demonstrate hybrid memory characteristic, which exhibits both threshold and memory switching, by controlling the oxygen concentration of NbO_x layer.

B. Multi-layered oxide based device

Highly non-linear property of $Ta_2O_5/TaO_x/TiO_2$ structure was reported [3]. By using multi-layered oxide stack, a high current density of $10^7 A/cm^2$ and a high selectivity ($\sim 10^4$) were achieved. To maximize the selector performance, we have performed extensive tunnel barrier engineering such as the adoption of various materials and control of oxidation conditions to optimize the oxide stoichiometry, film thickness, and electrode material. Furthermore, in order to confirm the feasibility for cross-point array application, selector device was vertically-integrated with ReRAM.

We have demonstrated excellent selector characteristics of threshold switching device and multi-layered tunneling oxide based device. Superior performances of selector devices show good promise for future high density ReRAM applications.

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4:40pm EM+MI+NS+SS+TF-TuA9 Crystallization study of SrTiO3 Thin Films Prepared on Si3N4, Al2O3 and Pt surfaces by Plasma-Assisted ALD, *V. Longo*, M.A. Verheijen, F. Roozeboom, W.M.M. Kessels, Eindhoven University of Technology, Netherlands
$SrTiO_3$ (STO) has received much attention due to its favorable properties as ferro-electric, para-electric and *high-k* dielectric material, related to its crystalline perovskite structure. Thin STO films are to be employed as the dielectric layer in metal-insulator-metal (MIM) structures, for example for DRAM and/or RRAM applications. When deposited by Atomic Layer Deposition (ALD), STO films are amorphous and require an annealing step to crystallize. Recent reports have shown that Sr-rich films yield a finer crystalline structure than stoichiometric films upon crystallization by rapid thermal annealing (RTA). The finer grain structure results in reduced nanocrack formation, thus less leakage and improved dielectric properties. A deeper understanding of the crystallization behavior of STO is therefore of crucial importance to further optimize the film properties.

In this work SrTiO3 thin films with different compositions ([Sr]/[Sr]+[Ti] from 0.50 to 0.65) were deposited by plasma-assisted ALD employing cyclopentadienyl-based precursors and an O2 plasma. The crystallization of the as-deposited amorphous films was obtained by RTA in N_2 at temperatures ranging from 550 °C to 650 °C. Different annealing times (60 to 600 s) were employed to characterize the crystallization process at different stages. An in-depth analysis of the microstructure of the crystallized STO was carried out by transmission electron microscopy (TEM). As a first step, the analysis was performed on STO films deposited

on Si_3N_4 TEM membranes, either bare or coated by ALD-grown Al_2O_3, due to the transparency of these materials to the electron beam. It was shown that the STO crystallites had grown in a *transrotational* manner and that an increased Sr-content resulted in films with reduced grain size and a more compact microstructure. Furthermore, two crystallization regimes were identified: 1) growth-dominated, where the crystallization process is dominated by growth of a low density of crystals, and 2) nucleation-dominated, where a high density of crystals is limited in lateral growth by their proximity. Finally, the STO films were also deposited on Pt-coated TEM windows (Pt prepared by plasma-assisted ALD) to compare the crystallization kinetics on a representative functional bottom electrode material as used in MIM structures. The TEM analysis and the X-ray diffraction patterns evidenced that these films show quite similar crystallization behavior as on Si_3N_4 and Al_2O_3 surfaces.

5:00pm EM+MI+NS+SS+TF-TuA10 Superconformal Coating and Filling by Two-molecule CVD, *W. Wang, N. Chang, T. Hitt, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana Champaign
An important fabrication challenge is to fill deep trenches or gaps with a dielectric material, such as shallow trench isolation or inter-metal dielectric in microelectronics. This is typically accomplished using chemical vapor deposition, which affords nearly conformal film growth, interspersed with one or more etching steps to prevent pinch-off of the feature opening. A superior alternative would be superconformal growth, in which the film thickness is inherently thicker towards the bottom of a deep feature than at the top, to afford complete filling in a single process.

We report a method, applicable to CVD processes that use two reactive molecules, to afford superconformal growth. It takes advantage of two insights. First, growth involves competitive adsorption on the film surface, such that the growth rate is maximum for a particular ratio of reactant fluxes (pressures) and falls on either side of this peak. Thus, there exists a regime in which *decreasing the pressure of one reactant will increase the film growth rate*. Second, the molecular (Knudsen) diffusion coefficient controls the rate of pressure drop down the axis of the feature. The reactant with the smaller diffusion coefficient (generally, the heavier molecule) will decrease in pressure faster than the other component. Combining these insights, we identify regimes of reactant pressure that afford superconformal growth in deep features.

We demonstrate superconformal growth, to a maximum depth beyond which the reactants are depleted, for two CVD systems. MgO is deposited at 220°C using the precursor $Mg(DMADB)_2$ with H_2O as the co-reactant; the growth rate increases from 1.0 nm/min at the trench opening to 1.8 nm/min at a depth/width ratio of 18. TiO_2 is deposited at 300°C using $TiCl_4$ and H_2O; the growth rate increases from 1.5 to 4.0 nm/min at depth/width ratio of 5. The TiO_2 coating inside trench is found to be stoichiometric and 88% of bulk density.

Finally, we describe a general model for the superconformal growth phenomenon. It uses as input the adsorption and reaction rate coefficients derived from growth on planar substrates, and suitable values for the molecular diffusivities. A first-order solution of the diffusion-reaction equation affords an analytic relationship that predicts the degree of superconformality in terms of the aspect ratio of the feature and the starting pressures of the reactants. It can be used to identify the regimes of useful operation and the necessary growth conditions. Given input data on reaction rates, this model can be used to predict which other two-molecule CVD systems would afford superconformal growth.

5:20pm EM+MI+NS+SS+TF-TuA11 Resistive Switching Random Access Memory (RRAM) - Materials, Device, Scaling, and Array Design, *Y. Wu, S. Yu, H.-Y. Chen, J. Liang, Z. Jiang, H-.S.P. Wong*, Stanford University **INVITED**
In this paper, we review our recent progress on resistive switching metal oxide memory (RRAM). We continue to explore the stochastic nature of resistive switching in metal oxide RRAM using the Kinetic Monte Carlo method. By including multiple conduction mechanisms, local field and local temperature profile, we substantially improved our stochastic model and studied the RRAM characteristics such as set/forming current overshoot, endurance and retention [1-3]. From an experimental perspective, we have demonstrated that HfOx-based RRAM devices can scale down to less than 10 nm diameter using electron beam lithography (e-beam) and atomic layered deposition (ALD) methods. The devices can switch more 10^8 cycles with fast speed (~10 ns), large resistance window (~100X), multi-level storage capabilities, and good retention. We also characterized the scaling behavior of the HfOx-based devices such as forming, set/reset voltages [4]. Two-layer stacked HfOx vertical RRAM was fabricated for 3D cross-point architecture. The vertical RRAM devices show excellent performance such as low reset current (<50 uA), fast switching (~50 ns), good endurance (~10^8 cycles), half-selected immunity (~10^8 cycles), retention (>10^5 s @125°C) [5]. Looking into the future, we investigated the impact of

wordline/bitline metal wire scaling on the read/write performance, energy consumption, speed and reliability in the cross-point memory array architecture. Possible solutions were suggested to incorporate and mitigate the scaling effects of metal wire interconnect for the next-generation non-volatile memory (NVM) [6-7].

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Magnetic Interfaces and Nanostructures
Room: 202 A - Session MI+AS+NS+SP-TuA

Advanced Probes in Magnetic Imaging and Characterization
Moderator: H. Ohldag, SLAC National Accelerator Laboratory

2:00pm MI+AS+NS+SP-TuA1 Electron Correlation Spectroscopy on Magnetic Surfaces, *F.O. Schumann*, Max-Planck Institut für Mikrostrukturphysik, Germany **INVITED**
The emergence of long range magnetic order is a consequence of the mutual interaction between electrons. A key postulate of quantum mechanics is the requirement of the wave function to be antisymmetric upon exchange. This inclusion leads to a modification of the Coulomb interaction which is termed exchange interaction. For ferromagnets this leads to parallel spins while for antiferromagnets an antiparallel alignment is prefered.

Electron pair emission from surfaces is an advanced tool to study the relation between electrons which goes beyond the capabilities of single electron spectroscopy e.g. photoemission. The power of this approach will be demonstrated by two case studies on Fe and NiO films. The angular distributions of emitted electron pairs reveal a region of reduced intensity which can be traced back to the exchange-correlation hole.[1] This concept was introduced by Wigner, Seitz and Slater more than 75 years ago. It plays an important role in modern solid state theory. We performed experiments on Fe films to unravel the spin-dependence of the exchange-correlation hole. We find that the contribution of exchange is more extended than the Coulomb contribution as suggested by Slater.[2]

The investigation of correlation effects in solids is an active field of research. In this context metal oxides like NiO are usually termed "highly correlated", because the material properties are decisively determined by the electron-electron interaction. The very existence of a finite electron pair emission requires a finite electron-electron interaction. This immediately leads to the question whether the intensity level provides insight into the correlation strength. A theoretical study of pair emission from a strongly correlated system modeled by the Hubbard Hamiltonian gives an affirmative answer.[3] We tested this conjecture and find that the coincidence intensity for NiO is roughly an order of magnitude larger compared to the Ag(100) substrate.[4] This also holds for the comparison of other transition metals and their oxide phases. This result suggests that the electron correlation strength is accessible via the pair emission intensity.

Our results demonstrate that electron pair emission is a unique tool to unravel the nature of the electron correlation in solids.

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4:00pm MI+AS+NS+SP-TuA7 Probing Magnetic Interfaces and Nanostructures with Hard X-ray and Standing-Wave Excited Photoemission Spectroscopy, *A.X. Gray*, SLAC National Accelerator Laboratory, *J. Minar,* Ludwig Maximillian University, Germany, *S. Ueda,* National Institute for Materials Science, Japan, *L. Plucinski,* Forschungszentrum Jülich GmbH, Germany, *A. Bostwick, E. Rotenberg,* Advanced Light Source, *C.M. Schneider,* Forschungszentrum Jülich GmbH, Germany, *H. Ebert,* Ludwig Maximillian University, Germany, *K. Kobayashi,* National Institute for Materials Science, Japan, *C.S. Fadley*, University of California, Davis **INVITED**

The ever-growing demand for miniaturization and increased speeds of next-generation electronic devices has taken science to the quantum frontier in which emergent phenomena at the nanoscale require a clear differentiation between surface, bulk and interface properties. Thus, for many technologically-promising novel materials electronic structure varies dramatically as a function of depth and proximity to other materials. Therefore, novel depth-resolved characterization techniques are required to disentangle these rich electronic behaviors, including magnetism and spin. In this talk I will describe several new directions in the field of x-ray photoelectron spectroscopy, made possible with the advent of third-generation synchrotron light sources and recent advances in the fields of x-ray optics and photoelectron detection. I will present several case-studies wherein hard x-ray photoelectron spectroscopy (HAXPES) in the multi-keV regime is used to probe the bulk properties of complex thin-film materials and heterojunctions, which would be otherwise impossible to investigate using conventional soft x-ray XPS. I will present the first results of hard x-ray angle-resolved photoemission measurements (HARPES), at excitation energies of 3 and 6 keV. Compared to the traditional ARPES, carried out in the UPS regime (20-100 eV), this new technique enables one to probe on average 10-40 times deeper into the bulk. Finally, I will introduce a new photoemission technique (SWARPES) which combines soft x-ray ARPES with standing-wave (SW) excited photoelectron spectroscopy, wherein the intensity profile of the exciting x-ray radiation is tailored within the sample in order to provide a depth-selective probe of the electronic structure of buried layers and interfaces.

4:40pm MI+AS+NS+SP-TuA9 Imaging Magnetization Dynamics on its Genuine Time Scale, *G. Meier*, University of Hamburg, Germany **INVITED**

A variety of excellent microscopies that provide magnetic contrast on the nanoscale matured to powerful tools. Today's scanning-probe techniques feature ultimate spin resolution, namely imaging of the magnetization of single adatoms [1]. The temporal resolution of optical and x-ray methods reaches down to femtoseconds. It is intriguing to have spatial and time resolution simultaneously. The relevant frequency scale for ferromagnets is given by the ferromagnetic resonance which lies in the GHz range. Thus the required time resolution is in the sub-nanosecond regime. Magnetic microscopies available at synchrotron sources enable real-time imaging and provide lateral resolution down to the nanometer scale [2,3].

We investigate the switching criteria of nanometer-scaled magnetic vortices in micron-sized Permalloy squares. The vortices are excited by high frequency magnetic fields. Continuous core reversal is demonstrated for a wide range of frequencies and amplitudes of excitation by ferromagnetic absorption spectroscopy and for selected frequencies and amplitudes with time-resolved scanning x-ray microscopy. The boundary of this switching regime is derived from the Thiele equation when a critical velocity of $v_{crit} \approx 250$ m/s is considered [4].

Complexity created by periodic arrangement of well-understood building blocks plays an important role in biochemistry, photonics, and nanoelectronics. The periodic arrangement of atoms or molecules as basis determines the physical and even the chemical properties of crystals. With the flexibility of nanometer-precise electron-beam lithography we engineer magnetic interactions yielding two-dimensional magnonic crystals that benefit from the magnetic vortex core as crystal basis. Using scanning transmission x-ray microscopy at the MAXYMUS beamline at BESSY II in Berlin, Germany we image the magnonic crystal dynamics. We observe self-organized vortex core state formation by adiabatic reduction of high frequency magnetic field excitation [5]. The experimental results are described analytically by coupled Thiele equations of motion and are compared to micromagnetic simulations.

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5:20pm MI+AS+NS+SP-TuA11 Towards Magnetic 3dim X-ray Imaging, *P. Fischer*, *M.-Y. Im, W. Chao, E.H. Anderson*, Lawrence Berkeley National Laboratory

Nanomagnetism research focused on a fundamental understanding and controlling spins on a nanoscale. As the next step beyond the nanoscale, mesoscale phenomena have been recognized[1], since those add essential parameters to meet future challenges in terms of speed, size and energy efficiency of spin driven devices. The development and application of multidimensional visualization techniques, such as tomographic magnetic imaging will be crucial to achieve mesoscience goals.

Magnetic soft X-ray microscopy is a unique analytical technique combining X-ray magnetic circular dichroism (X-MCD) as element specific magnetic contrast mechanism with high spatial and temporal resolution [2]. Three-dimensional (3D) soft X-ray tomography using Fresnel zone plate based full field and scanning transmission soft x-ray microscopies have been developed and are routinely used at various synchrotron sources but mostly for biological imaging [3]. However, magnetic X-ray tomography is of large interest to understand e.g. interfaces in magnetic multilayers, the inner structure of magnetic nanocrystals, nanowires or the functionality of artificial 3D magnetic nanostructures.

There are several approaches for 3D X-ray imaging, such as utilizing standing waves in Bragg conditions [3], X-ray imaging in reflection geometry [4], X-ray ptychography [5] or computational reconstruction of projection X-ray images [6]. We have developed and implemented at the full-field soft X-ray microscopy beamline 6.1.2 at the ALS in Berkeley CA a new stage for tomography, which allows recording an angular series (up to 360 deg) of high precision 2D projection images. Applying state-of-the-art reconstruction algorithms it is possible to retrieve the full 3D structure. We will present recent results on prototype systems, such as glass capillaries coated with magnetic films . We will also discuss the complementarity of magnetic X-ray tomography to other 3D imaging approaches such as electron microscopy [7].

