

Monday Afternoon, October 28, 2013

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 AgFeO₂ Thin Films with the Delafossite Structure by Combinatorial Sputtering.** *F. Mao, T. Nyberg, T. Thersleff, U. Jansson*, Uppsala University, Sweden

Delafossites AMO₂ (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 MO₆ octahedra. Consequently, the delafossites can be described as natural nanolaminates of MO₂ 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 ($\geq 700^\circ\text{C}$). 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 ($>400^\circ\text{C}$). 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 AgFeO₂ thin films using co-sputtering of silver and iron targets in a reactive Ar-O₂ 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 AgFeO₂ 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, O₂ flow rate, working pressure, etc. The XRD and TEM showed that the AgFeO₂ films grew epitaxially with the direction of (001) in the optimal sputtering condition.

2:20pm **MI+EM+MG-MoA2 MBE Growth and Properties of SrCrO₃ 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. SrCrO₃ was first reported to be a paramagnetic metallic oxide with a cubic structure, but the property measurements thereafter have been controversial. Almost all SrCrO₃ 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 SrCrO₃ films on LaAlO₃(001) substrates by molecular beam epitaxy using O₂ 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 SrCrO₃ films are in the 4+ oxidation state, although there is a small amount of Cr³⁺ 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 SrCrO₃ films will be compared to that of LaCrO₃ 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 topotactic 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, SrTiO₃ (STO) and LaAlO₃ (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 $3.3 \times 10^{14} \text{ cm}^{-2}$ (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 SrTiO₃/GdTiO₃(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 interfaces may be used to design semiconductor interfaces that could sustain similar 2DEGs.

Work performed in collaboration with L. Bjaalie, L. Gordon, K. Krishnaswamy, and A. Janotti, and supported by the ARO, ONR, and NSF.

[1] W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, *Phys. Rev. B* **18**, 4402 (1978).

[2] A. Janotti, L. Bjaalie, L. Gordon, and C. G. Van de Walle, *Phys. Rev. B* **86**, 241108(R) (2012).

[3] P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, *Appl. Phys. Lett.* **99**, 232116 (2011).

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

* Medard W. Welch Award Winner

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 Coherent 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 L1₀ tetragonal intermetallic phase which exhibits a high magnetocrystalline anisotropy of $K \sim 10^7$ to 10^8 ergs/cm³, 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 L1₀ and L1₂ 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 L1₀-L1₂ 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 L1₂ 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 L1₀ and L1₂ 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.

[†] W. Shockley, J. Chem. Phys. **6**, 130 (1938)

Tuesday Afternoon, October 29, 2013

Synchrotron Analysis Focus Topic

Room: 203 C - Session SA+AS+MG+SS-TuA

HAXPES Studies on Interfaces and Buried Layers

Moderator: A. Rossi, University of Cagliari

2:00pm SA+AS+MG+SS-TuA1 **Past and Present of Synchrotron Radiation, from Hard X-ray Photoemission to Soft X-ray and Back, P. Pianetta**, Stanford University **INVITED**

Synchrotron radiation has proven to be a very important tool for the study of materials in applications including earth sciences, energy and semiconductors. Most of the early applications focused on the study of surface phenomena using valence and core level spectroscopies using soft x-rays. Although one of the first studies at a multi-GeV synchrotron used hard x-rays, its practical use was limited by low counting rates. With the advent of high brightness synchrotron sources along with highly efficient electron energy analyzers, x-ray photoelectron spectroscopy using multi-keV x-rays has seen a rebirth for the study of buried interfaces and bulk materials properties. This talk will discuss the evolution of synchrotron radiation photoelectron spectroscopy from the early experiments to the present day.

2:40pm SA+AS+MG+SS-TuA3 **Practical use of Photoemission with Synchrotron Radiation in Nanotechnology: From Soft to Hard X-rays, O.J. Renault, E. Martinez**, CEA-LETI, France, *N. Barrett*, Cea Dsm Iramis Spcsi, France

Over the past 15 years, due to intrinsic limitations of laboratory X-ray sources, photoemission using synchrotron radiation has played an increasing role in solving issues of technologically-relevant materials and systems. With narrow spectral widths, synchrotron sources enable photoemission at uncomparable effective energy resolutions for refined assessment of chemical states at interfaces [1]. The broad energy range offers ultimate surface sensitivities with soft x-rays [2], and also much deeper photoelectron escape depths in the hard x-ray range which is crucial to investigate buried interfaces intrinsically found in devices. This contribution will highlight the advantages and achievements of hard x-ray photoemission (HAXPES) compared to soft x-ray photoemission, through a selection of recent studies performed on nanotechnological materials and devices (CMOS high-k/metal gate stacks, memory devices) [3]. Finally, we will briefly mention new developments: first, the extension of photoelectron spectroscopy (XPEEM) from chemical state and band structure imaging, to hard x-rays excitation (HAXPEEM) [4]. Second, the application of inelastic background analysis of HAXPES spectra.

[1] O. Renault *et al.*, Appl. Phys. Lett. 81 (2002), 3627; 90 (2007), 052112; J. Appl. Phys. 96 (2004) 6362; E. Martinez *et al.*, Appl. Surf. Sci. 285 (2012), 2107.

[2] K. Huang, P. Reiss, O. Renault *et al.*, ACS Nano 4 (2010), 4799; O. Renault *et al.*, Appl. Phys. Lett. 87 (2005), 163119.

[3] R. Boujama *et al.*, J. Appl. Phys. 111 (2012), 054110; P. Calka *et al.*, J. Appl. Phys. 109 (2011) 124507.

[4] C. Wiemann *et al.*, Appl. Phys. Lett. 100 (2012), 223106.

3:00pm SA+AS+MG+SS-TuA4 **Effective Attenuation Length for Titanium Nitride, Hafnium Oxide, Silicon, Silicon Dioxide, Lanthanum Lutetium Oxide, Lanthanum Calcium Manganite, and Gold from 1 keV up to 15 keV, J. Rubio-Zuazo, G.R. Castro**, SpLine Spanisch CRG beamline at the European Synchrotron Radiation Facility, France

