

Monday Morning, October 19, 2015

Novel Trends in Synchrotron and FEL-Based Analysis

Focus Topic

Room: 112 - Session SA-MoM

Imaging and Nanodiffraction (8:20-10:00 am) & Novel Insights in Correlated Materials, Organic Materials and 2D Solids (10:40 am -12:00 pm)

Moderator: Herrmann Dürr, Stanford University, Petra Rudolf, University of Groningen

8:20am **SA-MoM1 Nanoscale Chemical Imaging by Soft X-ray Spectro-microscopy and Spectro-ptychography**, *Adam Hitchcock*, X.H. Zhu, McMaster University, Canada, *J. Wu*, McMaster University, D. Shapiro, T. Tyliczszak, Lawrence Berkeley Lab, University of California, Berkeley

INVITED

Recent improvements in instrumentation and data analysis for soft X-ray spectromicroscopy and spectro-ptychography have made significant advances in spatial resolution and sensitivity. These improvements are providing researchers with new tools to contribute to solving real world technological issues as well as making fundamental discoveries. This presentation will give an overview of the performance of current instrumentation, report on exciting advances taking place in soft X-ray spectro-ptychography, and outline opportunities for *in situ* and *operando* studies. Spectro-ptychography studies of the magnetism of individual magnetosomes in magnetotactic bacteria by X-ray magnetic circular dichroism (XMCD). Results for 2D and 3D chemical analysis of polymer-electrolyte fuel cells will be presented.

Research performed at the Advanced Light Source, funded by DoE, BES, and at the Canadian Light Source, funded by CFI, NSERC, U. Saskatchewan, Saskatchewan, WEDC, NRC and the CIHR. The SHARP code used for ptychographic data analysis was developed by the Center for Applied Mathematics for Energy Research Applications (CAMERA) at LBNL, led by Jamie Sethian, in collaboration with Uppsala University.

9:00am **SA-MoM3 Imaging Single Cells in a Beam of Live Cyanobacteria with an X-ray Laser**, *Gijs van der Schot*, Uppsala University, Sweden

INVITED

Imaging live cells at a resolution higher than achieved using optical microscopy is a challenge. Ultra-fast coherent diffractive imaging¹ with X-ray free-electron lasers (XFELs) has the potential to achieve sub-nanometer resolution on micron-sized living cells². Our container-free injection method can introduce a beam of live cyanobacteria into the micron-sized focus of the Linac Coherent Light Source (LCLS) to record diffraction patterns from individual cells, with low noise at high hit rates³. We used iterative phase retrieval⁴⁻⁶ to derive two-dimensional projection images directly from the diffraction patterns. Synthetic X-ray Nomarski images⁷, calculated from the complex-valued reconstructions, show cells in a similar manner to what one would expect to see using a Nomarski microscope, only at higher resolution than currently available. In a first experiment, we collected diffraction patterns to 33-46 nm full-period resolution, and reconstructed the exit wave front to 76 nm resolution³. In a second experiment, we demonstrate that it is indeed possible to record diffraction data to nanometer resolution on live cells with an intense, ultra-short X-ray pulse as predicted earlier^{2,3}. These results are encouraging, and future developments to the XFELs and improvements to the X-ray area-detectors will bring sub-nanometer resolution reconstructions of living cells within reach.

We thank the Swedish Research Council, the Knut and Alice Wallenberg Foundation, the European Research Council, the Röntgen-Ångström Cluster, and Stiftelsen Olle Engkvist Byggmästare for supporting this work.

References

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3. van der Schot, G. *et al.* Imaging single cells in a beam of live cyanobacteria with an X-ray laser. *Nat. Commun.* **6**, 5704 (2015).
4. Gerchberg, R.W. & Saxton, W.O. Practical Algorithm for Determination of Phase from Image and Diffraction Plane Pictures. *Optik***35**, 237-246 (1972).