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5:40pm MI+AS+NS+SP-TuA12 Direct Visualization of Magnetoelectric Domains, *W. Wu*, *Y. Geng, X. Wang, S-W. Cheong*, Rutgers University, *C.J. Fennie*, Cornell University, *M. Mostovoy*, University of Groningen, Netherlands

The coupling between the magnetic and electric dipoles in multiferroic and magnetoelectric materials holds promise of conceptually new electronic devices[1-4]. The device miniaturization calls for development of local probes of the magnetoelectric response, in particular because such response is strongly affected by defects in magnetic and ferroelectric orders. For example, multiferroic hexagonal rare earth manganites exhibit a dense network of boundaries between six degenerate states of their crystal lattice, which are locked to both ferroelectric and magnetic domain walls. Here we present the first application of a newly-developed Magnetoelectric Force Microscopy (MeFM), which combines Magnetic Force Microscopy (MFM) with *in-situ* modulating high electric fields. This technique allowed us to directly image the magnetoelectric response of the domain patterns in hexagonal manganites. We found that this response changes sign at each structural domain wall. This MeFM result is corroborated by a symmetry analysis and a phenomenological model derived from microscopics and first-principles calculations[5], providing compelling evidence for a lattice-mediated magnetoelectric coupling. Furthermore, our measurements reveal a diverging magnetoelectric response near a critical point below 2 K originating from enhanced critical fluctuations and the high sensitivity of spin ordering to applied electric and magnetic fields. The direct visualization of magnetoelectric domains at mesoscopic scales opens up explorations of emergent phenomena in multifunctional materials with multiple coupled orders.

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Magnetic Interfaces and Nanostructures
Room: Hall B - Session MI-TuP

Magnetic Interfaces and Nanostructures Poster Session

MI-TuP1 Synthesis and Characterization of $Zn_{1-x}Co_xO/ZnO$ Hollow Nanosphere Structures, *D.R. Liu, W.-H. Cho, C.J. Weng*, ITRC, NARL, Taiwan, Republic of China

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnCoO is one of the most promising diluted magnetic semiconductors materials due to its high temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanosphere with different diameter (100nm~800nm) by atomic layer deposition (ALD). After removal of PS nanosphere by heating, ZnO hollow nanospheres were formed. Then the $Zn_{1-x}Co_xO$ (x=0~0.1) coatings were grown on ZnO hollow nanospheres by pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, the $Zn_{1-x}Co_xO/ZnO$ hollow nanospheres are polycrystalline with a preferential growth direction of (002). The surface and cross-section morphologies of the hollow nanospheres were analyzed using a field-emission scanning electron microscope (FE-SEM). The magnetic properties of the nanospheres were measured by a vibrating sample magnetometer(VSM) and x-ray magnetic circular dichroism (XMCD) spectroscopy. The results show the magnetic properties of $Zn_{1-x}Co_xO/ZnO$ hollow nanospheres strongly depend on the Co composition fraction and the size of nanospheres.

MI-TuP2 Exchange Bias Tuning with Temperature and Pt Ratios in Pt_xCo_{1-x}/CoO Bilayer, *M. Erkovan, M. Ozturk, E. Demirci, N. Akdogan, O. Erdemir, O. Ozturk*, Gebze Institute of Technology, Turkey

In this study, we report EB effect observed in Pt_xCo_{1-x} (x changes from 10 to 90 by 10 step)/ CoO bilayer thin films. PtCo alloys have very large magnetocrystalline anisotropy so they will be very good candidate for next generation data storage media. Besides EB effect is used in the read head sensors, so PtCo may find usage area in both the read head sensor and data storage media. Our goal was to determine how EB depends on Pt concentration in ferromagnetic PtCo layer and temperature.

All films were prepared at UHV conditions by magnetron sputtering deposition technique. The chemical ratios of PtCo layers and CoO layers for all composite films were characterized by Photoelectron Spectroscopy (XPS) technique. Quantum Design PPMS 9T vibrating sample magnetometer (VSM) was used to investigate EB properties of the films. Since the Néel temperature is about 290 K for antiferromagnetic CoO layer, Pt_xCo_{1-x} /CoO films were heated up to 320K before cooling down to the measurement temperature to observe Exchange bias effect. An in-plane magnetic field of 2 kOe was applied while cooling the samples to the measurement temperatures.

Temperature-dependent magnetization measurements show that strength and onset temperature of exchange bias are enhanced by increasing Pt concentration. We observed also two different results from magnetization measurement. One of them is that the blocking temperature (T_B) of both samples is lower than the expected bulk value. The other one is that decreasing Pt concentration within the FM PtCo layer reduces T_B to lower values. In order to determine the effect of Pt concentration on magnetic anisotropies, the samples have been investigated by using ferromagnetic resonance (FMR) technique at room temperature (RT). FMR experiments show uniaxial in-plane magnetic anisotropy at room temperature. This behavior becomes stronger when the Pt concentration is increased. According to these results, the manipulation of common interface between ferromagnetic and antiferromagnetic layers gives the possibility to tune the exchange bias with Pt concentration and temperature.

MI-TuP4 Internal Magnetic Friction of Gold-Nickel Alloy Substrates on a Quartz Crystal Microbalance, *K.M. Stevens, L. Pan, J. Krim*, North Carolina State University

The study of magnetic friction provides an opportunity to access bulk properties of the material and internal dissipation pathways. This gives benefits beyond that of surface studies, which assume a uniform substrate response and typically access phononic, conduction and charging pathways. This technique has been used successfully to study superconductivity-dependent friction [1,2] and nonhomogeneous magnetic microstructures[3-5].

We study gold-nickel alloys, as these provide an interesting spectrum of bulk magnetic properties. Samples with 5-20% nickel alloyed with gold were deposited as a homogenous solid-solution or as a two-phase FCC solid through the modification of annealing procedures. The solid solution is known to be paramagnetic for concentrations below 35% Ni [6], while the two phase solid maintains domains of ferromagnetism within bulk gold. These materials have been deposited onto a quartz crystal microbalance to allow properties to be monitored continuously by measuring the frequency and amplitude of the oscillator [7].

The two-phase Ni/Au material has demonstrated unique properties. Prior work has shown this to be an exceptional candidate for MEMS electrodes [8]. This work explores the impact of the bulk inhomogeneity. We have observed a "flexing" effect due to the application of an external magnetic field on two-phase alloy samples, which is measured as a discrete decrease of oscillator amplitude synchronized with the applied field; the effect is not seen on the solid solution samples of the same nickel-gold composition. The results are consistent with the formation of internal shear waves around the domains of nickel within bulk gold. An internal degree of freedom at the grain boundaries may decrease friction even in the absence of an external magnetic field.

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Wednesday Morning, October 30, 2013

Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+EM+MI+TF-WeM

APT Analysis of Semiconductor, Magnetic, and Oxide Materials
Moderator: T. Li, University of Sydney, Australia

8:00am AP+AS+EM+MI+TF-WeM1 Progress in Planar-Feature Spatial Reconstruction for Atom Probe Tomography, *D.J. Larson*, *B.P. Geiser, T.J. Prosa, T.F. Kelly*, CAMECA
In the last decade, the applicability of atom probe tomography (APT) has undergone a revolution [1] due to: 1) improved specimen preparation due to focused ion beam milling, 2) improved field of view due to the advent of a local electrode or other ion optical methods, and 3) reinvention of the use of lasers to induce field evaporation. This combination has created challenges in the area of spatial data reconstruction algorithms for APT for two reasons. Firstly, datasets collected at wider field of view are not accurately reconstructed using small angle approximation algorithms. Secondly, heterogeneous specimens containing multiple phases are more likely to yield, which creates challenges in reconstruction due to the non-hemispherical specimen shapes arising from field evaporation.

The most common algorithm for APT data reconstruction has been used with minimal changes for nearly twenty years [2] and has two main limitations: 1) the field evaporated surface is reconstructed as a hemispherical shape and 2) the atomic volume/depth increment is independent of X or Y. This abstract presents recent advances that have been made on APT data reconstruction, particularly in the areas of algorithm development and field evaporation simulation [3]. Various methods of improving APT reconstruction include: 1) post-reconstruction density correction [4], 2) methods which operate within the limits of the hemispherical projection, both pre- and post-reconstruction [5], and 3) methods which remove the hemispherical limitation, primarily based on simulation [6].

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8:20am AP+AS+EM+MI+TF-WeM2 APT Analysis of Superlattices, Nanowires, and Non-Planar Heterostructures, *L.J. Lauhon*, Northwestern University **INVITED**
I will describe pulsed laser atom probe tomography of semiconductors and semiconductor heterostructures in which the specimen or device geometry significantly limits the application of alternative analytical characterization techniques, thereby presenting unique opportunities for APT analysis. At the same time, geometry and other factors can complicate specimen preparation and APT interpretation. The talk will present both new scientific findings enabled by APT as well as challenges in data analysis, using three examples. First, I will describe the dopant distribution in semiconductor nanowires, for which APT studies have provided new understanding of dopant incorporation mechanisms. Additionally, advances in nanowire growth and design have enabled imaging of the entire nanowire diameter. Second, I will describe the analysis of InGaN/GaN superlattices extracted from light emitting diodes, for which APT is uniquely able to investigate fluctuations in indium mole fraction and the 3-D morphology of the InGaN quantum wells. In both GaN nanowires and thin-films, we have found that the surface polarity strongly influences the measured stoichiometry, but the indium mole fraction can be determined reliably. Finally, we have analyzed InGaN quantum wells grown on GaN nanowires. These are nonplanar heterostructures in which quantum wells are grown simultaneously on both polar and non-polar surfaces. Data from scanning transmission electron microscopy-based analytical methods will be compared with APT analysis, and the relative merits described. A comparison of these 3 examples will provide insights into the influence of intrinsic materials properties as well as specimen geometry on the capabilities and limitations of APT.

9:00am AP+AS+EM+MI+TF-WeM4 Atom Probe Analyses of Interfaces in Nd-Fe-B Permanent Magnets for Higher Coercivity, *T. Ohkubo*, *H. Sepehri-Amin, K. Hono*, National Institute for Materials Science, Japan **INVITED**
Nd-Fe-B permanent magnets are one of the most important engineering materials that are used for traction motors of (hybrid) electric vehicles. For these applications, coercivity at an operating temperature around 200°C must be higher than the demagnetization field in motors; thus, Nd atoms in the $Nd_2Fe_{14}B$ phase are partly substituted with heavy rare earth element (HREE). However, due to the limitation of natural resources of HREE, the development of high coercivity Nd-Fe-B magnets without HREE has become a new technical target in Japan. In order to understand the relationship between the microstructure and the coercivity, quantitative characterization of chemical compositions at various interfaces in Nd-Fe-B magnets have been needed. In this talk, we present how 3DAP analysis results of Nd-Fe-B magnets played crucial role in the development of high coercivity nanocrystalline anisotropy magnets with superior coercivity and comparable energy density.

One of the long-standing issues on the coercivity of Nd-Fe-B sintered magnets was the chemical and magnetic characteristics of the thin intergranular layer that emerge after the optimal post-sinter heat treatment. Although people thought that the intergranular layer is non-ferromagnetic, 3DAP analysis indicated it is ferromagnetic based on the concentration of the Fe within the phase [1]. We also found that the intergranular layer is formed by the Nd/NdCu eutectic reaction. This finding has been applied to nanocrystalline HDDR [2], melt-spun [3], and hot-deformed Nd-Fe-B magnets [4] to modify the grain boundary chemistry by the Nd-Cu eutectic diffusion process. Unlike the conventional HREE grain boundary diffusion process that has to be carried out above 900°C, this new low temperature process suppress the grain growth of the $Nd_2Fe_{14}B$ phase. Employing this new eutectic diffusion process, we have succeeded in developing bulk Nd-Fe-B magnets with sufficiently high coercivity and the energy product comparable to that of the conventional (Nd,Dy)-Fe-B magnets. In this talk, we will emphasize the role of the multi-scale characterization using 3DAP, (S)TEM, and SEM in the development of high coercivity Nd-Fe-B magnets.

This work was in part supported by JST, CREST.

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10:40am AP+AS+EM+MI+TF-WeM9 New Insights Into the Corrosion Behavior of Simulated Vitrified Nuclear Waste from Atom Probe Tomography, *D.K. Schreiber, J.V. Ryan, J.J. Neeway,* Pacific Northwest National Laboratory*, S. Gin*, CEA Marcoule, France
Atom probe tomography (APT) is being used to study the corrosion and alteration layers formed in borosilicate glass samples during long-term (1–26 years) water corrosion. The water environment and glass composition (SON68 – the non-activated surrogate of the French nuclear waste form R7T7 glass) were selected to generate novel insights into the rate-limiting mechanisms of glass corrosion that are relevant to the long-term storage of high-level nuclear waste in a geologic repository. APT concentration profiles across the corroded/pristine glass interface reveal significantly different interfacial widths for B and Na (~2-5 nm) than for Li and H (~15-30 nm), which suggests that multiple element-specific degradation mechanisms are occurring in parallel. Furthermore, the measured interfacial widths are much sharper than were measured previously by energy-filtered transmission electron microscopy and NanoSIMS. Accurate compositional APT analysis of this 26-component complex glass is, however, quite difficult. The implications of these findings and also practical considerations and limitations when performing these experiments will be discussed in some detail.

11:00am AP+AS+EM+MI+TF-WeM10 Advanced Applications in LEAP Microscopy, *H.G. Francois-Saint-Cyr*, *R. Ulfig*, CAMECA Instruments, Inc., *J. Valley*, *T. Ushikubo*, University of Wisconsin, Madison, *M. Miller*, Oak Ridge National Laboratory, *H. Takamizawa, Y. Shimizu*, Tohoku University, Japan, *L. Gordon, D. Joester*, Northwestern University, *A. Giddings, D. Reinhard, D. Lawrence, P. Clifton, D. Larson*, CAMECA Instruments, Inc.

The second revolution in atom probe tomography (APT), mainly due to the pursuit of sophisticated laser pulsed modes and focused ion beam based sample preparation, has broadened the range of new applications benefiting from three-dimensional, sub-nanometer compositional information [1]. Novel applications include dopant distribution analysis in metal-oxide-semiconductor (MOS) transistor, geological dating of zircon crystals, quantum dot (QD) assembly growth in Light-Emitting Diodes (LEDs), analysis of biological materials, and nano-scale phase behavior of metallic glasses using the LEAP 4000X[®].