Material composites, which combine different materials mostly multilayer hetero-structure, with specific and defined properties, are a promising way to create products with specific properties. In these materials the interfaces define many of their properties. The surfaces and interfaces play a fundamental role, and are the source of a great variety of new, and even unexpected, physical phenomena due to the existence of step changes in the structure and the electronic coordination. Third generation synchrotron radiation sources enables the extension of photoemission spectroscopy to higher electron kinetic energies (HAXPES, Hard X-ray Photoelectron Spectroscopy) compensating the decrease of the photoionization cross-section for excitation energies in the hard X-ray region. HAXPES allows the accessibility to buried interfaces and bulk materials due to the dramatic increase of the effective attenuation length (EAL). Electronic, compositional and chemical depth profiles can be then performed in a non-destructive way over the tens-of nanometers scale with nanometer depth resolution. Such an important application of HAXPES is crucial for many condensed matter experiments and requires reliable EALs for high kinetic

energy. EALs are well established for electrons with kinetic energies up to 2 keV. Even if EALs can be obtained by extrapolating well-known formulae, there is a lack of experimental data in the energy range between 1 and 15 keV. In the present study we have determined the EAL dependency on kinetic energy for titanium nitride (TiN), hafnium oxide (HfO₂), silicon (Si), silicon dioxide (SiO₂), lanthanum lutetium oxide (LaLuO₃), lanthanum calcium manganite (La_{0.66}Ca_{0.33}MnO₃), and gold (Au) from 1 keV up to 15 keV. A correlation between the EAL energy dependence and the material density is established. The EALs have been obtained by following either core level peak intensity dependence for a fixed kinetic energy as a function of the overlayer thickness or the core level peak intensity dependence with the photoelectron kinetic energy (i.e. photon energy) for a fixed overlayer thickness. The experimental set-up used is devoted to the combination of X-ray Diffraction (XRD) and HAXPES. Hence, we are able to determine the exact thickness and roughness of the layer from a fit of the X-ray reflectivity (Kiessig fringes) and simultaneously to obtain the EALs from the HAXPES signal evolution. It is important to stress that due to the simultaneous detection of the diffracted and photoemitted signal, the EALs, thickness and roughness determination correspond exactly to the same sample region.

4:00pm SA+AS+MG+SS-TuA7 **Hard X-ray Photoelectron Spectroscopy (HAXPES) Investigations of Electronic Materials and Interfaces, J.C. Woicik**, National Institute of Standards and Technology (NIST) **INVITED**

Photoelectron spectroscopy is a widely used technique that can uniquely measure the chemical and electronic structure of solids. Owing, however, to the historical use of low-energy photons and the resulting limited photoelectron inelastic mean-free path, the technique has found only general application to surfaces and shallow interfaces. With advances in both photon-source and electron-spectrometer instrumentation, hard x-ray photoelectron spectroscopy (HAXPES), where the photon energy is typically in the 2.1 – 10 keV range, has consequently emerged as a powerful tool for studying the bulk and interfacial properties of complex materials systems.

In this talk, we will discuss developments of the HAXPES technique at the NIST beamline X24A at the National Synchrotron Light Source for the study of electronic materials. Examples will include nitrogen treatment of HfO₂ gate stacks on Si, depth profiling of the HfO₂/SiO₂ interfaces, Ga and As “out-diffusion” at semiconductor/oxide interfaces, band offsets and Schottky barrier heights at semiconductor/oxide and diamond/metal interfaces, and oxygen vacancies in N doped TiO₂ and solid-oxide fuel cells. In all cases, the increased probing depth of HAXPES over traditional lab based XPS is crucial to study the electronic structure of entire overlayers and/or buried interfaces with thicknesses of industrial significance.

4:40pm SA+AS+MG+SS-TuA9 **HAXPES Study of Full High-κ/Metal Gate Stacks Deposited on Ge Substrates, C. Fleischmann, I. Kalpyris, T. Conard, C. Adelman, S. Sioncke**, IMEC, Belgium, *J.P. Rueff, J. Ablett*, Synchrotron SOLEIL, France, *W. Vandervorst*, IMEC, KU Leuven, Belgium

The introduction of Ge in CMOS devices beyond the 14 nm technology node requires effective passivation of the Ge gate stack. Besides the interface passivation, a highly scaled gate stack is needed for the next generation of CMOS devices. Scaling of the gate stack can be achieved by several means, for instance by changing process conditions. In this work, we investigate the influence of both the high-κ stack and the metal gate on the properties of a GeO₂S_y interfacial passivation layer by Hard X-ray Photoelectron Spectroscopy (HAXPES). Using high energy x-rays (4 to 8 keV), we are able to probe the buried interface between the high-κ layer and the Ge substrate, and hence to reveal direct information on the chemistry and the thickness of the GeO₂S_y passivation layer. Note that such a buried interface is not accessible using a “standard” XPS tool relying on Al K_α x-ray radiation.

In this study, we considered three high-κ materials (Al₂O₃, HfO₂ and an Al₂O₃/HfO₂ bi-layer) and three metal gates (TiN, TiW and Pt). Samples have been measured both directly after atomic layer deposition and after forming gas anneal, to investigate the effect of a thermal treatment on the interfacial properties. To disentangle the impact of the particular metal gate, comparison is made to a high-κ stack sample without metal gate.

We first demonstrate the importance of analyzing full stacks, as no effect of annealing was observed on the stacks without metal gates, while clear modification of the Ge/high-κ interfacial layer thickness is observed when a gate is present. We then show that this effect on interfacial layer thickness depends on both the high-κ and the metal gate material used. This can lead

for example to an increase (i.e. HfO_2/TiN) or to a decrease (i.e. $\text{Al}_2\text{O}_3/\text{TiN}$) of the interfacial layer thickness after annealing. As a global trend, the thinnest interfacial layers are obtained for pure Al_2O_3 . However, the interfacial layer thickness appears to be more sensitive to variations in the metal gate rather than the high- κ material. We also show that the introduction of a very thin Al_2O_3 layer ($\sim 2 \text{ \AA}$) between the Ge substrate and the HfO_2 layer strongly influences this observed sensitivity of the interfacial layer properties to the metal gate and forming gas anneal. Aside from quantifying the interfacial layer thickness, we will also analyze changes in the interfacial layer from a chemical point of view. As a conclusion, the final layer structure (hence, the Equivalent Oxide Thickness of the gate stack) is thus a complex interplay between the initial GeO_xS_y thickness before forming gas anneal and the chemistry of the high- κ and metal gate materials.

5:00pm **SA+AS+MG+SS-TuA10 X-ray Absorption Spectroscopy of Magnetic/Ferroelectric Complex Oxide Interfaces**, *M.B. Holcomb, J. Zhou, D. Chen*, West Virginia University, *C. Jenkins, M.A. Marcus*, Lawrence Berkeley National Laboratory, *Y.-H. Chu*, National Chiao Tung University, Taiwan, Republic of China

Magnetoelectric coupling (the electrical control of magnetic properties or vice versa) has promising applications in computer memory and logic, magnetic sensing and energy scavenging. Magnetoelectric interfaces are a potential new method to improving magnetoelectric coupling strength and controllability. We utilize x-ray absorption spectroscopy, photoemission electron microscopy, and second harmonic generation to understand both the order parameters of the individual layers and the resulting interface. This talk will focus on bilayers composed of ferromagnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and ferroelectric $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT). Through photoemission electron microscopy imaging, ME coupling was confirmed at the interface. X-ray absorption spectroscopy of Mn was taken across wedged samples of varying ferroelectric and ferromagnetic thicknesses. The change of Mn valences at different thicknesses of LSMO and PZT helps to understand ME coupling and impact of thickness on the ME properties. This work suggests a strategy for improving not only magnetoelectric devices, but also magnetic systems. This work is supported by West Virginia's Higher Education Policy Commission.