5. Fienup, J.R. Reconstruction of an Object from Modulus of Its Fourier-Transform. *Opt. Lett.***3**, 27-29 (1978).

6. Luke, D.R. Relaxed averaged alternating reflections for diffraction imaging. *Inverse Probl.***21**, 37-50 (2005).

7. Paganin, D. *et al.* X-ray omni microscopy. *J. Microsc.***214**, 315-327 (2004).

10:00am **SA-MoM6 Nanoscale Tomography and Spectroscopy with the HZB X-ray Microscope**, *Gert Schneider*, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany

The Helmholtz-Zentrum Berlin (HZB) operates a full-field transmission X-ray microscope (TXM) at the BESSY II electron storage ring. The advanced optical setup of the HZB-TXM permits NEXAFS spectroscopic applications as well as correlative fluorescence and nanoscale tomographic imaging of cryogenic fixed cells in a fully hydrated state. An overview of recent results in material and life sciences will be presented [1-8]. Investigations on TiO₂ nanostructures using NEXAFS spectromicroscopy at the Ti-L- and O-K-absorption edges will be shown [1,2]. Additionally, first results on the nanoscale morphology of organic solar cells will be discussed. Reconstructions taken from 3D X-ray datasets allow to visualize sub-cellular ultrastructures in mammalian and plant cells e.g. algae. Quantitative studies as e.g. the number of cell organelles in the cell volume are possible [4]. Scientific findings on the nucleation of hemozoin in *Plasmodium falciparum* by nanoscale tomography with the HZB-TXM will be demonstrated [5]. Studies of the interaction of viruses like the Herpes virus [6] or vaccinia virus [7] with mammalian cells will be presented. In addition, nanoscale X-ray tomography paves the way to a better understanding of the interaction of nanoparticles with cells [8].

[1] P. Guttman *et al.*, *Nature Photonics* **6** (2012), 25-29

[2] K. Henzler *et al.*, *Nano Letters* **13** (2013), 824-828

[3] G. Schneider *et al.*, *Nature Methods* **7** (2010), 985-987

[4] E. Hummel *et al.*, *PLoS ONE* **7** (12) (2012), e53293

[5] S. Kapishnikov *et al.*, *PNAS* (2012) DOI: 10.1073/pnas.1118120109

[6] C. Hagen *et al.*, *J. Struct. Biol.* **177** (2012), 193-201

[7] FCO J. Chichon *et al.*, *J. Struct. Biol.* **177** (2012), 202-211

[8] D. Drescher *et al.*, *Nanoscale* **5** (2013), 9193-9198

10:40am **SA-MoM8 Exploring All-optical Magnetic Switching with Resonant X-rays**, *Alexander Reid*, SLAC National Accelerator Laboratory

INVITED

The ability to write a magnetic 'bit', a stable magnetic domain, with a single sub-picosecond optical pulse is now known and demonstrated in magnetic materials from amorphous ferrimagnets, such as GdFeCo, to crystalline ferromagnets, such as FePt. However, understanding the underlying physics of this process remains a fundamental challenge in magnetism dynamics. The process of all-optical switching of magnetization begins with the absorption of the optical pulse by the magnetic material, this creates a highly non-equilibrium state. The evolution of this state is controlled by many factors, from fundamental coupling interactions to material heterogeneity. Resonant x-rays allow a powerful tool for exploring the evolution of this non-equilibrium state and beginning to answer questions about how and why reversed magnetic order can emerge deterministically. Powerful new x-ray sources, such as the Linac Coherent Light Source, produce femtosecond x-ray pulses with a high spatial coherence and brightness. Using such sources, and techniques such as x-ray circular magnetic dichroism, the transient elemental magnetism can be monitored during the switching process. Further, the intrinsically shorter wavelength of x-rays enables monitoring of the spatial aspects of the switching process down to length scales of a few nanometers. We detail recent measurement of the spatio-temporal dynamics of the switching process in the prototype materials GdFeCo and TbFeCo, which have led to new insights about the evolution of the optical magnetic switching process.