Elemental mapping from APT allows threshold voltage in 65 nm-node n-MOS transistors to be successfully correlated with the channel dopant concentration [2]. In geology, precipitates containing Y and Pb are visualized after APT reconstruction of zircon crystals and helped understanding the thermal history and mechanisms of mineral reaction, mineral exchange and radiation damage. Data analysis shows that $^{207}Pb/^{206}Pb$ ratios for nm-scale domains ($<2x\ 10^4$ atoms Pb) average 0.17 ± 0.04 and 0.43 ± 0.14 for 2.4 and 4.0 Ga zircons respectively [3], in agreement with SIMS ratios (0.1684 and 0.4269) derived from much larger analysis volumes (hundreds of μm^3 ($10^{-16}\ m^3$)). In the pillar arrangement of the Quantum Dots (QDs), as imaged in InAs/GaAs multi-layers, the strain field from one QD layer influences the growth of subsequent layers, although the apparent helical distribution has never previously been reported [4]. In biology, spatially organized collagen fibers in the dentin of elephant tusks have been unveiled. Three-dimensional imaging of apatite-derived calcium and phosphate species, inorganic substituents, and carbon/nitrogen containing fragments of organic macromolecules sheds some light on the source of strength for these materials [5]. Metallic glass $Fe_{76}C_{7.0}Si_{3.3}B_{5.0}P_{8.7}Cu_{0.7}$ used for low-cost transformer applications shows phase separation into a -Fe precipitates, ultrafine spheroidal e -Cu-rich precipitates, silicon-depleted $Fe_3(P,B,C)$, and Fe_3C after annealing for 30 minutes at 729 K [6].

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11:20am AP+AS+EM+MI+TF-WeM11 Gaining an Atomic Scale Understanding of Optoelectronic, Magneto- and Ionic-Transport in Nanostructured Materials using Cross-Correlative STEM and APT, *B. Gorman, D. Diercks, R. Kirchhofer*, Colorado School of Mines **INVITED**
Atomic scale characterization of internal interfaces such as grain boundaries and thin films is needed in order to fully understand the electronic, ionic, mechanical, magnetic, and optical properties of the engineered material. High resolution analytical TEM has given a significant amount of new information about these interfaces, but lacks chemical sensitivity below ~1 at% as well as 3-D information and light element sensitivity. Atom probe tomography in inorganic solids has shown that atomic scale, 3-D characterization is possible with 10 ppm chemical resolution, but a thorough understanding of the laser assisted field evaporation process is needed. Previous studies of inorganic photovoltaic devices have shown that APT is capable of quantifying dopant distributions and interface roughness at resolutions where junction models can be directly correlated.

In ionic conductors, grain boundaries are particularly important as they frequently have conductivities at least two orders of magnitude less than the bulk. Therefore, being able to quantitatively characterize the grain boundary nature to ascertain the reasons behind the decreased conductivity is indispensable for guiding future improvements. In this work an oxygen ion conductor $Ce_{1-x}Nd_xO_{2-x/2}$ and a proton conductor $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95}$ were analysed with particular emphasis on analysis of the grain boundary regions. In the Nd-doped ceria, cation and anion segregation at the grain boundary is quantifiable with sub-nm spatial resolution. The BCZY27 specimen was solid state reactive sintered using 2 wt% NiO and then operated in a reducing atmosphere for 1000 hrs. Most grain boundaries were observed to be compositionally no different than the bulk, h owever, some pockets of NiO were found at and near some grain boundaries.

Ferroelectric oxides are used in a wide variety of applications including capacitors, transistors, piezoelectric transducers, and RAM devices. The perovskite family has proven to be especially useful, with materials such as lead zirconium titanate (PZT) and barium titanate (BT) becoming the industry standards in dielectric and multiferroic applications. Through substitutions of niobium or lanthanum for some of the lead, PNZT and PLZT relaxor ferroelectrics are created. They have extraordinarily high piezoelectric and electrostrictive coefficients, respectively making them useful in electromechanical applications. It has been proposed that relaxor ferroelectrics achieve their electrostrictive properties through nanoscale phase separation. APT analysis of these relaxors illustrates that nanoscale phase separation of the B-site cations does occur in volumes less than $20nm^3$.

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG+EM+MI+MS-WeM

Materials Discovery and Optimization through Iterative Approaches
Moderator: M.B. Holcomb, West Virginia University, S. Jones, National Science Foundation

8:40am MG+EM+MI+MS-WeM3 Preparation of Ultra Stable Organic Glasses by Physical Vapor Deposition, *J.J. de Pablo*, University of Chicago, *L. Yu, M.D. Ediger*, University of Wisconsin-Madison **INVITED**
There is considerable interest in identifying structure-property relations in glasses. Structural studies of glassy materials have benefited from insights provided by molecular simulations of model glass forming liquids. In particular, simulations have provided support for the existence of dynamic and mechanical heterogeneity at the level of small groups of molecules or particles. In general, however, the cooling rates employed in simulations have been many orders of magnitude faster than in experiments, thereby adding some level of ambiguity to direct comparisons between theory and experiment. Recently, experiments have shown that glasses of organic molecules having unusually large thermal and kinetic stability can be prepared by a vapor deposition process. Such glasses exhibit higher onset temperatures, higher densities, and higher mechanical constants than those of ordinary glasses. In particular, vapor-deposited glasses have been shown to exhibit relaxation times that are many orders of magnitude longer than those of ordinary glasses. Inspired by such experiments, we have devised a strategy that allows one to prepare highly stable glassy materials, in silico, having thermal and kinetic characteristics that are superior to those obtained by gradual cooling of liquid samples. In this presentation, we will describe current experimental efforts to produce and characterize stable glasses, along with an overview of available theoretical and computational strategies aimed at understanding their properties. Emphasis will be placed on recent attempts to identify the structural origins behind the extraordinary stability of vapor deposited glasses, with the goal of providing new insights for design of stable amorphous materials deep in the potential energy landscape.

9:20am MG+EM+MI+MS-WeM5 Composition and Structure Manipulation for Energy Materials with Improved Properties, *S. Lany*, *H. Peng*, National Renewable Energy Laboratory, *V. Stevanovic*, Colorado School of Mines
Ideally, materials for energy applications like photovoltaics, photo-electro catalysis, or thermoelectrics should have a high performance, but be earth-abundant and manufacturable by low-cost processes. Given such demanding constraints, the list of promising materials that could potentially fulfill all requirements often shrinks to a few hopefuls. Then, the question arises whether we can start from materials that have both good and bad features, and manipulate the composition and structure such to cure their deficiencies. The role of theory is to assess the properties and identify promising alloying approaches.

We are presenting two recent examples for this approach: As a photovoltaic material, Cu_2O suffers from a high absorption threshold due to a relatively large band gap and a forbidden optical transition. Also, the p-type doping is 1-2 orders of magnitude below the optimal level. Our theoretical work identifies alloying of Zn, S and Se as a promising route to improve the optical and electrical properties of Cu_2O. Strong dopant-defect interactions lead to the unusual situation that the isovalent (S, Se) alloying increases the electrical doping, whereas the aliovalent (Zn) alloying changes the optical properties. The second example of MnO-ZnO alloys is based on the

prediction [Phys. Rev. B 85, 201202(R) (2012)] that MnO in a hypothetical tetrahedral structure (zinc-blende or wurtzite) should have a smaller band gap and superior carrier transport properties than the normal octahedral rocksalt structure. These features would make this hypothetical material interesting, e.g., for photo-electro-catalytic water-splitting. We predict that $Mn_{1-x}Zn_xO$ alloys assume the wurtzite structure above x = 0.38, and that such alloys preserve the beneficial properties of the tetrahedral MnO phase. Thus, the alloy approach presents a viable path to realize desirable materials properties that were originally identified for a hypothetical material.

9:40am MG+EM+MI+MS-WeM6 Accelerated Optimization of Solar Cell Materials, *A. Zakutayev*, National Renewable Energy Laboratory, *V. Stevanovic*, Colorado School of Mines, *S. Lany, J. Perkins, D. Ginley*, National Renewable Energy Laboratory

The rate of progress in the field of solar cells has been historically limited by the need for materials with desired functionality. Two complementary high-throughput approaches that have potential to facilitate such innovation are combinatorial thin-film experiments and predictive first-principles theory. Here we present examples of accelerated optimization of solar cell materials using the combined theoretical/experimental approach. The specific examples include (i) photovoltaic absorbers, and (ii) p-type contacts for solar cells

(i) PV absorbers are the key elements in any solar cells. Functionally, the absorbers are required to (1) absorb sunlight, and (2) facilitate extraction of charge carriers. We demonstrate accelerated progress towards (a) enhancement of optical absorption in Cu_2O, (b) improvement of electrical charge transport properties of Cu_3N, and (c) optimization of Cu-Sn-S material with respect to both optical and electrical properties. Our progress towards integration of these materials into thin film solar cell prototypes also will be discussed.

(ii) p-type contacts are needed for next-generation thin-film photovotlaics. Functionally such p-type contacts are required to (1) transmit sunlight, and (2) conduct holes. To accelerate the progress, we show (a) formulation of design principles (d6 oxide spinels) to guide the candidate selection [1, 2, 3], (b) down-selection of the most promising materials (Co_2ZnO4 and Co_2NiO4) from ~30 candidates using predictive theory [4], (c) optimization of the selected best-of-class materials (Co-Zn-O, Co-Ni-O) using thin-film combinatorial experiments [5], and (d) integration of the optimized materials (Zn-Ni-Co-O) as hole transport layers in organic photovotlaic devices [6].

In summary, combination of high-throughput theoretical and experimental methods demonstrated here can significantly accelerate the development of materials for thin film solar cells. This approach should be also suitable for discovery and optimization of materials for other technological applications.

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10:40am MG+EM+MI+MS-WeM9 The "Materials Genome" Project: Accelerated and Large-Scale Materials Discovery through Computation, *G. Ceder*, MIT **INVITED**
Novel materials design has become a critical capability to address several urgent societal problems. The need for novel materials is the technological Achilles Heel of our strategy to address the energy and climate problem facing the world, and over-reliance on critical elements has inspired large efforts to develop accelerated materials design strategies. The Materials Genome Project, originally started at MIT (www.materialsproject.com), has as its objective to use high-throughput first principles computations on an unparalleled scale to provide basic materials property data on all known and many potential new inorganic compounds, thereby facilitating the search for new materials.

I will show successful examples of high-throughput calculations in the field of lithium batterier, and show several new materials that have been discovered. I will discuss the public release version of the Materials Genome project which is making large quantities of computed data freely available to the materials community. The Materials Project is rapidly growing as a large collaborative environment for computed materials data.

11:20am MG+EM+MI+MS-WeM11 Multifunctional Interfacial Materials by Design, *C. Eom*, University of Wisconsin-Madison **INVITED**
Complex oxides materials have been fertile ground for new discoveries, due particularly to their wide-ranging electronic, optical, and magnetic properties. Interfaces between complex oxides and related materials create juxtapositions between different symmetries and ordered states, and it has become clear that these interfaces are new materials in their own right and lead to dramatically different properties from those in bulk. But interfacial materials encompass a virtually unexplored territory, one in which theory or experiment alone cannot be successful. New approaches must be implemented to understand basic principles, categorize competing interactions, and design and synthesize complex oxide interfaces with advanced functionalities. Our project focuses on an iterative cooperation between forefront theory and experiment that determines the fundamental principles controlling new physical phenomena at oxide interfaces, uses these principles to design couplings between multiple orders at interfaces to generate new functionalities, and experimentally synthesizes and investigates designed interfacial materials for novel electronic devices. These atomic-scale interfacial materials lead to, for example, new classes of electric-field controllable electronic and magnetic phenomena, and enable the development of new technologically important devices that exploit these couplings. Using a predictive theory and modeling, and feedback to theory from experiments, we have designed and synthesized novel oxide hetero-interfaces that have unique properties not presently available. This work has been done in collaboration with M.S. Rzchowski, C.J. Fennie, E.Y. Tsymbal, L.Q. Chen, X.Q. Pan, S. Ryu, T. Hernandez, T. R. Paudel, H. Zhou and D. D. Fong.

Synchrotron Analysis Focus Topic
Room: 203 C - Session SA+AS+MI+SS-WeM

Synchrotron and Imagery: PEEM, Nano-ARPES and Others (8:00-9:40 am)/Synchrotron TXRF and Related Techniques (10:40 am-12:00 pm)
Moderator: M.C. Asensio, Synchrotron SOLEIL, France, J. Kawai, Kyoto University, Japan

8:00am SA+AS+MI+SS-WeM1 LEEM, PEEM and ARPES Studies of Epitaxial Graphene on SiC(0001), *U. Starke*, Max Planck Institute for Solid State Research, Germany **INVITED**
Large area epitaxial graphene (EG) can be grown on SiC(0001) by heating in Ar atmosphere [1]. However, such graphene layers are *n*-doped due to the influence of a covalently bonded carbon interface layer. This influence can be completely eliminated and the graphene layers be decoupled from the substrate by atomic intercalation. The electronic structure can be tuned in various ways for these decoupled graphene layers. Detailed investigations of the π-band structure, the spatial arrangement, chemical bonding and local surface order are shown based on angle-resolved photoemission spectroscopy (ARPES), low-energy electron microscopy (LEEM), photoemission microscopy (PEEM) combined with microscopic X-ray photoelectron spectroscopy (μ-XPS) and low-energy electron diffraction (μ-LEED), as well as scanning tunneling microscopy (STM) experiments.

By annealing the EG samples in atmospheric H_2, atomic hydrogen reacts under the interface layer, so that the underlying SiC layer becomes passivated [2]. The interface layer alone transforms into a quasi-free standing monolayer while monolayers and bilayers turn into decoupled bilayers and trilayers [3,4]. As a result, charge neutral quasi-free standing graphene layers can be obtained. By intercalation of Germanium the graphene layers can also be decoupled. In this process both *p*- and *n*-doping can be produced, depending on the amount of Ge material intercalated. By preparing both phases in coexistence on the surface, lateral *p-n* junctions can be generated on a mesoscopic scale [5]. Intercalation of Cu induces a coincidence superstructure on top of the SiC surface, which originates from periodic regions of different bond configuration for the carbon atoms in the graphene layer. As a result, a long range periodic potential is imposed onto the graphene layer, which leads to a profound modification of its electronic spectrum. A surprisingly strong doping and the development of mini-Dirac cones are observed [6].

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8:40am **SA+AS+MI+SS-WeM3 An Imaging NEXAFS Detector for Compositional and Structural Analysis**, *C. Weiland*, Synchrotron Research, Inc., *Z. Fu, C. Jaye, D. Fischer*, National Institute of Standards and Technology (NIST), *K. Scammon*, University of Central Florida, *P. Scobol, E. Principe*, Synchrotron Research, Inc.
We present the development of the second generation Large Area Rapid Imaging Analytical Tool (LARIAT MKII) for near edge x-ray absorption fine structure (NEXAFS) surface chemical and structural analysis. This analyzer utilizes magnetostatic electron optical elements to maintain the lateral distribution of electrons into a 16 mega channel detector, while providing a near 180° collection angle for high collection efficiency enabling rapid parallel imaging. A series of electrostatic lenses can be used to tune the energy and depth sensitivity of the imaged electrons allowing for 3D analysis of the near surface region (<7nm). The first LARIAT MKII will be installed on the NIST SST beamline at NSLS II; initial testing is currently being performed at NSLS beamline U8B.

The first generation LARIAT has demonstrated capabilities in determining simultaneously the concentration and orientation of single-strand DNA micro array sensors, organic electronic combinantorial device arrays, and semifluorinated molecular gradients. Additionally, LARIAT MKI was used to identify cancerous versus non-cancerous dermal tissue through spectroscopic analysis. LARIAT MKII advances these capabilities by improving the lateral resolution of the analyzer to below 7 µm and improving collection efficiency through a series of gridless electrostatic lenses. Here we will present an overview of LARIAT MKII and its capabilities, as well as some of the initial data recorded from the system.