5:20pm **SA+AS+MG+SS-TuA11 Local-Structure Determination Using Combined Fitting of EXAFS and Neutron Total Scattering Data**, *I. Levin*, National Institute of Standards and Technology **INVITED**

The functional responses of many industrially-relevant materials are controlled by their *local structure* – a term that refers to the atomic arrangements on a scale ranging from atomic (sub-nanometer) to several nanometers. Today, multiple experimental techniques exist for probing the local atomic order. Nonetheless, finding accurate comprehensive structural solutions still remains a challenge, because any one of the existing methods yields only a partial view of the structure. In this talk, we will discuss recent advances in local-structure determination using simultaneous fitting of EXAFS, X-ray/neutron total scattering, and electron diffuse scattering data. Examples will include several representative perovskite systems that find use as dielectrics and ferroelectrics.

Wednesday Morning, October 30, 2013

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, Cu₂O 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 Cu₂O. 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 Cu₂O, (b) improvement of electrical charge transport properties of Cu₃N, 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 photovoltaics. 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 (Co₂ZnO₄ and Co₂NiO₄) 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 photovoltaic 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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[1] V. Stevanovic et al Phys. Rev. Lett. 105, 075501 (2010)

[2] V. Stevanovic et al J. Am. Chem Soc. 133, 11649 (2011)

[3] J. Perkins, A. Zakutayev et al Phys. Rev. B 84, 205207 (2011)

[4] T. Paudel, A. Zakutayev et al Adv. Func. Mat. 21, 4493 (2011)

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[6] A. Zakutayev et al MRS Comm. 1, 23 (2011)

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 battery, 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. Tsybal, L.Q. Chen, X.Q. Pan, S. Ryu, T. Hernandez, T. R. Paudel, H. Zhou and D. D. Fong.

Wednesday Afternoon, October 30, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG+EN+MS-WeA

Education for Interactive R&D & Industrial Implementation

Moderator: C. Eom, University of Wisconsin-Madison, B. Nelson-Cheeseman, University of St. Thomas

2:00pm **MG+EN+MS-WeA1 21st Century Skills and Educating the Next Generation Workforce for Expedited Innovation and Deployment, C.C. Broadbridge**, Southern Connecticut State University **INVITED**

The goal of the Materials Genome Initiative [MGI] is to expedite materials discovery, innovation and deployment via the development of new approaches to materials research that exploit interdisciplinary collaboration and innovation. Successful implementation will require a workforce possessing 21st Century Skills including critical thinking, problem solving, communication, collaboration, technological fluency and creativity. To address the need for US competitiveness in a global economy, educational reform has been initiated at the K-12 level with the development of 21st Century Skills Standards [1], Common Core Standards [2] and the Next Generation Science Standards [3]. Similar reform is needed at the university and post-graduate [PG] professional development levels to assure the optimal development of a STEM educational pipeline. At the university level, reform has been initiated with the development of novel approaches to all university [non-major] requirements as well as courses and programs for majors (e.g., [4,5]). For the effective implementation of the MGI, it is important to realize the natural synergies that exist between these efforts and those within the materials science education and research communities. Arguably, individuals acquire and refine these necessary skills best via exposure to, and active participation in, authentic science research. NSF funded Materials Research Science and Engineering Centers [MRSECs] support interdisciplinary and multidisciplinary materials research and education of the highest quality [6]. All MRSECs include education and outreach components that effectively integrate the collaborative and innovative aspects of materials research. Components are developed and implemented at the K-PG levels and also include programs that educate the general public. For this presentation, educational reform at all levels will be reviewed with an emphasis on approaches with the greatest potential positive impact on the implementation of the MGI. In particular, an interdisciplinary team-based approach to materials research effectively leveraging programs within the Center for Research on Interface Structures and Phenomena (CRISP) MRSEC will be described that integrates materials science education and research while maximizing on the attainment of the 21st Century Skills necessary for successful implementation of the MGI.

1. <http://www.p21.org/overview/skills-framework/351>
2. <http://www.corestandards.org/>
3. <http://www.nextgenscience.org/>
4. <http://www.aacu.org/resources/generaleducation/index.cfm>
5. <http://www.tms.org/pubs/journals/jom/0910/thornton-0910.html>
6. <http://www.mrsec.org/>

2:40pm **MG+EN+MS-WeA3 High-Performance Ceramics – Challenges for Next Generations, W. Rossner, S. Lampenscherf**, Siemens AG, Germany **INVITED**

Ceramics play an important role in system engineering for demanding industrial applications because they provide functionality of key components that are critical for overall system performance and operational benefit. The continuous development of high performance ceramics over the last decades was aiming mainly towards ‘better’ properties and ‘deeper’ understanding of material behaviour.

For today’s applications in areas such as power engineering, medicine, automotive, aircraft and high-end electronics the time-to-market aspect is an important success factor. Product cycles become shorter while R&D cycles especially including materials development are not able to keep up with such pace. The complex relationship between ceramic performance and processing plays a special role for accelerating the R&D process. An additional time-consuming factor is the need for extensive qualification and testing of high-performance ceramics to guarantee functionality and reliability under desired operation conditions.

Based on the very much improved understanding of the dependencies of processing, performance and application as well as the availability of

advanced computational methods and tools materials engineering can be a vital part to overcome today’s limitations for accelerating materials development and product implementation.

In the talk we discuss these aspects in the context of current industrial examples for next generation high performance ceramics.