11:20am **SA-MoM10 Ultrafast Dynamics in Magnetic Systems**, *Gerhard Grubel*, Magnetic Dynamics, Germany

INVITED

Ultrafast Dynamics in Magnetic Systems

Gerhard Grubel

DESY and The Hamburg Centre for Ultrafast Imaging (CUI)

Hamburg, Germany

Understanding ultrafast magnetization Dynamics on the nano-scale is a forefront problem in modern magnetism research with direct impact on the quest for faster and smaller storage devices. Probing the magnetization

element-specifically and on the nanometer length-scale is a pre-requisite when probing technologically relevant material systems with complex composition.

X-ray free electron laser (FEL) sources with their unique properties delivering ultrashort and super intense soft X-ray pulses allow for the first time to address magnetization dynamics on the relevant time-and length scales.

We present recent results obtained on multi-domain Co/Pt magnetic multilayer samples with perpendicular magnetic anisotropy, pumped with short IR and THZ pulses. As a probe we use small angle X-ray scattering from the magnetic domains which, via X-ray magnetic circular dichroism at the Co M-edge, allows us to simultaneously obtain information on the magnitude of the local magnetization and the characteristic length scale of the domains. The FEL sources FLASH at DESY (Hamburg) and FERMI at ELECTRA (Trieste) were used at a wavelength of 20.8 nm corresponding to the CO M-edge.

Monday Afternoon, October 19, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-MoA

Ambient Pressure X-ray Photoelectron Spectroscopy Studies for Catalytic and Energy Materials in Gas Phase

Moderator: Peter Crozier, Arizona State University, Franklin (Feng) Tao, University of Kansas

2:20pm **IS+AS+SA+SS-MoA1 In situ Electron Spectroscopy for Energy Science, Robert Schlögl**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

The use of volatile renewable electricity in larger amounts in our energy systems requires grid-scale technologies for integration electricity in material energy carrier streams. Several systemic options always suffer from our conceptual weakness to convert free electrons in chemical bonds. This can be achieved with accumulators for limited applications and should be done through water splitting and synthesis of solar fuels in almost unlimited applications. Complex interfacial chemistry is the underlying scientific challenge. To tackle this old challenge with new concepts it is essential to improve our ability to study chemical, electronic and geometric structures of nanoscopic objects in-situ meaning under operation conditions. A whole train of dedicated instrumentation from specimen formation, data acquisition and auxiliary analyses plus sample manipulation is necessary for this task. The presentation gives some aspects of priority challenges and uses examples of operation studies of water splitting catalysts and of CO₂ reduction systems to illustrate the present status of insight. In the outlook the possibilities of the novel experiment EMIL at BESSY will be discussed.

3:00pm **IS+AS+SA+SS-MoA3 Catalysis on Singly Dispersed Bimetallic Sites on Oxide Support, Luan Nguyen**, University of Kansas, A. Frenkel, Yeshiva University, J. Li, Tsinghua University, China, F. Tao, University of Kansas

Reaction events of heterogeneous catalysis occur on specific catalytic sites. Atoms of a catalytic site arrange in a specific geometric/electronic configuration for adsorbing/dissociating reactant molecules and subsequent coupling to form product molecules. Bimetallic catalysts play significant roles in chemical and energy transformations due to their tunable catalytic properties through ligand, geometric, bi-functional, or lattice strain effect.

When a bimetallic site (M_1A_n , M and A: metal elements, $n \geq 1$) is one of the continuous sites on the surface of a bimetallic NP, this site is in a metallic state. However, when M_1A_n sites are *separately* anchored on a surface of a transition metal oxide support, these isolated bimetallic sites are in cationic state. Such change in electronic structure could cause these bimetallic sites to have stronger chemisorption to reactant or/and intermediate molecules, thus facilitating its dissociation and subsequent coupling. In addition, singly dispersion of metal M in M_1A_n minimizes the potential binding configurations of reactant molecules hence may enhance catalytic selectivity toward a specific reaction pathway. Here we present singly dispersed bimetallic catalyst Rh_1Co_3 prepared on Co oxide support, which exhibits 100% selectivity for the production of N₂ in NO reduction with CO.