9:00am **SA+AS+MI+SS-WeM4 Recent Advances in High Resolution Real and Reciprocal Space Photoelectron Emission Microscopy**, *K. Winkler*, B. Kroemker, Omicron NanoScience, Germany, *N.J. Weber, M. Escher*, FOCUS GmbH, Germany, *N. Barrett*, Cea Dsm Iramis Spcsi, France
Conventional electron spectroscopy methods are limited in providing simultaneous real and reciprocal or k-space information from small areas under laboratory conditions. Therefore, the characterization of materials with only micron scale sample homogeneity requires new instrumentation. Recent improvements in aberration compensated energy-filtered photoelectron emission microscopy (PEEM) can overcome the known limitations in both synchrotron and laboratory environments.

We present first results from real and reciprocal space photoelectron emission microscopy (PEEM) e.g. on Ag (111) showing high k and high energy resolution using a laboratory based He I and II radiation at room temperature and temperatures below 40K. The combination of a recently developed LHe cooled sample stage with an improved aberration compensated energy-filter allows 30 meV energy resolution while a new type of event counting detector improves the signal to noise ratio of the detector.

9:20am   **SA+AS+MI+SS-WeM5   Quantum Material Spectroscopy Center at the Canadian Light Source**, *S. Gorovikov, B. Yates*, Canadian Light Source, *A. Damascelli, H. Davis*, University of British Columbia, Canada, *R. Reininger*, Advanced Photon Source, *K.I. Blomqvist*, Consultant, *M. Sigrist, S. Chen, E. Hallin*, Canadian Light Source
We report on the concept and design features of the Quantum Material Spectroscopy Center (QMSC), a state-of-the art XUV and soft X-ray beamline facility currently under construction at the Canadian Light Source. The QMSC will operate within the photon energy from 15 to 1200 eV and is intended for spin- and angle-resolved photoemission spectroscopy (SARPES and ARPES).

A distinctive feature of the QMSC is the combination of two independent end stations dedicated to SARPES and ARPES experiments with a unique source consisting of a pair of 4 m long APPLE type undulators. The low- and high-energy undulators will be installed side by side in a switch yard arrangement and will provide the highest possible photon flux within this photon energy range. Complete polarization control in both linear and circular modes will be available. Moreover, the quasiperiodic magnetic structure of the low-energy undulator will result in optimized suppression of the higher order harmonics.

The optical design of the beamline is based on the Variable Line Spacing Plane Grating Monochromator (VLS PGM) design and will deliver 10^{12} -

10^{13} photons/second at the experimental stations with a resolving power higher than 10^4 over the full photon energy range.

The theoretical performance of the beamline will be presented. Research capabilities of the beamline will be illustrated.

9:40am **SA+AS+MI+SS-WeM6 Nano-ARPES Beamline at SOLEIL: A Powerful and Innovative Probe for Nanoscience**, *M.C. Asensio*, Synchrotron SOLEIL, France
Over the last decades, we have witnessed exponential advances in a wide diversity of new nanotechnologies. These advances, seen particularly in nanoelectronics, nanomagnetism and nanochemistry, among others, affect almost every aspect of our lives. Following the fundamental step in the creation of nano-objects and even if these "building blocks" have shown remarkable properties, they would have remained unexploited if, at the same time, we had not developed new tools capable of analyzing, viewing and scrutinizing objects on a wide range of scales, from a few microns to a few tens of nanometers.

Recently, great progress has been made as a result of the rapid expansion in the range of modern microscopies. However, if they have achieved nanometer spatial resolution, the challenge still remains to provide powerful high-energy-resolution spectroscopic tools for probing nano- and micro-areas. The challenge then, is to quantify and analyze the electronic properties of advanced materials on a nano- and mesoscopic-scale. For such a result, analysis of the electronic structure must be comprehensive, not only with regard to detection of core levels, but especially to study the structure of electronic states of the valence bands, directly responsible for chemical bonds, electrical transport and the thermal and mechanical properties.

In this presentation, the latest results of the ANTARES microscope beamline at the synchrotron SOLEIL will be disclosed. In particular, nano-ARPES findings describing the electronic band structure of mono-atomic thick graphene films grown on copper substrates by chemical vapor deposition will be presented[1]. This end-station, with a spatial resolution of several tens of nanometers, has already been able to carry out direct imaging of core levels, their chemical shifts and the band electronic structures of several ordered materials. High precise Chemical images and valence band information of nano-objects like exfoliated grapheme, granular materials and Nanowires will be reported.
1.- J. Avila et al., Sci. Rep. 2013, 14, August 3 : 2439 | DOI: 10.1038/srep02439

10:40am **SA+AS+MI+SS-WeM9 Grazing Incidence and Grazing Exit X-ray Spectroscopy of Ultra Shallow Arsenic Implants in Silicon**, *F. Meirer*, Utrecht University, Netherlands   **INVITED**
Grazing incidence (GI) and grazing exit (GE) geometries exhibit exotic geometries in x-ray fluorescence (XRF) spectroscopy and are mainly used to restrict the information depth of the analysis to the sample surface. For samples with sufficiently small surface roughness, variation of the angle of incidence within the range of the critical angle of total (external) reflection of x-rays allows obtaining information about the depth distribution of elements within the sample's surface. In total reflection x-ray fluorescence analysis (TXRF) the effect of total reflection is utilized adjusting the measurement angle below the critical angle. TXRF offers excellent detection limits and is routinely used for chemical trace analysis and surface contamination control.

The use of synchrotron radiation (SR) is highly beneficial for TXRF and for angle-dependent XRF in general, because its properties (e.g., high intensity, linear polarization, small source size, and natural collimation) make it ideally matched to the requirements of these techniques. Furthermore, when using SR as x-ray source these methods can be combined with x-ray absorption spectroscopy (XAS) analyzing the local coordinate structure of an element of interest in the sample. This extends XAS to the trace element level (ppb) in samples where only small amounts are available or where the sample is confined in or on the surface of a substrate material.

In this presentation I will review strengths and weaknesses of SR induced TXRF, GI-XRF and GE-XRF and their combination with XAS on the basis of the analysis of state-of-the-art ultra shallow arsenic implants in silicon produced by plasma immersion ion implantation and deposition (PIIID) and subsequent LASER annealing.

11:20am **SA+AS+MI+SS-WeM11 Basic Principles and Applications of Time Resolved Grazing Incidence EXAFS Experiments for Surface Studies in the 50 ms Range**, *D. Lützenkirchen-Hecht, J. Stötzel, O. Müller, R. Frahm*, Bergische Universität Wuppertal, Germany
The surfaces of materials play a decisive role for many fundamental physico-chemical processes such as e.g. acqueous and gaseous corrosion, catalysis, or coating procedures. Many of those processes proceed in non-vacuum environments, so that classical surface analytical techniques like

XPS or scanning electron microscopy are not suited for in-situ investigations. Furthermore, all of the above mentioned processes are strongly time dependent, so that fast surface sensitive in-situ probes are necessary to study the respective phenomena. EXAFS can be made surface sensitive by using the grazing incidence geometry: For incidence angles below the critical angle of total reflection, the penetration depth of the X-rays amounts to only some few nanometers, and the reflected X-ray beam only contains information about the near surface region of the studied samples. Here we have combined the grazing incidence geometry with the Quick-scanning EXAFS (QEXAFS) data collection. Recent experimental developments of QEXAFS have substantially improved the time resolution to about 50 ms for a single spectrum, thereby enabling completely new surface science experiments.

In this contribution, we will briefly discuss the experimental setup and present results obtained in-situ during the film deposition by sputtering. The growth of gold and copper thin films on float glass substrates and Si wafers were investigated as examples. We will show that the evolution of the film structure can be followed with a subsecond time resolution, and a detailed modelling of the experimental data using the distorted wave Born approximation yields e.g. the film composition, thickness and roughness as a function of time. First experiments showed the need for an automated analysis, and we will also introduce appropriate software solutions for the processing of huge amounts of data acquired in a typical time resolved experiment with several thousands of spectra. Furthermore, we will also discuss the oxidation of the Cu thin films by their exposure to ambient air at different temperatures. The results clearly show that the dynamics of the oxidation are strongly depending on the actual temperature of the samples.

11:40am SA+AS+MI+SS-WeM12 Portable versus Synchrotron TXRF Analysis, *J. Kawai, Y. Liu, S. Imashuku*, Kyoto University, Japan
Total reflection X-ray fluorescence (TXRF) analysis is a micro (absolute amount is less than pg) and trace (relative concentration is less than ppb) analysis method. When synchrotron X-rays are used, the minimum detection limit becomes down to fg for transition metals. However the synchrotron radiation is an elemental selective method, and thus overall elements are not detectable. On the other hand, synchrotron radiation can eliminate the interference of elements whose analytical lines overlap, such as Ba and Ti, As and Pb. The TXRF spectrometers can be classified into three categories: (i) synchrotron radiation TXRF, (ii) high power X-ray tube (kW) TXRF, and (iii) low power (1-50 W) desk top TXRF. Type (i) achieves highest sensitivity, with WD-TXRF spectrometer (wavelength dispersive), down to fg, however ED (energy dispersive type) is also used, where polarization is additionally used to reduce the scattering of incident X-rays. Type (ii) is used for routine analysis of Si wafer analysis (ISO standard methods), but due to the recent progress of the semiconductor processing, the detection limit is not enough for the advanced semiconductor processing systems. Type (iii) is again classified into monochromatic and non-monochromatic types. Monochromatic type needs 50 W X-ray tube (cooling by fan), but non-mono type is possible only by 1 W X-ray tube. The sensitivity is comparable. Type (iii) is mainly used for environmental analysis, toxic elements analysis, and water quality analysis. We must also consider the sensitivity of elements for mass spectrometry such as SIMS and ICP-MS. These methods are sometimes more sensitive than synchrotron radiation TXRF. Most versatility method is the non-monochromatic X-ray tube (1 W) type portable TXRF spectrometer, by which we can analyze something toxic materials, whether it is truely toxic or not toxic. Several examples which show the ability of the low power TXRF, such as laboratory hazard analysis, will be presented.

Thin Film
Room: 102 C - Session TF+MI-WeM

Magnetic Thin Films and Nanostructures
Moderator: S. Gupta, The University of Alabama

8:00am TF+MI-WeM1 Recent Advances and Challenges in Magnetic Recording Media, *M. Desai, C. Papusoi, K. Srinivasan, R. Acharya*, Western Digital Corporation   **INVITED**
For perpendicular magnetic recording (PMR) beyond areal density of 700 Gb/in^2, signal to noise ratio (SNR) and write-ability improvements are becoming extremely challenging to realize. The present exchanged coupled composite (ECC) recording medium has become quite complex and consists of multiple magnetic layers. To enable 1Tb/in^2 areal density, it is required to (i) improve grain isolation for SNR (ii) increase magnetic anisotropy for thermal stability and (iii) reduce all the dimensions, such as thicknesses of the magnetic layers and media grain size. Improvement in grain isolation with maintaining magnetic anisotropy poses challenges on material

selection and process optimization and higher anisotropy materials limits the write-ability of the media. It was estimated that the media grain size <8nm can achieve higher SNR due to reduced jitter and transition noise. However, for last several years, the media grain size has hardly changed in optimized PMR media. The increased inter-granular exchange coupling in small grain size media degrades recording media noise characteristics. Also, thermal stability is compromised on media with small grain size. Here, we discuss recent developments and efforts on perpendicular recording media with small grain size and will present our major findings in terms of SNR, write-ability and thermal stability characteristics. We will also discuss advanced ECC media structure with multiple exchange break layers that offers advantages towards enabling reduced grain size. We also describe advanced characterization methods to quantify the effect of inter granular interactions and their relation with materials and sputtering processes.

8:40am TF+MI-WeM3 FePt Nanopillars for Advanced Media by Glancing Angle Deposition, *H. Su, A. Montgomery, S. Gupta*, The University of Alabama
Granular L1$_0$ FePt films are leading candidates for next generation magnetic recording, for instance, heat assisted magnetic recording (HAMR). This is due to its high magnetocrystalline energy constant (~7.0 x 10^7 erg/cm^3), which can maintain thermal stability even with a reduced grain size of 3nm [1]. However, post-deposition annealing at high temperatures or substrate heating during deposition is required to obtain the L1$_0$ –phase. Meanwhile, glancing angle deposition (GLAD) is a physical vapor deposition method in which the incoming flux from the source impinges on the substrate at oblique angles, causing increased shadowing and forming nanorods and other nanostructured films [2-5]. Herein we report for the first time the fabrication of FePt, utilizing glancing angle deposition (GLAD) with lower annealing temperatures to obtain L1$_0$ phase FePt. The samples were co-sputtered using elemental iron and platinum targets. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and alternating gradient magnetometry (AGM) were employed to characterize the structural and magnetic properties. SEM micrographs indicated that the nanorods were approximately 12 nm in diameter, the angle between the substrate plane and the growth direction was about 78 degrees, while the lengths of the nanorods varied, depending on deposition time. The angles between the substrate plane and incident flux ranged from 47 degrees to 82 degrees as the substrate presented itself at different angles to the target during the planetary deposition. After annealing, M-H loops showed that the planetary GLAD samples had higher coercivity than that of normally deposited samples. XRD confirms the L1$_0$ structure for FePt. Our preliminary results indicate a novel and promising approach to L1$_0$-phase FePt for HAMR that is the subject of intense research in the data storage industry.

Acknowledgements

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9:00am TF+MI-WeM4 Mössbauer Study of Disordering in Thin Sputtered FeCo–SiO$_2$ and FeCo Films, *S.S. Maklakov, S.A. Maklakov, I.A. Ryzhikov,* Institute for Theoretical and Applied Electromagnetics, Russian Federation, *V.A. Amelichev, K.V. Pokholok,* M.V. Lomonosov Moscow State University, Russian Federation, *K.N. Rozanov, A.V. Osipov, A.N. Lagarkov,* Institute for Theoretical and Applied Electromagnetics, Russian Federation
Thin ferromagnetic films possess perspective applications for a data recording devices, magnetic field sensors, and microwave devices[1]. Thin nanocomposite films, which are prepared of a dielectric matrix and ferromagnetic filler, show interesting magnetic properties. In the case, magnetic properties are determined by exchange interactions and dipole-dipole interactions between ferromagnetic nanoparticles. Among the other techniques, magnetron sputtering results in the composite films with high uniformity. The report demonstrates structural modification in a solid solution Fe$_{70}$Co$_{30}$ which is caused by additional energy flux towards the

substrate during a $(Fe_{70}Co_{30})_{95}(SiO_2)_5$ composite growth comparing with the metal film growth.

Thin metal films ($h = 130$ nm) were deposited via DC magnetron sputtering onto a PET substrate; the DC magnetron operating regime (time, pressure and discharge parameters) was identical during the composite synthesis. To sputter SiO_2, a RF magnetron was applied; both magnetrons were sputtering simultaneously. To derive structure information, a Mossbauer spectroscopy, X-ray diffraction (GIXD) and electron microscopy data were gathered. Magnetic properties were studied using VSM and a coaxial line technique for a microwave permeability.