4:00pm **MG+EN+MS-WeA7 Educating for High-Impact Computation – Skills vs. Acceptance, W.E. Windl**, The Ohio State University **INVITED**

As an integral part of the Materials Genome Initiative (MGI), the task of materials computation, in concert with experiment and theory, is to help accelerate the discovery and maturation of new materials by at least a factor of two. During the first rounds of MGI-related solicitations, two major groups of challenges that always existed became very evident. For one, the obvious question about the skill set available in the Materials Research community to actually perform the necessary computations. Secondly, and much less apparent on the surface, was the frequent lack of acceptance of computational work as a valid input, maybe foremost in the experimental community, which can lead to awkward situations, missed opportunities, and frustration in collaborative projects. Beginning with the 2012-2013 academic year, The Ohio State University has moved from a quarters-based academic calendar to a semesters-based calendar. As part of this change, the Department of Materials Science and Engineering has elected to revise degree program curricula in a significant manner. A key objective in our revision was to respond to the challenges in lack of acceptance of computational work from Integrated Computational Materials Engineering and MGI described above. We have developed a curriculum that attempts to integrate congruently database use, visualization, simulation and computational approaches in materials science with other core educational content. At the undergraduate level, our goal was to produce graduates who are cognizant of the broad range of computational tools available to materials engineers and what they can do to solve engineering problems, and who are able to use a number of those tools proficiently to solve problems of practical importance themselves. The MSE core curriculum includes 9 credit hours (four courses), or 20% devoted to these topics. Students may take an additional 4 credit hours (two courses) in elective content on computational methods in materials science. In this presentation, details will be presented on the specific course offerings, course content, exercises, and software packages used. How the courses are postured in the curriculum will also be addressed. The experiences, challenges, and recommendations resulting from the first year of teaching will finally be discussed, where the author was involved in four different courses relying on different combinations of traditional teaching with reverse and peer teaching approaches as well as with significant fractions of active-learning work.

4:40pm **MG+EN+MS-WeA9 MGI in the Laboratory: Closing the Feedback Loop in Aerospace Materials Design and Development, E. Sapper, P. Kinlen**, Boeing Research & Technology **INVITED**

The aerospace industry has continuously driven major developments in material science as technology has evolved from wood and fabric to lightweight metal alloys and advanced polymer composites. Future aerospace materials systems will require even more advanced technologies, such as those afforded by smart and responsive systems like electroactive polymers and composites. The unique properties of these materials provide the ability to construct intelligent systems which produce a defined, predictable response to an input.

Concurrent with state-of-the-art chemical technology, the increasing availability of high-performance computing power has facilitated the entry of various computational simulation and modelling methods into the research and development production cycle. Quantum mechanics, molecular dynamics, and multi-scale simulation approaches, developed and applied within a Materials Genome Initiative paradigm, are providing insight into aerospace material properties of interest, such as species-specific transport rates, electrochemical response, service lifetime prediction, material color and appearance, and quantitative structure-property relationships.

The ultimate goal of a coupled experimental-computational approach is the closed and tightened feedback loop between laboratory results and computational predictions. This leads to the incorporation of more theory into experimental practice as well as more heuristics into computational method development, expressed in the form of semi-empirical models and empirically-pinned property response surfaces. This presentation will review some of the challenges involved in applying advanced computational methods alongside state-of-the-art laboratory procedures. The development of novel, more environmentally friendly aerospace coatings that release site-specific corrosion inhibitors on-demand will be presented as a case-study in closed-loop computation-experimentation.

5:20pm **MG+EN+MS-WeA11 Condensed Matter Physics in an Age of Computation**, *M. Marder*, University of Texas at Austin **INVITED**

Condensed matter physics and materials physics have grown so enormously that no one can hope to know everything done in the last five years let alone the last fifty. This does not relieve researchers of the charge of educating new generations of students. I will discuss the balance between acquisition of skills and acquisition of knowledge, and the way that computing power changes what is taught and how.

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/PbTiO₃ 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-throughput 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')BO₃ 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 *Pca*2₁, with a sizeable polarizations, which are supported by preliminary experiments. 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

*Work supported in part by DOE under grant DE-FG02-07ER15842.

Thursday Afternoon, October 31, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG-ThA

Theory, Computation and Data-Enabled Scientific Discovery

Moderator: T. Mueller, Johns Hopkins University

2:00pm MG-ThA1 High-throughput Quantum Chemistry and Virtual Screening for Materials Solutions, M.D. Halls, D.J. Giesen, H.S. Kwak, A. Goldberg, T.F. Hughes, Y. Cao, Schrödinger Inc.

For the past 20 years the standard approach to drug discovery has been the automated computational screening of chemical structure libraries to identify lead systems for further investigation and experimental development. Recent advances in the power of computational resources and the improvements in the efficiency and stability of first-principles simulation packages has made it possible to apply this paradigm to challenges in material science. It is now possible for multi-step property calculations using accurate quantum-based methods to be executed automatically for diverse chemical libraries, with the results collected in a growing data record. This record can then be sorted and mined to identify exemplary candidates and establish critical structure-property limits within a chemical design space. To date very few studies have been reported in which quantum chemical calculations are carried out in a high-throughput fashion to compute properties and screen for optimal materials solutions, however with time virtual screening will become central to advanced materials chemistry research.

In this presentation, the use of high-throughput quantum chemistry to analyze and screen a chemical structure library is demonstrated for key materials applications including organic light-emitting diode (OLED) and organic photovoltaic (OPV) materials, and precursors for optimal thin film deposition in semiconductor device fabrication.

2:20pm MG-ThA2 Computational Materials Design: Precious Material Free Catalyst for NO Dissociation, H. Kasai, A.A. Padama, Osaka University, Japan

We entered the 21st Century witnessing remarkable progress in Science and Technology. Novel materials and devices that were once considered the stuffs of *science fiction* are becoming a reality. It would not be an exaggeration to say that we are coming to the **Age of Designer Materials**. **Complex materials** are designed to have desired properties, with both basic and technological applications. A **Designer Material** has to be **Functional**. To realize this and to test the concepts and principles developed for realizing designer materials, we use **Surfaces** as our testing ground. These give access to the appropriate reduced dimensionality and means to manipulate the degree of complexity, and emergence of function.

Specifically, we were able to design catalyst for NO dissociation that is free from precious materials. NO is emitted from the combustion of fossil fuels and converts to nitric acid in the atmosphere which leads in the formation of acid rain. The dissociation of NO is known to be the rate limiting process for its reduction due to the strong N-O bond [1]. Precious metals such as Rh, Pd and Pt are efficient catalysts for such purpose but their high cost prohibits their massive production [2]. Through first principles investigation, we were able to confirm that Cu-based surface is capable of dissociating NO molecule [3, 4]. The analysis is made with reference to a clean Cu surface. In Cu(111), dissociation of NO is accompanied by a large activation barrier and NO desorption is more likely to happen. This is due to the filled d states of the Cu atoms which limits their interaction with the adsorbate. In the contrary, the local density of states profile of the d orbital of the Cu atoms in Cu₂O(111) shows that the states are shifted to the Fermi level region which explains the good adsorption and easy dissociation of NO. We also found that the reaction path of NO on Cu₂O surface is comparable with that of Rh surface which is characterized by a transition state lying below the reference level (surface and NO_{gas}) [5]. Nevertheless, the activation barrier for NO dissociation is lower in Cu₂O indicating the easier dissociation of NO on the alternative catalyst. Furthermore, the adsorption energy of N and O atoms from the dissociated molecule is also lower on Cu₂O which is desirable for the succeeding steps in the reduction process.