Thin $Fe_{70}Co_{30}$ and $(Fe_{70}Co_{30})_{95}(SiO_2)_5$ films show differently broadened Mossbauer sextet. Composite film possess unusually high effective field at iron nuclei $H_e = 371(3)$ kOe. We propose a model which describes H_e values depending on environment of a reference iron atom[2]. With this construction, $Fe_{70}Co_{30}$ solid solution possesses higher *CsCl*-type ordering degree when in form of the composite. Such modification is the result of surface processes during film growth. SiO_2 injection also decreases FMR frequency from 10 to 3 GHz, depending on a composition.

The results reported may be applied to design thin film microwave devices.

Literature

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2. *S.S. Maklakov, S.A. Maklakov, I.A. Ryzhikov, V.A. Amelichev, K.V. Pokholok , A.N. Lagarkov.* Mossbauer study of disordering in thin sputtered FeCo–SiO2 and FeCo films. // J. Alloys. Compd. 536 **(2012)** 33-37

9:20am TF+MI-WeM5 Comparing Deep Reactive Ion Etching vs. Ion Milling for Block Copolymer Templating for Bit Patterned Media, *A. Owen, S. Gupta, A. Highsmith, A. Montgomery, H. Su, R. Douglas*, University of Alabama

Block copolymer templating has been used to pattern perpendicular magnetic anisotropy Co/Pd multilayers.[1] A multilayer stack of Ta 5Pd 5/[Co 0.3/Pd 1]$_{20}$ /Pd 5 nm nanolayers was sputter deposited onto a bare silicon wafer. The block copolymer used was polystyrene polyferrocenyldimethylsilane[2] (PS-b-PFS). This was spin coated onto the wafer and annealed to cause phase separation.[2] The wafer was ashed in an oxygen plasma to remove the polystyrene matrix and reveal the PFS nanospheres. The Co/Pd multilayer films were subsequently etched using an ion mill and a deep reactive ion etching tool.[3] In order to optimize the size tuning of the PFS nanospheres and the coercivity of the magnetic films,response surface methodology was performed to optimize the power, etching times and ashing time of the block copolymer mask and magnetic film. This statistical Design of Experiments was used for both ion milling and deep reactive ion etching. We will discuss some of the shapes of the resulting nanopillars from the different etching techniques. Magentometry was taken to characterize the films before and after patterning, showing a significant improvement in the coercivity, increasing from 1.5 kOe to 3.6 kOe.

Acknowledgements

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10:40am TF+MI-WeM9 Atomic Layer Deposition Enabled Synthesis of Nanostructured Composite BiFeO3/CoFe2O4 Thin Films for Multiferroic Applications, *C. Pham, J.P. Chang*, University of California at Los Angeles

Multiferroic materials are a class of material which exhibit two or more forms of ferroic order such as (anti)ferroelectricity, (anti)ferromagnetism, or ferroelasticity and have been proposed for use in future devices in which magnetism is switched upon the application of a electric field. While the existence of intrinsic multiferroic materials, such as $BiFeO_3$, have been demonstrated, composite multiferroics offer improved switching performance, consisting of a piezoelectric and a magnetostrictive material coupled together via interfacial strain. In addition, nanoscale composites have been shown in literature to have even greater coupling when compared to other composites. For this project, atomic layer deposition (ALD) is used

to enable the precise control of the composition and thickness by manipulating the pulsing sequence of the precursors. In addition, two approaches to multiferroic composites emphasize the flexibility of the ALD technique; for a 2D composite approach, the ability to deposit nanoscale laminates; while for a 3D composite approach, the ability to uniformly coat films over a nanoscale porous template.

In this work, $BiFeO_3$ (BFO) and $CoFe_2O_4$ (CFO) were deposited by ALD to synthesize 2D nanoscale multiferroic composite multilayers. The ALD processes used the metallorganic precursors $Bi(tmhd)_3$, $Co(tmhd)_2$, and $Fe(tmhd)_3$ alongside oxygen atoms produced from a microwave atomic beam source. The ALD BFO and CFO films were able to be grown with a stoichiometric ratio Bi:Fe close to unity and Co:Fe close to 1:2, respectively, and with a controlled linear growth rate. The ALD BFO and CFO processes were then combined to deposit multilayer nanolaminates which repeated between the two oxides at varying thicknesses between 5-20 nm and number of repeating layers. Additionally, ALD BFO was integrated with a 3D mesoporous CFO template consisting of approximately 14 nm diameter pores, which was synthesized using a di-block copolymer self-assembly technique. The conformal aspect of ALD deposition was demonstrated by covering the pores at varying thicknesses until the pores were completely filled.

To compare the material performance of the ALD enabled BFO/CFO films to previously reported benchmarks, measurements of magnetic and ferroelectric properties were accomplished using SQUID magnetometry and Sawyer-Tower circuit methods, respectively. For the 3D mesoporous composite, SEM and XPS confirmed that BFO was able to be deposited onto the nanoscale high aspect-ratio structure of the CFO conformally. The magnetoelectric coupling properties in the composite films were studied by taking magnetic measurements with and without an *ex-situ* electric poling.

Wednesday Afternoon, October 30, 2013

Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+MI+NS+SS-WeA

APT and FIM Analysis of Catalysts and Nanoscale Materials
Moderator: P.A.J. Bagot, Oxford University, UK

2:00pm **AP+AS+MI+NS+SS-WeA1 Atom Probe Tomography Characterization of Engineered Oxide Multilayered Structures**, *S.A. Thevuthasan*, *M.I. Nandasiri, A. Devaraj, D.E. Perea, T. Varga, V. Shutthanandan*, Pacific Northwest National Laboratory
There has been growing interest in developing materials which possess high oxygen ionic conduction at low temperatures for solid oxide fuel cell applications. In our group, we have been developing trivalent element doped creia/zirconia multilayer thin film structures for this purpose. We have grown (i) multilayers of high quality samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) films, and (ii) samaria and gadolinia co-doped high quality ceria films using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These films exhibit significantly higher oxygen ionic conduction at intermediate temperatures in comparison to bulk materials. Although we have demonstrated that these structures possess high oxygen ionic conduction at low and intermediate temperatures, we haven't established the mechanisms associated with the enhancement in oxygen ionic conduction through these engineered heterogeneous interfaces.

Atom Probe Tomography (APT) can provide quantitative three-dimensional chemical analysis of materials with lateral and depth resolutions in the order of 0.2-0.3 nm and chemical sensitivity up to parts-per-million levels with field-of-view on the order of $100 \times 100 \times 100$ nm^3. Although APT has been extensively used to characterize metals, it is in its infancy in characterizing oxides and insulators. In addition, multilayer structure adds additional complications to the characterization of the doped ceria/zirconia multilayers. In this study, we have synthesized high quality SDC and ScSZ multilayers and used surface impedance spectroscopy to carry out detailed analysis of oxygen ionic conductivity as a function of individual layer thickness and dopant concentration. As a part of this study we attempted coupled scanning transmission electron microscopy and atom probe tomography to study the oxygen vacancy and dopant distributions along with the inter-diffusion and dopant segregation at the interfaces. These STEM/APT findings are correlated to the conductivity measurements and these results will be discussed.

2:20pm **AP+AS+MI+NS+SS-WeA2 Correlative Atom Probe Tomography and Transmission Electron Microscopy of Metal-Dielectric Composites**, *A. Devaraj*, *R.J. Colby, D.E. Perea, S.A. Thevuthasan*, Pacific Northwest National Laboratory **INVITED**
Metal-dielectric composite materials are ubiquitous in several important engineering applications ranging from catalysis to semiconductor devices. The technological advances in such fields heavily depend upon the development of three-dimensional characterization capabilities that can accurately identify composition and structure at sub-nanometer spatial resolution and ppm-level composition sensitivity. Atom probe tomography (APT) has already demonstrated its potential in three-dimensional characterization of bulk metals and alloys, however the theoretical understanding of the evaporation behavior of dielectrics and metal-dielectric composites, as well as possible artifacts during laser assisted APT, is still at its infancy. 3D transmission electron microscopy (TEM) tomography on the other hand is currently restricted by long acquisition times and reconstruction artifacts. A correlative TEM-APT approach can help in extending the applicability of APT analysis and TEM beyond the current boundaries by providing not only complementary information but also a deeper understanding of the possible artifacts. This presentation will focus on such a correlated TEM-APT approach to investigate the field evaporation behavior of metal dielectric composites with metallic nanoparticles embedded inside oxides as well as planar structures with metallic thin films on single crystalline oxide substrates. Aberration-corrected TEM high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to image the APT samples before and after APT analysis. STEM imaging after interrupted APT analysis was used to capture snapshots of evolving tip shape. Such understanding, when combined with novel APT reconstruction processing, can greatly aid in expanding the capabilities of APT analysis to novel complex heterogeneous metal-dielectric composite materials.

3:00pm **AP+AS+MI+NS+SS-WeA4 High Temperature *In Situ* Diffusion Studies of Gas – Solid Reactions with Atom Probe Tomography**, *S. Dumpala*, *S.R. Broderick*, Iowa State University, *P.A.J. Bagot*, University of Oxford, UK, *K. Rajan*, Iowa State University
The diffusion couples of in-situ metal-oxygen reactions are analyzed through laser pulsed atom probe tomography (APT) reactions and experiments. Using ternary metal compounds, the relative diffusion and segregation of the different species with oxidation is assessed. This provides a further level of information beyond typical diffusion profiles by considering relative changes in metallic species, providing basic material descriptions at a higher resolution then ever previously measured.

The oxidation experiments were performed in-situ and at temperatures of ~450 ^{O}C and at 10^{-3} torr pressures. Given atom probe's atomic scale spatial resolution, chemical diffusion over a nanometers wide range across the chemical interface is assessed with exceptional accuracy, and the identification of compound formation is quantified. By performing all reactions within an in-situ APT reaction cell along with initial (in-situ) cleaning of the samples, any effects due to native oxidation or contamination are eliminated, which is particularly important when considering atomic scale spatial resolution and femto-scale chemical resolution. The challenges associated with performing in-situ reactions and the potential of this new experimental set-up to study a far wider range of treatment conditions, particularly when coupled with a laser-pulsed APT are discussed.

3D results of binary and ternary catalytic alloys are presented and the advancements in studying catalytic reactions are discussed. Aluminum and silicon samples were also oxidized and chemically-mapped atomic scale imaging of the material was processed to identify the preferred stoichiometry of aluminum oxides as a function of the distance from the aluminum-oxygen interface. This demonstrated ability of the APT to simultaneously image and chemically quantify gas-metal interactions at the atomic level enables us to systematically quantify these interactions as a function of material chemistries, crystallographic orientations and important microstructural features.

4:00pm **AP+AS+MI+NS+SS-WeA7 Atomic Scale Characterisation of Catalyst Material**, *T. Li*, *P.A.J. Bagot, S.C.E. Tsang, G.D.W. Smith*, Oxford University, UK **INVITED**
Bimetallic heterogeneous catalysts have proven remarkably successful in catalysing a wide range of important processes, in fuel-cells, exhaust emission control and in hydrocarbon processing. However, the effects of the operating environment on the surface composition, structure and stability of the noble metal catalysts are poorly understood at the atomic-scale. This knowledge will be required to produce the improved catalysts needed for future energy- and materials-efficient technologies.

Atom probe tomography offers a unique method for studying these materials, offering atomic-scale chemical identities of the catalyst surfaces and chemisorbed species. We have used APT to show a rich variety of behaviour in Pt-based alloys, investigating the effects of high temperature/pressure oxidation. These reveal pronounced surface segregation behaviour, strongly dependent on the treatment conditions, crystallographic plane and alloy composition. Furthermore, while subsequent reduction treatments remove formed oxides, the marked changes to the metallic surface compositions remain. Such results suggest using sequential oxidation and reduction treatments as an alternative synthesis method for designing and preparing nano catalysts with controlled surface compositions.

Another aspect of our work focuses on the investigation of the use of APT for characterizing catalyst nanoparticles either in colloidal dispersions or on the carbon supports. It is very challenging to fully characterize these complex 3D architectures by conventional electron microscope technique. In this work, we have for the first time demonstrated the use of APT for the analysis and characterization of such materials in atomic detail. Alongside a description of the preparations, we will also present a range of results from these catalysts materials, highlighting the correction between catalytic efficiency and the atomic-scale chemical/structural information uniquely provided by APT.

4:40pm AP+AS+MI+NS+SS-WeA9 From Field Ion Microscopy of Tips to 3D Atom Probe Tomography of Real Catalyst Nanoparticles, *N. Kruse*, Université Libre de Bruxelles, Belgium **INVITED**

This contribution will address some major achievements made in the application of Field Ion Microscopy (FIM) and 1D/3D Atom-Probe (AP) techniques to study catalysis-related problems. In particular, we shall demonstrate the unique capabilities of FIM to image reaction-induced morphological reshaping of single metal nanoparticles conditioned in the form of tips. As an example, we show how a nearly hemispherical Rh nanoparticle is transformed into a polyhedral morphology in the presence of oxygen gas.

In a second example, we shall inspect the use of 1D AP as a tool to provide a detailed kinetic analysis of adsorption/thermal desorption processes. As an example, measurements of the mean life time of NO molecules adsorbing on $\sim$ 60 atomic sites of a (111) Pt facet will be presented. A quantitative evaluation of the data in terms of activation energies for desorption along with pre-exponential factors becomes possible by temperature variation.

Third, we shall consider the combined approach of FIM and 1D AP in imaging the dynamics of surface reaction processes while mapping the local chemistry during these processes. As an example, we shall present results of the catalytic reaction between oxygen and hydrogen on the surface of a Rh nanoparticle. Moving reaction fronts are followed here by using video techniques. The observed patterns demonstrate a strong non-linearity merging into oscillating reaction behavior between oxygen and hydrogen. 1D atom-probe measurements during oscillations allow distinguishing between oxygen- and hydrogen-covered surface patches. They also indicate the participation of sub-surface oxygen species in a feedback process. The oscillatory behavior has been successfully modeled using theoretical models of non-linear processes along with DFT.

Finally, we show that 3D AP can also be used for a chemical mapping of single nanosized grains of real catalysts. Using focused ion beam techniques, "CoCuMn" real catalyst particles as used for the selective production of 1-alcohols from synthesis gas (CO/H_2), can be conditioned in the form of tips. A 3D AP analysis of a single catalyst grain demonstrated the occurrence of a core-shell structure with Co forming the core. Interestingly, all three metals are found to be present in a 2nm thick shell which is otherwise dominated by large amounts of Cu. Such information is most important when it comes to establish relationships between catalytic activity/selectivity and surface chemical composition.

5:20pm AP+AS+MI+NS+SS-WeA11 NO_2 Reduction over Pt and Rh Single Nanoparticles: Imaging with Nanometric Lateral Resolution, *C. Barroo*, S. Lambeets, Y. De Decker, F. Devred, T. Visart de Bocarmé, N. Kruse*, Université Libre de Bruxelles, Belgium

Nitric oxides (NO_x) emissions from vehicles are harmful to human beings and may cause severe health issues. NO_x abatement is therefore highly desirable, but the development of viable solutions still represents a major challenge for catalyst makers, especially in the case of lean-driven vehicles. NO is known to be oxidized to NO_2 under lean-burn conditions in automotive engines, and subsequently reduced into N_2 during the rich-burn regime. In this work, we have investigated the catalytic reduction of NO_2 over platinum and rhodium field emitter tips by means of Field Emission Microscopy (FEM). Real-time FEM is a powerful method for studying the dynamics of catalytic reactions that take place on the surface of the top of a nanosized metal tip, which acts as a catalytic particle. These studies are performed during the ongoing catalytic reaction which can be imaged in real time and space. Nanoscale resolution is achieved, providing a local indication of the instantaneous surface composition. Reaction-induced structural changes of the catalyst's surface can also be assessed with step-site resolution. FEM is based on the emission of electrons from the sample which can be affected by the presence of various adsorbates. Local variations of the work function are reflected in the form of a brightness pattern and the surface composition of the sample can be qualitatively investigated during the ongoing catalytic process, allowing for the determination of the elementary processes involved.

The microscope is run as an open nanoreactor, through a constant supply of gaseous reactants and constant gas-phase pumping of the reaction chamber, ensuring that the system is kept far from thermodynamic equilibrium. This may lead to non-linear dynamics. Among others, oscillating phenomena observed during the NO_2 reduction by H_2 over both Pt and Rh nanocrystal (whose diameter is $\approx$40 nm) are presented.

Data have been characterized by Fourier transforms, temporal autocorrelations and dynamical attractors that demonstrate the existence and robustness of the kinetic oscillations. Furthermore, the optimal parameters obtained for the reconstruction of the dynamical attractor from the experimental time series, give important information that can lead to a better understanding of the mechanism of the catalytic reduction of NO_2 over PGM nanoparticles.

5:40pm AP+AS+MI+NS+SS-WeA12 Quantitative Three-Dimensional Compositional Analysis of Geologic Minerals using Atom-Probe Tomography, *J. Liu, D.E. Perea, R.J. Colby, B. Arey, O. Qafoku, A. Felmy*, Pacific Northwest National Laboratory

Carbon capture and sequestration within deep geological formations has become one of the most important options to mitigate the ever-growing environmental CO_2 emissions. The olivine group of minerals, X_2SiO_4 where X = Mg or Fe, hold promise as potential media to sequester carbon. Upon reaction of supercritical CO_2 (sc-CO_2) with fayalite (Fe_2SiO_4) or forsterite (Mg_2SiO_4), various oxide and carbonate phases result accompanied by a complex change in surface morphology. A combination of atom probe tomography (APT) and scanning transmission electron microscopy (STEM) is being used to map the complex composition across various site-specific interfaces in order to better understand the complex phases that form upon reaction with sc-CO_2. The advantage of APT analysis is that it can provide a unique 3-D atomic-scale compositional map with a part-per-million sensitivity to allow tomographic mapping of low-level impurities such as Li. Optimization of the APT analysis conditions will be discussed leading to the optimal stoichiometric composition. The results demonstrate the viability of using APT analysis to study the composition geological minerals for energy and environmental applications.

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* NSTD Student Award Finalist

Thursday Morning, October 31, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG+MI+NS-ThM

Theoretical and Computational Methods
Moderator: K. Cook-Chennault, Rutgers, the State University of New Jersey, L. Madsen, National Science Foundation (NSF)

8:40am **MG+MI+NS-ThM3 Application of Computational Methods to Material Design and Discovery**, *S.B. Sinnott*, University of Florida **INVITED**

Modeling of materials is an integral component in the design and discovery of materials as outlined in the Materials Genome Initiative. Illustrative examples are discussed where computational methods are used in conjunction with cutting-edge experimental methods. In the first example, electronic-structure, density functional theory calculations and empirical, atomic-scale simulations are used in conjunction with experimental synthesis and characterization to identify the features of Pt electrode/$PbTiO_3$ dielectric interfaces that lead to the degradation of devices. The results specify how the microstructure of the interface might be designed to improve performance. In the second example a combination of simple, electrostatic calculations, high-through-put experiments, and materials informatics is used to investigate the tribological properties of inorganic materials. The results are used to design a simple model to identify material properties that are indicative of solid-state lubrication. This work is supported by the National Science Foundation under grant DMR-1207293 and the Office of Naval Research

9:20am **MG+MI+NS-ThM5 New Ferroelectrics and Antiferroelectrics by Design**, *K.M. Rabe*, Rutgers, the State University of New Jersey **INVITED**

I will describe our work on the design and discovery of new classes of ferroelectric and antiferroelectric materials using a combined crystallographic database / first principles approach. For ferroelectrics, using the design principle that any polar structure type can have ferroelectric representatives if the barrier to switching is lowered by appropriate chemical variation, we have recently identified a new family of ferroelectrics in the intermetallic LiGaGe structure type. For antiferroelectrics, we used a design principle based on the close relationship between ferroelectrics and antiferroelectrics to identify a previously unrecognized class of antiferroelectrics, related to the LiGaGe-type ferroelectrics, in the MgSrSi structure type. The further development of design principles and their application will be discussed. The discovery of new classes of antiferroelectrics is expected to open the way to increased recognition and application of antiferroelectrics as functional materials.

10:40am **MG+MI+NS-ThM9 Disruptive Design Strategies for Emergent Ferroics**, *J.M. Rondinelli*, Drexel University

There are two main routes to accelerate materials discoveries for advanced electronic and sustainable energy technologies: serendipitous realization through conventional synthesis or computationally guided growth of novel materials through, *e.g.*, artificial structuring of bulk compounds at the atomic scale. Recently, the launch of the Materials Genome Initiative (MGI) at the national level has reinvigorated the search for new routes to accelerate the discovery of advanced materials for rapid deployment—the aim being to evolve a "hunter and gatherer" discovery paradigm into the cultivation of materials by design. This discovery process may be accelerated by merging applied theoretical crystallography, where the objective is transformed into (*i*) identifying suitable topologies – approximate geometric arrangements of structural building units – that lift particular symmetries, with electronic structure methods to (*ii*) search for microscopic mechanisms and external conditions that energetically stabilize those geometries. Such information may guide experimental explorations, whereby the synthetic efforts are focused on a more manageable (and largely reduced) structural data set by the theoretical (symmetry) considerations.

Here, we describe report an Ensemble Computation Materials Protocol (ECMP) with predictive capability to design and accelerate the discovery of a new class of *A*-site cation-ordered perovskite ferroelectrics from combinations of the centric, non-polar, transition metal–oxygen octahedra that form the perovskite framework. First, we describe the microscopic origin for the loss of inversion symmetry and the electric polarization in layered (*A,A'*)BO_3 perovskite oxides. We then show that the mechanism can be translated to $A_nB_nO_{3n+1}$ (*n*=1,2) Ruddlesden-Popper (RP) oxides with disconnected layers of corner-sharing octahedra. We use the group theoretical methods to enumerate the structural criteria required to remove the mirror symmetry elements. Feasible chemistries are proposed using Bayesian inference methods. We then evaluate the stability of the possible ground state structures with density functional theory (DFT) calculations. We predict that ordering of divalent and trivalent cations in a layered RP manganite leads to a polar phase, space group $Pca2_1$, with a sizeable polarizations, which are supported by preliminary experimentsal. We anticipate that these findings and methodology will contribute to our understanding of not only new ferroic materials, but also that this general approach of physical properties by atomistic structure design within the MGI is immediately amenable to other material functionalities.

11:00am **MG+MI+NS-ThM10 Computational Design of Materials for Catalysis: Interface Matters**, *T.S. Rahman*, University of Central Florida **INVITED**

An important ingredient in computational design of functional materials is back and forth feedback between theory and experiment, which necessarily involves modeling of realistic environments, using accurate methods. In this talk, I will present results of our density functional theory based calculations which together with experimental observations help isolate catalyst descriptors for specific reactions, in particular for supported nanoparticles. For example, for methanol oxidation on Au nanoparticles on titania [1], the higher activity of interfacial sites can be traced to charge-transfer-induced Coulomb interaction among the gold, reactant, and reducible TiO2 support, brought about through the formation of an ionic O−Au bond between gold and methoxy in such sites, which turns the participating perimeter gold atom cationic. A direct result of such charge-transfer-induced repulsive interaction between cationic gold and positively charged C moiety of methoxy is activation of the positively charged C moiety of methoxy, as manifested by the pronounced elongation of O−C bond length and the tilting of the methoxy axis, which facilitate reaction of methoxy through C−H scission with the bridge oxygen atoms that are readily available from the reducible support. I will use the above guidelines to predict the reactivity of several titania supported metallic/bimetallic nanoparticles for oxidation of organic molecules with the structure of R−O−R', where R and R'are (saturated) hydrocarbons. Similarly, I will analyze the role of the interface (with the support) for a set of nanometer and sub-nanometer sized Pt nanoparticles on titania and alumina and point to the variations in the physical and chemical characteristics as a function of size, shape, and chemical environment (H and OH coverage). Through detailed comparison with XANES data [2], I will provide an understanding of the descriptors that control specific nanoparticle property.

[1] S. Hong and T. S. Rahman, J. Am. Chem. Soc., dx.doi.org/10.1021/ja4010738 (2013)

[2] F. Behafarid, L. K. Ono, S. Mostafa, J. R. Croy, G. Shafai, S. Hong, T. S. Rahman, Simon R. Bare and B. Roldan Cuenya, Phys. Chem. Chem. Phys., 2012, **14**, 11766–11779

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Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+BI+MI+NS+SS-ThM

Advances in Scanning Probe Imaging
Moderator: S. Allen, The University of Nottingham, UK, A.P. Li, Oak Ridge National Laboratory

8:00am **SP+AS+BI+MI+NS+SS-ThM1 Inelastic Imaging of Single Molecule Dynamics**, *W. Ho*, University of California, Irvine **INVITED**

A greater part of chemistry is designed to probe the encounter of reactants to form products through a sequence of reaction steps that involve reaction complexes as intermediates. The detection of these complexes is an important step to reveal the reaction mechanisms and advance our understanding and control of chemistry. While sophisticated spectroscopic techniques have been developed to provide properties of the complexes in the energetic and temporal domains, much less is known about the spatial properties. Advances made over the last 15 years in scanning tunneling microscopy (STM) have led to direct characterization and imaging of reaction complexes that are formed by controlled manipulation of the reacting molecules to separate from each other at distances from non-interaction to those approaching the transition state. Changes in their vibrational properties can be monitored as a function of the spatial

separation by inelastic electron tunneling spectroscopy (IETS) with the STM. Both spectroscopic information (vibrational energies, intensities, and lineshapes) and inelastic images can be obtained by STM-IETS. These results provide sub-THz spectral characterization and spatial visualization of chemical reactions with sub-Angstrom spatial resolution.

8:40am SP+AS+BI+MI+NS+SS-ThM3 Tunneling Resonances Into Engineered Nanoscale Cavities on a Noble Metal Surface, *A. DiLullo, D. Acharya,* Ohio University, *N. Takeuchi,* Universidad Nacional Autónoma de México, *S.-W. Hla,* Ohio University
Variations in surface topologies such as step edges and surface defects are known to alter the electrochemical properties of the surfaces. The ability to directly alter surface topologies on the nanoscale in order to achieve desired properties is useful. We report on the direct modification of local surface topologies and the resulting changes in local electronic properties. Surface vacancies on a Ag(111) surface are created by probe manipulations using a scanning tunneling microscope operated at 78 K. Tunneling resonances, found at certain probe-sample biases, are determined by analysis of spatial height-differential mapping (dz/dV). The resonances, when considered over paths crossing the induced surface vacancies, significantly shift when comparing clean terraces to vacancy positions. These resonances originate as a result of field emission where the emitted electron has greater energy than the surface potential (work function) at the probe lateral position. By fitting these resonances to the Gundlach equation describing resonant tunneling it is possible to extract the tip work function, sample work function at probe position, and absolute tip height from the sample. The shift in resonances at vacancy locations is related to the variation in the work function due to local topology. It is important to be able to tune the work function as it plays a large role in many surface processes and properties. The created surface vacancies may then be considered local wells having work functions differing from the supporting substrate, with resonances tunable by probe manipulations, and may be useful for nanotechnological applications.

9:00am SP+AS+BI+MI+NS+SS-ThM4 Real-space Spectroscopy and Microscopy of Tunneling Electron Induced Light Emission from Single Gold Nanoclusters, *S.W. Li, A.X. Yu, G. Czap, W. Ho,* University of California, Irvine
Historically, gold has been treasured for its beauty and permanence. In the quantum regime, gold nanoclusters gain even more reputation from their unique power as photocatalysts. To better understand the optical properties of nanoclusters, we investigated Scanning Tunneling Spectroscopy and tunneling electron induced light emission of single Au nanoclusters deposited on Al_2O_3 / NiAl(110) surface. In this electron-in-light-out experiment, optical phenomena are probed with sub-Ångström spatial resolution.

9:20am SP+AS+BI+MI+NS+SS-ThM5 Spatial Mapping of Surface Plasmons in Nanoscale Ag Islands on Graphite using Scanning Probe Energy Loss Spectroscopy, *K. Bauer, S. Murphy, L. Tang, R.E. Palmer,* University of Birmingham, UK
A scanning STM tip operated at high voltage can be used to obtain localized spectroscopic information from surfaces via energy loss measurements [1]. In this technique, known as Scanning Probe Energy Loss Spectroscopy (SPELS), the STM tip is used as a localized source of field-emitted electrons, which, upon backscattering from a surface, are analyzed by an energy-dispersive detector to obtain localized energy loss spectra. Characteristic surface excitations such as plasmons and excitons (as well as secondary electrons) can be probed with a spatial resolution below 50 nm and an energy resolution approaching 0.3 eV [2].

We report the development of a new generation SPELS instrument utilizing a 400-channel electron detector. This allows sufficiently fast sampling of the energy loss spectra to obtain 2D spatially-resolved maps of energy loss features in a reasonable timeframe. We demonstrate the new instrument by mapping plasmons in (thermally evaporated) Ag nano-islands on the surface of graphite and illustrate the various mechanisms give rise to the contrast obtained in the energy-resolved maps.

[1] A. Pulisciano, S.J. Park and R. E. Palmer, Appl. Phys. Lett. 93, 213109 (2008).

[2] F. Festy and R. E. Palmer, Appl. Phys. Lett. 85, 5034 (2004).

9:40am SP+AS+BI+MI+NS+SS-ThM6 Development of a Synchrotron X-Ray Assisted STM, *H. Kersell, S.-W. Hla,* Ohio University, *N. Shirato, V. Rose,* Argonne National Laboratory
Scanning tunneling microscopy (STM) yields substantial information about surface properties of conductive materials by probing the electronic properties of samples under investigation. However, the nature of STM's reliance on the sample density of electronic states often limits the elemental

contrast of resulting images. By targeting samples with high energy X-rays, such as those generated by a synchrotron light source, core level electrons may be excited and subsequently measured as a contribution to the tunneling current in STM. Since core level energies are chemically specific, this technique can be used to gain elemental sensitivity in STM imaging, providing enhanced understanding of molecule-substrate and intermolecular interactions. We present the development of a synchrotron-assisted STM (SXSTM), for this purpose.