References:

- [1] S. Gonzalez et al., J. Catal. 239 (2006) 431.
- [2] H.J. Kwon et al., Chem. Eng. Sci., 62 (2007) 5042.
- [3] A.A.B. Padama et al., J. Phys.: Condens. Matter, 24 (2012) 175005.

[4] H. Kishi et al., J. Phys.: Condens. Matter, 24, 262001 (2012).

[5] H. Kasai et al., J. Jpn. Petroleum Institute, (2013) *accepted for publication*.

2:40pm MG-ThA3 Computer-aided Design of Materials for CO₂ Utilisation, N.H. de Leeuw, Unaffiliated, A. Roldan, N. Hollingsworth, J. Goodall, University College London, UK

INVITED

Despite the high thermodynamic stability of CO₂, biological systems are capable of both activating the molecule and converting it into a range of organic molecules, all of which under moderate conditions. It is clear that if we were able to emulate Nature and successfully convert CO₂ into fuel or useful chemical intermediates, without the need for extreme reaction conditions, the benefits would be enormous: One of the major gases responsible for climate change would become an important feedstock for the fuel, chemical and pharmaceutical industries!

Iron-nickel sulfide membranes formed in the warm, alkaline springs on the Archaean ocean floor are increasingly considered to be the early catalysts for a series of chemical reactions leading to the emergence of life. The anaerobic production of acetate, formaldehyde, amino acids and the nucleic acid bases - the organic precursor molecules of life - are thought to have been catalyzed by small cubane (Fe,Ni)S clusters which are structurally similar to the surfaces of present day sulfide minerals such as greigite (Fe₃S₄) and mackinawite (FeS).

Contemporary confirmation of the importance of sulfide clusters as catalysts is provided by a number of proteins essential to modern anaerobic life forms, e.g. ferredoxins or (de)hydrogenases, all of which retain cubane (Fe,Ni)S clusters with a greigite-like local structure, either as electron transfer sites or as active sites to metabolise volatiles such as H₂, CO and CO₂.

We have used a combination of computation, synthesis and electrochemistry to mimic Nature and produce Fe-S and Ni-doped Fe-S nanoparticles to catalyse the conversion of CO₂. Careful and sensitive testing of the computationally designed materials, prepared through novel synthesis routes, shows that the nanoparticles have the power to adsorb CO₂ and reduce it to formic acid - a useful chemical intermediate. A particularly promising aspect is that the catalytic conversion of CO₂ takes place at room pressure and temperature and at the sort of low voltages that could be obtained from solar energy, thus making it a sustainable process.

3:40pm MG-ThA6 Surface Technology Solutions: Materials Design for Aero-Engine Gas Turbine Applications, J.R. Rodgers, Toth Information Systems Inc., Canada

INVITED

Erosion damage of aero-engine compressor gas path components occurs to aircraft operating in sandy environment. Erosion can lead to gradual changes in surface finish and component geometry, which consequently alters the dynamic response characteristics of compressor airfoils, causing premature failure. One of the approaches to deal with erosion problems in gas turbine engines is to apply protective hard coating on the component surface. Hardness and ductility are two of the key values for the design and characterization of materials that are used for surface protection. These key values largely depend on the elastic properties of the material, as described by the elastic stiffness tensor. Materials informatics approaches and high-throughput computational materials science methods have been employed, to explore chemistry and property space, to aid the prediction, synthesis, characterization and property optimization of promising candidate materials, for protective hard coatings systems, with enhanced erosion resistance for application to gas turbine airfoils. These generic methods have been employed to explore multidimensional property space, at a previously unavailable level of detail and to rapidly calculate thermophysical properties that are difficult to measure. Given these vast resources of structure and property data it is possible to extract trends on the structure of materials and their properties and use these results at the materials selection and design stages. These informatics approaches, coupled with *ab initio* quantum mechanics methodologies, provide many of the tools needed to guide materials selection via computational experiments. Examples for the application of these methods coupled with the use of experiments for the design of materials for industrial applications will be presented. The results presented will highlight the potential of this combined - informatics, theoretical and experimental - research strategy to aid the manufacturing process.

4:20pm MG-ThA8 Exploring Electronic Structure in the Search for New Functional Materials, M. Klintonberg, Uppsala University, Sweden

INVITED

The Electronic Structure Project (ESP/ELSA)[1-3] is an initiative that dates back to 2001 [4,5] and today contain tens of thousands of materials that

have been investigated using robust and high accuracy electronic structure methods (all-electron full-potential linear muffin-tin orbital approach, FP-LMTO). A short history of the project, the present capabilities of ESP/ELSA including some examples of successful studies using ESP as well as future developments and outlook will be presented.

[1] <http://www.materialsgenome.se> (re-directed to <http://gurka.fysik.uu.se/esp>).

[2] A high accuracy fermi-surface database can be found at <http://gurka.fysik.uu.se/esp-fs>

[3] "Data mining and accelerated electronic structure theory as a tool in the search for new functional materials", C. Ortiz, O. Eriksson and M. Klintonberg. *Comput. Mater. Sci.* 44, 1042-1049 (2009)

[4] "A systematic search for new scintillators using electronic structure calculations", M. Klintonberg, S. E. Derenzo and M. J. Weber, *Nanotech*, 2, 427 (2002). Technical Proceedings of the 2002 International Conference on Computational Nanoscience and Nanotechnology, <http://www.nsti.org/procs/ICCN2002/16/W62.11>

[5] "Potential new scintillators identified by electronic structure calculations", M. Klintonberg, S. E. Derenzo and M. J. Weber, *Nucl. Inst. Meth. A*, 486, 298 (2002), <http://www.sciencedirect.com/science/article/pii/S0168900202007234>

5:00pm **MG-ThA10 Data-Driven Discovery of Physical, Chemical, and Pharmaceutical Materials**, *B.A. Jones*, IBM Almaden Research Center
INVITED

Data-driven insights have aided materials discovery in the pharmaceutical and related chemical areas for some years now, with even commercial products available. I will describe some successes in these areas, and derive lessons which might be applicable to the areas of condensed matter and polymeric materials. Three points which I will be emphasizing are that a) Just as experiment, theory, and computation must guide each other for MGI to succeed, a triangle of inter-relationships, for MGI it is really a tetrahedron, with computer science forming the fourth vertex. I will discuss the benefits which modern computer science can bring in the areas of modern data mining, machine learning, and big data analytics techniques. The volume of data on materials is fast-growing and scattered across many sources. While new tools and platforms have allowed the processing of vast volumes of data, our ability to integrate heterogeneous and unstructured data sets is still developing. The ability to correlate data from multiple sources deepens the value of data and allows new insights to emerge. b) The elements of accelerated materials discovery are different in the different scientific fields. Pharmaceutical discovery involves extracting chemical constituents and structures from patents; polymer data is scattered, unstructured, statistical and often ambiguous; and in condensed matter we tend to look at materials properties as a function of some parameter such as doping or temperature, often in graph form. Understanding the needs of both soft and hard condensed matter will help common tools and synergies to develop. c) There are many challenges ahead in fully incorporating data-enabled scientific discovery, as well as learning on both computer science and materials science sides. Getting scientific insights from both computer scientists and from data mining and databases is not yet common, and requires some work ahead in both communities to familiarize themselves with opportunities and to optimize the tools needed for future materials by design.