10:40am SP+AS+BI+MI+NS+SS-ThM9 High-Speed AFM Studies of Cell Membrane Dynamics, *A. Slade, S.C. Minne,* Bruker Nano Inc.
Bacterial membranes have a much more complex structure than mammalian cell membranes. As such, knowledge of bacterial membrane composition and organization, as well as characterization of the molecular-level responses to drug interactions, is critical to the development and assessment of effective antibacterial drug formulations. Cellular drug responses involve highly dynamic processes. However, the ability to image live cells with nanometer resolution on timescales relevant to dynamic cellular events has proven challenging. With traditional AFM systems, the typically longer image acquisition times required to obtain a single high-resolution image (~minutes) has limited the ability to investigate dynamic biological processes. While recent years have shown significant progress in the development of high-speed atomic force microscopy (HS-AFM), the nature of the instrumentation that has been developed has several drawbacks in specimen size, requiring small scan sizes and flat sample surfaces. As such, the majority of biologically-related HS-AFM studies have concentrated on imaging single biomolecules with little focus on using HS-AFM to examine cellular processes. With the rapidly growing antibiotics crisis, antimicrobial peptides (AmP) are increasingly being investigated as therapeutic alternatives. Key to their success is an understanding of the mechanisms by which AmPs interact with the cell membrane and facilitate cellular death. Using HS-AFM, we have obtained the first high-resolution time sequence images of the native structure of a bacterial outer membrane, obtained directly on the surface of live *Escherichia coli* cells. The increased time resolution of HS-AFM allowed us to observe dynamic changes in the nanoscale structure of the outer membrane in direct response to the AmP CM15, at timescales relevant to the mechanism of AmP-induced cell death. To understand how CM15 interacts with the bacterial inner membrane, we also conducted HS-AFM imaging on supported model membranes that mimic the composition of the inner membrane of *E. coli*. Our results revealed the formation of circular, pore-like defects within specific lipid domains upon exposure to the AmP. The results of these HS-AFM studies have provided the first opportunity to resolve the dynamics of AmP-mediated cell death in a native cell membrane environment in real-time and with nanoscale resolution.

11:00am SP+AS+BI+MI+NS+SS-ThM10 Photothermal Excitation for Reliable and Quantitative AFM, *A. Labuda, D. Walters, D. Bocek, M. Rutgers, J. Cleveland, R. Proksch,* Asylum Research, an Oxford Instruments Company
Since the advent of atomic force microscopy, cantilevers have predominantly been driven by piezos for AC imaging and data acquisition. The ease of use of the piezo excitation method is responsible for its ubiquity. However, the well-known "forest of peaks", which is clearly observed while tuning a cantilever in liquids, renders AC imaging in liquids problematic because the peaks move around with time (see Figure). Effectively, these shifting peaks result in a setpoint that changes with time causing stability problems while AFM imaging. Furthermore, the same "forest of peaks" prevents the quantitative interpretation of forces in liquids[1], air[2], and vacuum environments[3], even if the cantilever tune looks clean. Dissipation studies in all these environments have especially suffered due to piezo excitation of the cantilever.

Photothermal excitation is an alternative method for exciting a cantilever by heating/cooling the base of the cantilever to drive the cantilever. Photothermal excitation results in a repeatable, accurate and time-stable cantilever tunes, as seen in the Figure. Therefore, the setpoint remains truly constant while imaging, preventing tip crashes, or unwanted tip retractions. A true atomic resolution image of calcite in water, shown in the inset of the Figure, were made for hours with no user intervention, testifying to the stability of photothermal excitation. Unlike other specialized drive methods, photothermal excitation is compatible with almost any cantilever and with all AFM techniques. The introduction of a blue laser into the AFM also enables several other functionalities, such as tuning the temperature of the cantilever. Furthermore, because the photothermal tune represents the true cantilever transfer function, existing AFM theories can be applied to accurately recover conservative and dissipative forces between the tip and the sample. This is especially important for force spectroscopy, dissipation studies, as well as the frequency modulation AFM techniques.

Our recent developments in perfecting photothermal excitation [4] and its benefits to the AFM community will be discussed in this talk.

[1] A. Labuda, K. Kobayashi, *et al*. AIP Advances **1**, 022136 (2011)

[2] R. Proksch and S. V Kalinin, Nanotechnology **21**, 455705 (2010)

[3] A. Labuda, Y. Miyahara, *et al*. Phys. Rev. B **84**, 125433 (2011)

11:20am **SP+AS+BI+MI+NS+SS-ThM11 Minimally Invasive AFM for Imaging Biomolecules in Liquid**, *B.W. Hoogenboom*, University College London, UK   **INVITED**

Atomic force microscopy (AFM) is a unique tool in combining nanometre spatial resolution and high temporal resolution with the ability to visualise biological molecules in their native environment, i.e., aqueous solution. Its ultimate resolution on such samples depends on the strength of the interaction between the sample and the AFM probe: Too weak an interaction means low contrast, too high an interaction usually results in molecules being distorted or dislodged. I will discuss our recent work on minimising the invasiveness of AFM in liquid, resulting among others in the first observation of the DNA double helix on a single molecule in aqueous solution [Nano Lett. 2012, 12(7), pp. 3846-3850].

Thursday Afternoon, October 31, 2013

Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+BI+EM+MI+NS+SE+SS-ThA

Probe-sample Interactions, Nano-manipulation and Emerging Instrument Formats

2:00pm SP+AS+BI+EM+MI+NS+SE+SS-ThA1 Antibody Movement on Regular Antigen Clusters: Fab Arms are Made for Walking, *J. Preiner*, Johannes Kepler Univ. & Ctr for Adv. Bioanalysis GmbH, Austria*, N. Kodera*, Kanazawa Univ., Japan, *J. Tang*, Chinese Academy of Sciences*, A. Ebner*, Johannes Kepler Univ., Austria, *M. Brameshuber*, Vienna Univ. of Tech., Austria, *D. Blaas*, Medical Univ. of Vienna, Austria, *N. Ilk*, Univ. of Natural Resources & Applied Life Sci. Vienna, Austria, *H.J. Gruber*, Johannes Kepler Univ., Austria, *T. Ando*, Kanazawa Univ., Japan, **P. Hinterdorfer**, Johannes Kepler Univ. & Ctr for Adv. Bioanalysis GmbH, Austria **INVITED**

Antibodies are key molecules for the immune system of vertebrates. The Y-shaped IgGs exhibit C2-symmetry; their Fc stem is connected to two identical Fab arms binding antigens. The Fc part is recognized by the complement system and by phagocytic cells. Antibodies can be considered molecular calipers; bivalent binding of the two Fab arms to adjacent antigens can only occur within a distance of roughly 6 to 12 nm. This leads to much higher avidity and slower dissociation rates as compared to monovalent binding. Here we show that antibodies exhibit "bipedal" walking on antigenic surfaces and static binding of both Fab arms of an antibody may hold true only for a time scale of ~ 0.04 s. The walking speed depends on the lateral spacing and symmetry of the antigens. On 2D-crystalline surfaces, such as found on bacteria and viruses, steric strain thus appears to be the main reason for short-lived bivalent binding. Importantly, the collision between randomly walking antibodies was seen to reduce their motional freedom. It leads to formation of transient antibody clusters even at low antibody density. Interestingly, such assemblies are known nucleation sites for docking of the complement system and/or phagocytes.

2:40pm SP+AS+BI+EM+MI+NS+SE+SS-ThA3 Development of a Novel Single-Molecule Force Based Approach for Fragment Screening, *G.A. Milson*, University of Nottingham, UK

The discovery and development of new chemical entities is complex and time consuming, and of great expense to the pharmaceutical industry[1]. High throughput screening (HTS) is the main method used for lead identification, allowing significant numbers of compounds to be tested. However, productivity levels are still below those desired[2]. Due to this, interest in a relatively new process termed fragment based drug discovery (FBDD) has developed[3]. The FBDD process starts from small, efficiently binding fragments elaborated to more drug-like molecules[4]. However, with fragments being smaller components of the traditionally screened small molecules they have lower affinities and as a result require sensitive detection systems[5].

It has been proposed that the atomic force microscope (AFM) could be used as a novel system in fragment screening. The AFM benefits from the ability to probe single molecular interactions[6] using only small volumes of solution that need not be of high purity. Single molecule force recognition spectroscopy (SMFRS) is the commonly termed process where an AFM tip is functionalised with probe molecules that are known to recognise specific target molecules on the opposing surface. Fragments can theoretically be screened against their potential target on the surface and if they bind will block the natural ligand on the tip from occupying the active site.

Here, the well-characterised interaction between streptavidin and biotin was used as a model in which fragments of biotin were screened using an AFM probe functionalized with a biotin-mimetic peptide. It was seen that the AFM was capable of measuring the specific interaction between the biotin mimetic peptide and streptavidin. Each competition assay worked well, with the peptide-streptavidin interaction being blocked by fragments in a concentration dependent manner. Analysis of the percentage adhesion-versus-concentration data resulted in a ranking of the fragments, which matched their known or measured affinities to streptavidin. Despite the fact that this is still in the early stages of development, the results are promising and it is hoped that with further development the approach will be introduced into drug discovery fragment screening methods.

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3:00pm SP+AS+BI+EM+MI+NS+SE+SS-ThA4 Popping Nano-Balloons on TiO$_2$(110) Surface with the STM Tip, *D.V. Potapenko*, Z. Li, *R.M. Osgood*, Columbia University

Argon-filled subsurface nano-cavities can be created on TiO$_2$ rutile(110) surface by the means of Ar-ion bombardment combined with temperature treatment of the sample. The presence of the nano-cavities is manifested by the elliptical protrusions on the surface up to 1 nm high and 5 – 30 nm wide. We have developed a micromechanical model that can predict the shape and the depth of individual nano-cavities from the geometry of the corresponding protrusions. To evaluate the validity of the model 7 – 9 V, 1 – 10 ms voltage pulses from the STM tip were used to cause controllable explosions of the nano-cavities, thus allowing the direct independent measurements of their depth. The explosions are caused by the combination of local heating due to the voltage pulse and the high mechanical strain of the TiO$_2$ crystal lattice in the volume of the protrusion. We discuss the general mechanisms of the nanoscale surface modification produced by voltage pulses from the STM tip and show that at certain conditions the mechanical contact between the tip and the surface occurs. This work is an example of an unusual application of scanning probe microscopy for deep subsurface exploration.

3:40pm SP+AS+BI+EM+MI+NS+SE+SS-ThA6 Manipulating Magnetism One Atom at a Time, *S. Loth*, Center for Free-Electron Laser Science, Germany **INVITED**

Magnetic materials consist of atoms that interact very locally – often on atomic length scales. In nanoscopic systems the details of these interactions become increasingly important. We use scanning tunneling microscopy to test how far classical concepts of magnetism can be extended into the nanoworld and how they emerge from the quantum mechanical behavior of individual spins.

We have developed a complete toolset to explore magnetization dynamics in artificial few-atom nanostructures:

Magnetic atoms can be assembled into precisely defined arrays by atom manipulation with the STM tip. The atomic spins interact with each other and form collective magnetic states that can be tailored by modifying the atomic arrangements. Elastic and inelastic electron tunneling spectroscopy is used to quantify magnetic properties such as excitation energies, anisotropy barriers and spin-polarization as the nanostructure is being built up [1]. Crucial information on the stability of a nanostructure and influence of the environment can be obtained from the spin system's dynamical response to an external stimulus. For this purpose we use an all-electronic pump probe measurement scheme that excites the nanostructure repeatedly by spin-transfer torque and measures its response by spin-polarized tunneling [2].

With this technique we identified a new route to create stable magnetic states using antiferromagnetic spin-spin interaction. While individual Fe atoms exhibit a spin relaxation time on the order of 1 ns, linear antiferromagnetic chains with as few as eight Fe atoms show magnetic states that are stable for several minutes [3]. This dramatic change in dynamic behavior is indicative of a cross-over from quantum mechanical spin states to a ground state with classical magnetic order.

These experiments show a promising route towards rapid prototyping of quantum magnetic spin structures with control over static and dynamic properties by atom assembly in the STM.

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4:20pm SP+AS+BI+EM+MI+NS+SE+SS-ThA8 High-speed AFM with a Light Touch, *M. Miles*, R. Harniman, D.J. Phillips, L.M. Picco, O. Payton, M. Antognozzi, S. Simpson, S. Hanna, D.J. Engledew, University of Bristol, UK, *G. Gibson, R. Bowman, M.J. Padgett*, University of Glasgow, UK **INVITED**

AFM offers unique characteristics amongst microscopy techniques, and offers many benefits such has high-resolution 3D imaging in many environments including liquids. However, there are three areas in which

conventional AFM has limitations: (i) a low imaging rate, (ii) the probe-sample force interaction, and (iii) the planar nature of the sample. We are developing two high-speed force microscopy techniques to overcome the first two of these, (i) and (ii).

(i) One high-speed AFM (HS AFM) technique is a DC mode in which an automatic feedback mechanism essentially arising from the hydrodynamics of the situation maintains a tip-specimen separation of about 1 nm. This technique routinely allows video-rate imaging and has achieved imaging at over 1000 fps. Damage to specimens resulting from this high-speed DC-mode imaging is surprisingly less than at normal speeds. The behavior of the cantilever and tip at these high velocities has been investigated and super lubricity is a key component in the success of this technique [1,2].

(ii) The second high-speed force microscope is a non-contact method based on shear-force microscopy (ShFM). In this HS ShFM, a vertically-oriented, laterally-oscillating probe detects the sample surface at about 1 nm from it as a result of the change in the mechanical properties of the water confined between the probe tip and the sample. With this technique, very low normal forces are applied to the specimen. Information on the molecular water layers as a function of position [3,4].

(iii) AFMs require planar samples because the probe scans in a plane. The tip only 'sees' the sample from above. We have overcome this limitation by steering the tip of a nanorod in a three dimensional scan with six degrees of freedom using holographically generated traps such that it is possible to scan around a sample from any direction. We use various probe types: including silica nanorods, rod-like diatoms, and two-photon polymerized 3D structures [5,6].

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5:00pm SP+AS+BI+EM+MI+NS+SE+SS-ThA10 Multimodal and Multispectral Nano-imaging: Accessing the Structure Underlying the Function of Polymers, organic Photovoltaics, and Biomaterials, *M.B. Raschke*, University of Colorado at Boulder **INVITED**
The properties of many functional soft-matter systems, including polymer heterostructures, organic photovoltaics, and biomembranes are typically defined on the mesoscopic few nm to sub-micron scale. Scattering scanning near-field optical microscopy (s-SNOM) has demonstrated its ability to access the relevant spatial regime. In combination with IR-vibrational spectroscopy s-SNOM provides molecular structural information. However, a yet higher degree of specificity, sensitivity, and selectivity with respect to specific molecular functional features is desired. We will discuss the combination of scattering scanning near-field optical microscopy (s-SNOM) with other nano-optical and scanning probe modalities. That together with the multi-spectral features of different coherent and incoherent IR sources including tunable continuous-wave lasers, femtosecond sources, broadband synchrotron radiation, and thermal near-field radiation provides the desired enhanced dynamic range to probe at the level of the intra- and intermolecular interaction. This results in a unprecedented degree of specificity, sensitivity, and selectivity with respect to specific molecular functional features, as we will discuss for several specific block-copolymer, organic photovoltaic, protein, self-assembled monolayer, and biomineral systems we investigated.

5:40pm SP+AS+BI+EM+MI+NS+SE+SS-ThA12 Mapping Local Dipole Domains within Two-Dimensional Plastic Lattices, *J.C. Thomas, J.J. Schwartz, H.S. Auluck, G. Tran, J. Gilles, S. Osher,* University of California at Los Angeles*, C.A. Mirkin,* Northwestern University*, P.S. Weiss*, University of California at Los Angeles
We have observed aligned dipoles forming two-dimensional plastic lattices in self-assembled monolayers of carboranethiols on Au{111}. We have used scanning tunneling microscopy (STM) and simultaneously acquired local barrier height images of 9,12-dicarba-*closo*-dodecaborane *o*-9-carboranethiol (**O9**) monolayers on Au{111} at 4K in extreme high vacuum to determine the local structures and dipole orientations within the monolayers. The molecular structure of **O9** is that of a symmetric cage; a two-dimensional plastic lattice of aligned dipoles is formed through favorable intermolecular dipole-dipole interactions after chemisorption. Local barrier height images juxtaposed with the simultaneously recorded topography reveal directional dipole offsets within domains. New imaging analysis methods were used to overlay the multimodal data and determine molecular dipole orientations. We employ Monte Carlo simulations to model the dipole-dipole interactions, and to predict alignment at low temperature. We compare and contrast topographic and simultaneously acquired local barrier height images of 1,7-dicarba-*closo*-dodecaborane *m*-1-carboranethiol (**M9**) on Au{[111] in which the largest dipole is due to the sulfur-gold bond (as opposed to the cage) and is aligned to topographic maxima in STM images.

Friday Morning, November 1, 2013

Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+EM+GR+MI+NS+SS-FrM

Probing Electronic and Transport Properties
Moderator: S. Allen, The University of Nottingham, UK

8:20am **SP+AS+EM+GR+MI+NS+SS-FrM1 STM Mapping of Thermoelectric Power on Graphene across Defects and Boundaries**, *J. Park*, Oak Ridge National Laboratory, *G. He, R.M. Feenstra,* Carnegie Mellon University, *A.P. Li*, Oak Ridge National Laboratory
We present the spatially resolved thermoelectric power on epitaxial graphene on SiC by a scanning tunneling microscopy (STM) method. A thermovoltage is induced by a temperature difference between tip and sample and variations of thermovoltage are distinguished at defects and boundaries with atomic resolution. The epitaxial graphene shows a high thermoelectric power of 42 µV/K with a big change (9.6 µV/K) at the monolayer-bilayer boundary. Also, the thermopower is modified by Friedel oscillations of the charge density in graphene. Besides the change at monolayer and bilayer graphene boundary, the thermopower also provides spectroscopy maps which reveal domain structures induced by collapsed graphene wrinkles that not obvious in STM images. The thermopower distribution measurement with STM thus allows probing the electronic, thermoelectric, and structural properties down to the individual defect level.

8:40am **SP+AS+EM+GR+MI+NS+SS-FrM2 New Milestones in Scanning Probe Microscopy: Graphene on Rh(111) Studied by DFT, STM and NC-AFM**, *A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany
Graphene and is its interface with metallic substrates is proposed to be used in many technological applications. It can act as a protection layer for the underlying substrate, as a spin-filtering material separating two layers of a ferromagnetic material, or, in case of its growth on a lattice mismatched surfaces [for example, Ir(111), Rh(111), or Ru(0001)], as a template for the preparation of ordered arrays of clusters.

For graphene on Rh(111) [Fig.1(a-c)] several regions of different arrangements of carbon atoms above a Rh(111) substrate can be found: ATOP [A; carbon atoms are above Rh(S-1) and Rh(S-2) atoms], HCP [H; carbon atoms are above Rh(S) and Rh(S-2) atoms], FCC [F; carbon atoms are above Rh(S) and Rh(S-1) atoms], and BRIDGE [B; Rh(S) atoms bridge the carbon atoms]. These places are marked in Fig.1(a) by circle, down-triangle, square, and stars, respectively. Among them, the BRIDGE positions are expected to be the most energetically favorable for the nucleation of deposited atoms on top of a graphene layer.

In this contribution we present the combined study of the graphene/Rh(111) system via application of the state-of-the-art DFT calculations, STM, and NC-AFM. The calculated imaging contrast for STM between all high-symmetry positions for graphene/Rh(111) is in very good agreement with experimental results and this contrast does not depend on the sign of the bias voltage applied between a tip and the sample. As opposed to the latter observation, the imaging contrast in atomically-resolved AFM measurements depends on the frequency shift of the oscillating tip that can be understood on the basis of measured force-spectroscopy curves.

For this the KolibriSensor™, a new quartz sensor that excels in its performance reliability is used either for RT to HT studies in an SPM Aarhus 150 or for LT studies in the new Tyto™ scan head mounted into a JT-SPM. It is controlled by the Nanonis Control System.

9:00am **SP+AS+EM+GR+MI+NS+SS-FrM3 Electric Field Tuning of 2-dimensional Electrons in Graphene and Topological Insulators**, *J.A. Stroscio, J. Ha*, National Institute of Standards and Technology **INVITED**
The recent advances in classification of matter in terms of topological band theory have spurred a great deal of interest in synthesizing new materials demonstrating new topologically related properties. In a large class of these materials there are robust surface states on the spatial boundaries with vacuum. These surface states possess linear dispersive bands with chiral properties, similar to graphene. In this talk I will review our scanning tunneling spectroscopy measurements of graphene in applied electric field and magnetic fields [1-4] and compare them to some new results of applying electric fields in tunneling spectroscopy measurements of topological insulators [5,6].

Gate mapping tunneling spectroscopy has proved to be a powerful probe of the 2-dimensional electron system in graphene. In the presence of moderate disorder the charging of graphene quantum dots localized in the disorder potential has been observed with graphene on SiO_2 [1]. Intrinsic many body effects were observed in the renormalization of the dispersion velocity when substrate disorder was reduced using boron nitride spacer layers between graphene and SiO_2 [4]. In contrast, removing the substrate and creating suspended graphene membranes was seen to generate pseudomagnetic fields localizing the carriers in response to the strain generated from the forces between the probe and graphene membrane [3].

In the topological insulator Sb_2Te_3, we achieved gate tunable devices which are suitable for low temperature scanning tunneling microscopy (STM) studies by designing sample holders with back gating capability [5]. Thin films are epitaxially grown on pre-patterned $SrTiO_3$ substrates which are mounted on the specially designed sample holders. This allows *in-situ* gating on epitaxial films without any *ex-situ* processing of the sample [5]. In 3 QL thick Sb_2Te_3 films we observe a gap opening at the Dirac point due to the coupling of the top and bottom surface states [6]. More importantly, the gap is found to be tunable by the gate field, indicating the possibility of observing a topological phase transition in this system. A comparison of the data with an effective model of 3D topological insulators suggests that 3QL Sb_2Te_3 belongs to the quantum spin Hall insulator class.

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9:40am **SP+AS+EM+GR+MI+NS+SS-FrM5 SPM: Manipulating Spin to Operating Molecular Nanomachines**, *S.-W. Hla*, Argonne National Laboratory **INVITED**
We combine scanning tunneling microscope (STM) imaging, manipulation and spectroscopy to investigate and manipulate magnetic, electronic, and mechanical properties of atoms and molecules on surfaces. This talk will highlight advances achieved by STM studies at atomic and molecular scale [1-3]. In spintronic area, we will present imaging and manipulation of atomic spin using a spin-polarized STM tip [1]. Here, individual cobalt atoms assembled as a chain on a Mn monolayer on W(110) surface appear different shapes due to their spin directions. In nanoscale superconductivity area, donor-acceptor type $(BETS)_2GaCl_4$ molecular clusters on a Ag(111) surface opens up the possibility to explore superconducting phenomena locally [2]. In this part, electronic structure evolutions at molecule-metal boundaries and manipulation of superconducting clusters will be presented. Quenching of surface state electrons due to the molecular superconducting state will also be discussed. Finally, operations of complex molecular motors using STM manipulation on a Au(111) surface will be shown. Interestingly a selective tunneling into specific rotor arms result in a controlled directional rotation of the motor. The inherent molecular design is critical to achieve such directional control. These innovative experiments are tailored to address several critical issues covering both for fundamental understanding, and for demonstration of novel molecule based nanodevices on materials surfaces.

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10:20am **SP+AS+EM+GR+MI+NS+SS-FrM7 New Experiments and Applications Made Possible by a Low Temperature 4-Tip STM with UHV-SEM Navigation**, *A. Bettac, B. Guenther, J. Chrost, J. Hilton, J. Koeble, A. Feltz*, Omicron NanoScience, Germany
A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scale electrical circuits required to control and characterize their functional properties. Local electrical probing by multiple probes with STM precision can significantly improve efficiency in analyzing individual nano-electronic devices without the need of a full electrical integration. Recently we developed a microscope stage that merges the requirements of a SEM

navigated 4-probe STM and at the same time satisfy the needs for high performance SPM at low temperatures.

Besides SEM/STM probe fine navigation and imaging with atomic resolution at temperatures of T<5K, the pm-stability of the LT NANOPROBE expands applications to tunneling spectroscopy and even the creation or modification of nanostructures or single atoms by a sharp and precise SPM probe. A further milestone in the development of the instrument was the implementation of the Qplus- NC-AFM mode for imaging on insulating surfaces. The Qplus measurement becomes important if nanowires/nanostructures are deposited on an insulating substrate for a better electrical decoupling of the nanowire from the substrate. In this case the Qplus sensor can be employed to locate the nanostructures and, after finding the structure, to carry out conductance measurements.

In this contribution we will present first Qplus results obtained with the LT Nanoprobe at low temperatures. Furthermore we will focus on measurements that prove the performance level of the instrument as well as on tunneling spectroscopy and atom manipulation experiments on Ag(111) at temperatures of T < 5K.

10:40am **SP+AS+EM+GR+MI+NS+SS-FrM8** **Electrical Characterization of GaAs Nanowires with a 4-tip STM**, *B. Voigtlaender*, *S. Korte*, *V. Cherepanov*, Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany, *M. Steidl, W. Zhao, P. Kleinschmidt, T. Hannappel,* TU Ilmenau, Germany, *W. Prost*, University of Duisburg-Essen, Germany

III-V semiconductor nanowires are promising building blocks for novel semiconductor devices in future electronic and opto-electronic applications such as solar cells. In this context the distribution of the dopant over the nanowires is of great importance. Resistance profiles of as-grown freestanding GaAs nanowires were measured with a multitip scanning tunneling microscope (STM) used as nanoprober. Four point probe resistance measurements were performed along the nanowire. The dopant induced carrier concentration along the wire was determined from the resistance measurements and geometrical data. It was found that in the high temperature growth region (450°C) the carrier concentration is about one order of magnitude lower than in the low temperature regime (400°C). The NWs exhibit high mechanical elasticity, they can be deformed by the STM tips and revert to their original shape when released. Even extreme bending of a NW did not show a significant influence on its conductivity. These measurements were performed using a multi-tip scanning tunneling microscope (STM) in which four independent STM units are integrated on a diameter of 50 mm, resulting in an unsurpassed mechanical stability, enabling atomic resolution imaging with each tip. The heart of this STM is a new type of piezoelectric coarse approach called KoalaDrive. The coarse positioning of the tips is done under the control of an SEM. This multi-tip instrument is suited to perform electrical measurements such as local potential measurements at the nanoscale.

11:00am **SP+AS+EM+GR+MI+NS+SS-FrM9 Atomic and Electronic Structure of an Alloyed Topological Insulator $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$**, *W. Ko, I. Jeon, H.W. Kim, H. Kwon,* Samsung Advanced Institute of Technology, Republic of Korea, *S.-J. Kahng,* Korea University, Republic of Korea, *J. Park, J.S. Kim,* Pohang University of Science and Technology, Republic of Korea, *S.W. Hwang, H. Suh,* Samsung Advanced Institute of Technology, Republic of Korea

The alloyed compound $Bi_{2-x}Sb_xTe_{3-y}Se_y$ has been argued to exhibit both topological surface states and insulating bulk states, but not yet been studied with local probes on the atomic scale. Here we report on the atomic and electronic structures of $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$ studied using scanning tunnelling microscopy (STM) and spectroscopy (STS). Although there is significant surface disorder due to the alloying of constituent atoms, cleaved surfaces of the crystals present a well-ordered hexagonal lattice in STM topographs with 10 Å high quintuple layer steps. STS results reflect the band structure and indicate that the surface state and Fermi energy are both located inside the energy gap. In particular, the surface states do not show any electron back-scattering; due to their topological nature they are extremely robust. This finding demonstrates that alloying is a promising route to achieve full suppression of bulk conduction in topological insulators whilst keeping the topological surface state intact.

11:20am **SP+AS+EM+GR+MI+NS+SS-FrM10 Schottky Barrier Height Measurements of Cu/Si(001), Ag/Si(001), and Au/Si(001) Interfaces Utilizing Ballistic Electron Emission Microscopy and Ballistic Hole Emission Microscopy**, *R. Balsano*, *V.P. LaBella*, College of Nanoscale Science and Engineering

The Schottky barrier heights of both n and p doped Cu/Si(001), Ag/Si(001), and Au/Si(001) diodes were measured using ballistic electron emission microscopy (BEEM) and ballistic hole emission microscopy (BHEM), respectively. Measurements using both forward and reverse BEEM and

BHEM injection conditions were performed. The Schottky barrier heights were found by fitting to a linearized Bell-Kaiser and Prietsch-Ludeke model. The sum of the n-type and p-type barrier heights are in good agreement with the band gap of silicon and independent of the metal utilized. These findings may help to improve models for Schottky barrier heights of non-epitaxial diodes.

11:40am **SP+AS+EM+GR+MI+NS+SS-FrM11 A STM Study of a Self Assembled Cu-Si Nanoisland on Si(110)**, *P.K. Ng*, University of Illinois at Chicago, *B. Fisher, N.P. Guisinger,* Argonne National Laboratory, *C.M. Lilley*, University of Illinois at Chicago

The surface of a self-assembled copper-silicide (Cu-Si) nanoisland on a silicon (Si) substrate with (110) orientation was studied using surface tunneling microscopy (STM). Self-assembled Cu-Si nanostructures on Si are of technological interested because of their potential use in nanoscale devices. Self-assembled Cu-Si nanoislands were fabricated by electron beam evaporation of Cu onto a 600°C annealing Si substrate in ultrahigh vacuum (UHV) environment. In prior work, we used transmission electron microscopy (TEM) to analyze material composition of Cu-Si nanostructures via x-ray energy dispersive spectroscopy (XEDS) [1]. The XEDS data of a Cu-Si nanowire show a Cu_3Si phase [2]. The size of these nanostructures was on the scale of hundreds of nanometers and high resolution analysis was focused on the cross-sectional (or bulk) material. However, the surface of these self-assembled Cu-Si nanoislands has not yet been studied. Figure 1(a) in the attached supplemental document (and all the referring figures therein) shows a scanning tunneling microscopy (STM) micrograph of a self assembled Cu-Si nanoisland on Si(110). The facets on the nanoisland indicates a single crystal. As seen in Figs. 1(b)-(c), a higher resolution scan and analysis on the same nanoisland indicates a surface periodicity between scan points A to B of ~6.8 Å. These results corroborate that the faceted nanoisland is a single crystal. The surface of the nanoisland appears to have unknown absorbates, possibly from water or hydrogen contaminations, see Fig. 1(b). Interestingly, some of these absorbates do not randomly form on the surface but also in a periodical manner. As such, the surface may have a periodical affinity for certain absorbates. A full discussion of this study will be presented in the AVS proceeding.

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