Friday Morning, November 1, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic

Room: 202 B - Session

MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM

Novel Synthesis Approaches and Innovative Characterization Techniques Coupled with Theory & Computations

Moderator: E.B. Svedberg, The National Academies, M.B. Holcomb, West Virginia University

8:20am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1 MWCT and Piezoelectric Thick Film Composites that Incorporate Graphene Electrodes, K. Cook-Chennault, S. Banerjee, R. Kappera, M. Chhowalla, Rutgers University**

Three-phase, PZT-Epoxy- Multi-walled Carbon-Nanotube (MWCNT) flexible thick films prepared by a combination of solvent and spin coating technique were prepared, where materials were spin coated onto flexible substrates. The substrates investigated included; stainless steel, graphene and graphene with PMMA. Graphene and graphene/PMMA films which were grown by a chemical vapor deposition process, and the film thicknesses were ~ 200 μm . The volume fraction of the MWCNTs was varied from 1% to 6%, while the PZT volume fraction was held constant at 30%. The strain coefficient and capacitance were measured as a function of the MWCNT volume fraction and used to determine the effective dielectric constant. Samples that incorporated graphene electrodes rendered higher dielectric properties in comparison to samples with graphene-PMMA. The maximum values of dielectric constant were ~ 4353, ~1945 and ~ 61, for samples with graphene, graphene/PMMA and no electrode respectively. Sample surface morphology and sample composition were observed using SEM and measured using Raman Spectroscopy respectively. Improved dielectric properties observed for samples with graphene coatings are due to graphene's high carrier mobility and its ability to readily conform to the surface of the sample.

8:40am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2 Morphological and Structural Characterization of Size-Selected Pt NPs Supported on TiO₂(110) and SiO₂/Si(111) via Polarized Total Reflection Fluorescence XAS in UHV, F. Behafarid, L.R. Merte, University of Central Florida, R. Gordon, Argonne National Laboratory, B. Roldan Cuenya, University of Central Florida**

A combination of polarized total reflection x-ray absorption spectroscopy (XAS) and atomic force microscopy (AFM) data have been used to determine the morphological properties of the size-selected micelle-prepared Pt nanoparticles (NPs) supported on TiO₂(110) and SiO₂/Si(111) in an ultrahigh vacuum (UHV) environment. The Pt NPs were cleaned in UHV using an O₂-plasma followed by annealing in O₂ (1x10⁻⁶ mbar) at 600°C after the *ex situ* sample transfer. Extended X-ray absorption fine-structure (EXAFS) measurements were carried out at Argonne National Laboratory in fluorescence mode. Measurements along different orientations, namely one perpendicular and two parallel to the sample surface were carried out on the Pt NPs supported on TiO₂(110). Our analysis revealed that while the Pt NPs on SiO₂ remained spherical, the NPs on TiO₂ wetted the substrate and adopted an epitaxial relationship with the support. It will be shown that the first shell EXAFS analysis of the data acquired along different directions provides valuable information regarding the size and aspect ratio of the NPs as well as the degree of disorder and strain in their structure. FEFF simulations were carried out on model NP shapes and the theoretical data compared with experimental EXFAS data.

9:00am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM3 Materials Control on a Nanoscale: Artificial Oxide Structures, D.H.A. Blank, MESA+Institute for Nanotechnology, University of Twente INVITED**

In general, nanotechnology provides the tools for controlling key parameters for thin films performance: chemical composition (and crystalline structure at nano-sized domains), thickness and topography (including nano-scale patterning of thin films' surface) and controlled interfaces at the nanoscale.

As research in nanotechnology develops, new characterization and production tools, new materials and process models as well as more computational power will become available. Nanotechnology is giving a new boost to thin films' application development.

Pulsed Laser Deposition (PLD) is one of the attractive research tools for complex materials because it is fast and one can easily investigate a wide range of different materials and compositions. Currently, a major issue in the growth of oxide materials with PLD is the control of the surface morphology. For most materials it is necessary to control the thickness and roughness of the thin films down to an atomic scale. Such well-controlled growth can also be used to manufacture artificially layered structures. In this way it is possible to create a whole new class of materials.

Much effort is put in the deposition of excellent textured layers without grain boundaries. In general the properties of highly oriented films approximate the properties of single crystals. Single or multi-layer structures require a well-conditioned process technique. The deposited layers must have a large homogeneity with well-defined material properties, smooth surfaces, and, in the case of oxides, the correct oxygen stoichiometry. Important is the possibility to combine PLD with standard *in-situ* diagnostic techniques, like *high pressure* Reflecting High Energy Electron Diffraction (RHEED).

With our development of pulsed laser deposition with control at atomic level we are able to control the growth of complex materials and to introduce new growth manipulations, like pulsed laser interval deposition. At present, new superlattices can be synthesized that exhibit rare properties, like multiferroics. Extremely sharp and homogeneous interfaces can be realized and this is, for example, yet utilized in SrTiO₃-LaAlO₃ interfaces and artificial ferroelectric structures. In this presentation I like to show this unique technique and their use in obtaining complex materials systems 'on demand'.

9:40am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM5 Catalytic Micro-/Nano- Motors Propelled by Bubbles, M.T. Manjare*, University of Georgia, Athens, B. Yang, University of Texas, Arlington, Y.P. Zhao, University of Georgia, Athens**

Catalytic Micromotors are micro- or nano- objects that use catalytic reaction, most commonly H₂O₂ --> H₂O + 1/2 O₂, to propel themselves in fluid environment. The motion of the motors can be controlled by designing different motor geometries and functionalizations and to perform variety of tasks such as cargo towing and biosensing. One of the mechanisms by which the motors move is bubble propulsion, i.e., the O₂ generated in the reaction forms bubbles and propel the motors by ejecting or bursting the bubbles. Bubble propulsion is proven to be the most efficient and fastest way to drive the motors. Here we report our new discoveries on bubble propelled catalytic motors. For spherical particles, electron beam evaporation method is used to coat half of their surface with Pt and to make them as Janus motors. A new bubble propelled quasioscillatory translational motion is observed only for big motors. The motion coincided with bubble growth and burst resulting from catalytic reaction. A physical model was proposed which explained that bubble growth imparts a growth force on the motor to move it forward and instantaneous local pressure depression due to bubble burst causes the motor to move backward. The competition of the two processes generates a net forward motion. The bubble propulsion mechanism involves hydrodynamics, growth kinetics, and mass/momentum transport. In order to understand the detailed mechanism, we have investigated the mass transport in microtubular jet engines, a major bubble propelled motor. A one dimensional mass transport model using basic principles of diffusion and reaction is built to explain the effect of environmental factors such as fuel concentration and of geometry on the motion. Numerical investigations of the motion-related parameters, such as O₂ flux, bubble generation rate and frequency, and average speed of the microjet motors during bubble growth, are found to depend closely on the length and opening radius of the microjet and the concentration of H₂O₂ in the surrounding environment. The theoretical results are in good agreement with the motion of Graphene oxide tubular microjet motors we have fabricated.

10:00am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM6 Erosion Resistant Physical Vapor Deposition Coatings for High Temperature Polymer Matrix Composites Applications, S. Dixit, M. Chin, R. Dixit, Plasma Technology Inc.**

The advantages of replacing metals in aircraft turbine engines with High-Temperature Polymer Matrix Composites (HTPMC's) include weight savings accompanied by high strength to weight ratio, and lower manufacturing costs. Most of the nacelle of a modern aero gas turbine is made of HTPMC, a component that accounts for approximately 25% of the weight and 20% of the cost of the power plant. Unfortunately, they are limited to applications where they are not exposed to high-temperature

* TFD James Harper Award Finalist

oxidizing atmospheres and/or particulates from ingested air. This is because oxidation and erosion occur on the surface, leading to weight loss, and/or cracking on the surface and a consequent decline of mechanical properties over time. Resistance to surface erosion is one rarely reported property of HTPMC's in engine applications because HTPMC's are generally softer than metals and their erosion resistance suffers.

Although prior research has shown that oxidation can be slowed down when metallic or ceramic coatings are applied onto HTPMC's, there remains a need for erosion-resistant coatings that protect HTPMC's from high-velocity particulates in the engine flow path. These erosion-resistant coatings could extend the life of polymer composites and also reduce the overall cost of the turbine assembly. Hence in this paper we report the development of coating materials that are compatible with HTPMC's such as Avimid N and AFR-PE-4 using Cathodic Arc Physical Vapor Deposition (CAPVD). We report the feasibility of applying multilayer PVD TiN coatings onto the HTPMC substrates and characterize their adhesion, microstructure and erosion resistance. We also show the effectiveness of duplex process of thermal spray and PVD to enhance the overall adhesion of the multilayer coating.

10:20am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM7 Poking Tips at Surfaces: Mechanical and Electronic Properties of Atomically Defined Interfaces.** *P. Grutter*, McGill University, Canada **INVITED**

How does stuff break? An important step in this process is inelastic deformation of the material, the formation of a first dislocation. We report on the for the first experiments which due to the small size and atomic scale control of the indenter allow a direct quantitative comparison with molecular dynamics simulations and state-of-the-art electronic transport theory.

We have studied the formation of the smallest permanent indentation in the Au(111) model surface by a combination of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) in ultrahigh vacuum (UHV). We use field ion microscopy (FIM) to characterize the nanometer scale spherical apex of the W(111) indenter in UHV prior to the indentation experiments [1,2]. Knowledge of the indenter geometry is necessary to extract quantitative parameters such as contact pressures and stresses within the sample during indentation.

Traditional nanoindentation measures depth to high precision, but typically does not possess the force resolution (nN) to detect initial plastic events [3]. Indentation with standard AFM allows for excellent force resolution, but large piezo displacements required to load the contact with a soft cantilever hamper the extraction of true indentation depth because of quantitative optical beam deflection calibration issues (beam placement, sensitivity to mode shape, etc.) and piezo creep. I will describe how our set-up overcomes these limitations and allows us to quantitatively assess elastic and plastic behaviour in an indentation curve.

We report on the transition from elastic to plastic deformation in the indentation of Au(111). This is done by producing arrays of indentations to forces near the plastic yield point and examining the resulting force-displacement curves for both elastic and plastic indentation sites. Plasticity can be identified by features in the force displacement curves, such as the sudden displacement excursions of the tip (pop-ins), the work done by the indenter, and the sink-in depth measured at mild repulsive loads. These indicators of plasticity can also be correlated with the permanent impressions in the surface imaged by STM. The measured forces at the initial yield points correspond to shear stresses lower than those expected for the homogeneous dislocation nucleation. We suggest that heterogeneous nucleation involving surface effects and atomic scale indenter roughness is likely to play a role in the observed plastic behaviour.

[1] W. Paul et al. *Nanotechnology* 23, 335702 (2012) [2] D. J. Oliver et al., *PNAS* 109, 19097 (2012) [3] Minor et al., *Nature Materials* 5, 697 (2006)

11:00am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM9 Functionalized Shape Memory Polyester Biomaterials.** *V. Sheares Ashby*, University of North Carolina at Chapel Hill **INVITED**

Functionalized Shape Memory Biomaterials

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Shape memory polymers (SMPs) are a class of smart materials that can change their shape in a predetermined fashion when exposed to the appropriate external stimulus. Since Langer and Lendlein first demonstrated the tremendous potential of SMPs in biomedical applications there has been a growing interest in utilizing these materials as intelligent medical devices and minimally-invasive implants. Our research focuses on several areas: micro- and nanotopography, reactive functionality and switching stimuli.

Recently, we have developed thermally responsive micro-patterned poly(ϵ -caprolactone) (PCL) shape memory films to examine the interaction of human mesenchymal stem cells (hMSCs) with dynamic surface patterns using PRINTTM (pattern replication in non-wetting templates). We have also begun research on novel polymer structures containing functionality with the goal of developing SMPs capable of micro- or nanoscopic shape memory and post-functionalization. Finally, there have been several examples of dual (one temporary shape) and triple shape memory (two temporary shapes). Our efforts focus on the synthesis of novel bifunctional monomers and biodegradable polyester prepolymers containing photo-responsive side groups (cinnamide or cinnamate) using a polycondensation method to allow uniform repeat units each possessing a photo group, followed by end-functionalization and crosslinking to create networks with photo and thermal shape memory switches. The synthesis of these materials, which has led to shape memory polymers with switching temperatures near physiological temperature and unique functionality, in addition to characterization of thermal and shape memory properties, will be presented. Fabrication of the patterned surfaces, initial cytotoxicity and cellular response to dynamic shape switching will also be discussed.

Authors Index

Bold page numbers indicate the presenter

— A —

Ablett, J.: SA+AS+MG+SS-TuA9, 3
Adelmann, C.: SA+AS+MG+SS-TuA9, 3

— B —

Balchandran, P.: MI+EM+MG-MoA10, 2
Banerjee, S.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1,
12
Barrett, N.: SA+AS+MG+SS-TuA3, 3
Behafarid, F.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2,
12
Bhattacharya, A.: MI+EM+MG-MoA10, 2
Blank, D.H.A.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM3,
12
Broadbridge, C.C.: MG+EN+MS-WeA1, 7

— C —

Cammarata, A.: MI+EM+MG-MoA10, 2
Cao, Y.: MG-ThA1, 10
Castro, G.R.: SA+AS+MG+SS-TuA4, 3
Ceder, G.: MG+EM+MI+MS-WeM9, 5
Chambers, S.A.: MI+EM+MG-MoA2, 1
Chen, D.: SA+AS+MG+SS-TuA10, 4
Chhowalla, M.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1,
12
Chin, M.: MG+AS+EM+NS+SA+SE+SP+SS+TF-
FrM6, 12
Chu, Y.-H.: SA+AS+MG+SS-TuA10, 4
Colby, R.J.: MI+EM+MG-MoA2, 1
Comes, R.B.: MI+EM+MG-MoA11, 2
Conard, T.: SA+AS+MG+SS-TuA9, 3
Cook-Chennault, K.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1,
12

— D —

de Leeuw, N.H.: MG-ThA3, 10
de Pablo, J.J.: MG+EM+MI+MS-WeM3, 5
Dixit, R.: MG+AS+EM+NS+SA+SE+SP+SS+TF-
FrM6, 12
Dixit, S.: MG+AS+EM+NS+SA+SE+SP+SS+TF-
FrM6, 12
Du, Y.: MI+EM+MG-MoA2, 1

— E —

Ediger, M.D.: MG+EM+MI+MS-WeM3, 5
Eom, C.: MG+EM+MI+MS-WeM11, 5

— F —

Fitz-Gerald, J.M.: MI+EM+MG-MoA11, 2
Fleischmann, C.: SA+AS+MG+SS-TuA9, 3
Floro, J.A.: MI+EM+MG-MoA11, 2

— G —

Giesen, D.J.: MG-ThA1, 10
Ginley, D.: MG+EM+MI+MS-WeM6, 5
Goldberg, A.: MG-ThA1, 10
Goodall, J.: MG-ThA3, 10
Gordon, R.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2,
12
Grutter, P.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM7,
13

— H —

Halls, M.D.: MG-ThA1, 10
Hoffman, J.: MI+EM+MG-MoA10, 2
Holcomb, M.B.: SA+AS+MG+SS-TuA10, 4
Hollingsworth, N.: MG-ThA3, 10
Hughes, T.F.: MG-ThA1, 10
Hwang, H.: MI+EM+MG-MoA8, 1

— J —

Jansson, U.: MI+EM+MG-MoA1, 1
Jenkins, C.: SA+AS+MG+SS-TuA10, 4
Jones, B.A.: MG-ThA10, 11

— K —

Kalpyris, I.: SA+AS+MG+SS-TuA9, 3
Kappera, R.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1,
12
Kasai, H.: MG-ThA2, 10
Kinlen, P.: MG+EN+MS-WeA9, 7
Klintonberg, M.: MG-ThA8, 10
Kwak, H.S.: MG-ThA1, 10

— L —

Lampenschurf, S.: MG+EN+MS-WeA3, 7
Lany, S.: MG+EM+MI+MS-WeM5, 5;
MG+EM+MI+MS-WeM6, 5
Lee, H.N.: MI+EM+MG-MoA3, 1
Levin, I.: SA+AS+MG+SS-TuA11, 4

— M —

Manjare, M.T.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM5,
12
Mao, F.: MI+EM+MG-MoA1, 1
Marcus, M.A.: SA+AS+MG+SS-TuA10, 4
Marder, M.: MG+EN+MS-WeA11, 8
Martinez, E.: SA+AS+MG+SS-TuA3, 3
Merte, L.R.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2,
12

— N —

Nelson-Cheeseman, B.: MI+EM+MG-MoA10, 2
Nyberg, T.: MI+EM+MG-MoA1, 1

— P —

Padama, A.A.: MG-ThA2, 10
Peng, H.: MG+EM+MI+MS-WeM5, 5
Perkins, J.: MG+EM+MI+MS-WeM6, 5
Pianetta, P.: SA+AS+MG+SS-TuA1, 3

— R —

Rabe, K.M.: MG+MI+NS-ThM5, 9
Rahman, T.S.: MG+MI+NS-ThM10, 9
Renault, O.J.: SA+AS+MG+SS-TuA3, 3
Rodgers, J.R.: MG-ThA6, 10
Roldan Cuenya, B.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2,
12
Roldan, A.: MG-ThA3, 10
Rondinelli, J.M.: MG+MI+NS-ThM9, 9;
MI+EM+MG-MoA10, 2
Rossner, W.: MG+EN+MS-WeA3, 7
Rubio-Zuazo, J.: SA+AS+MG+SS-TuA4, 3
Rueff, J.P.: SA+AS+MG+SS-TuA9, 3

— S —

Sapper, E.: MG+EN+MS-WeA9, 7
Sheares Ashby, V.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM9,
13
Shutthanandan, V.: MI+EM+MG-MoA2, 1
Sinnott, S.B.: MG+MI+NS-ThM3, 9
Sioncke, S.: SA+AS+MG+SS-TuA9, 3
Soffa, W.A.: MI+EM+MG-MoA11, 2
Steiner, M.A.: MI+EM+MG-MoA11, 2
Stevanovic, V.: MG+EM+MI+MS-WeM5, 5;
MG+EM+MI+MS-WeM6, 5

— T —

Thersleff, T.: MI+EM+MG-MoA1, 1

— V —

Van de Walle, C.G.: MI+EM+MG-MoA6, 1
Vandervorst, W.: SA+AS+MG+SS-TuA9, 3

— W —

Windl, W.E.: MG+EN+MS-WeA7, 7
Woicik, J.C.: SA+AS+MG+SS-TuA7, 3

— Y —

Yang, B.: MG+AS+EM+NS+SA+SE+SP+SS+TF-
FrM5, 12
Yu, L.: MG+EM+MI+MS-WeM3, 5

— Z —

Zakutayev, A.: MG+EM+MI+MS-WeM6, 5
Zhang, H.: MI+EM+MG-MoA2, 1
Zhao, Y.P.:
MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM5,
12
Zhou, H.: MI+EM+MG-MoA10, 2
Zhou, J.: SA+AS+MG+SS-TuA10, 4