Preparation of isolated bimetallic sites Rh_1Co_3 on Co_3O_4 nanorods begins with the formation of hydroxide species $Rh(OH)_n$ on the surface of Co_3O_4 , followed by calcination at 150°C in O₂ to form Rh-O-Co bonds between singly dispersed $Rh(OH)_n$ species and the surface of Co_3O_4 , and concluded with a carefully controlled reduction to remove oxygen atoms between Rh and Co and thus a simultaneous formation of Rh-Co bonds. In-situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to monitor the oxidation and reduction steps and to avoid over or under-reduction.

Formation of singly dispersed Rh atoms was visualized using HAADF-STEM. The bonding environment of Rh to three Co atoms was confirmed using in-situ EXAFS. For reduction of NO with CO, Rh_1Co_3/CoO exhibits high activity at 110 °C with 100% selectivity toward N₂ production. In contrast, Rh-Co alloy NP/CoO has much lower activity and selectivity (10%) under the same condition. In-situ AP-XPS investigation shows that Rh atoms are at cationic state instead of metallic state. Along with this, DFT calculations suggest that a strong adsorption of intermediate N₂O molecules on Rh_1Co_3 site prevents its desorption as a byproduct and provides a dissociation pathway of N₂O to N₂ with a low activation barrier (~0.21 eV), thus leading to a 100% selectivity to N₂ production.

3:20pm **IS+AS+SA+SS-MoA4 Oxidation and Recovery of WC Thin Film Surfaces, E. Monazami**, University of Virginia, J.B. McClimon, University of Pennsylvania, N. Johansson, P. Shayesteh, S. Urpelainen, J. Schnadt, Lund University, Sweden, Petra Reinke, University of Virginia

Transition metal carbide (TMC) surfaces are coveted as catalytic materials, electrodes and hard protective coatings. A bottleneck in their use is surface oxidation, which leads to a decay in performance. Our work establishes the feasibility of surface recovery by using a carbon-rich WC layer where recarbonization of the surface is initiated by an annealing step. Thin carbon-rich tungsten carbide layers are grown by co-deposition of W and C₆₀ on a MgO(001) surface at 1100 K. The MgO substrate serves as a diffusion barrier for carbon, and the films have a well-defined carbon inventory controlled by the deposition rates of the reactants. The film surfaces were studied by in-situ Scanning Tunneling Microscopy and Spectroscopy. Raman spectroscopy confirmed the presence of highly defective graphitic carbon. The oxidation-recarbonization (O-R) cycles were studied in the ambient pressure endstation SPECIES at MAX-Lab (J. Synchr. Rad. 701, 19 (2012)) in a pressure of 0.3 mbar of O₂. Oxidation with $p(O_2)$ of 10^{-5} mbar were performed at SPECIES for direct comparison to low $p(O_2)$ STM experiments.

The carbon-rich WC films exhibit a relatively rough surface, which allows only in a few instances true atomic resolution, but graphite as well as graphene layers can be identified. Oxidation at $T > 550$ K leads to etching of surface carbon and the growth of a W-oxide layer and STS maps show the oxide evolution. The oxidation in the low $p(O_2)$ pressure regime progresses slowly and the surface carbide is recovered by annealing.

The use of the SPECIES endstation enabled a quantitative study of the O-R cycles including a detailed analysis of the respective bonding environments which are modified at different times in the O-R cycle. The oxidation in the ambient pressure environment was monitored using the ratio of W-carbide to W-oxide in the W4f core level during the reaction. The steady state thickness of oxide is a function of sample temperature and order of annealing cycles. The surface carbide concentration can be fully recovered in a subsequent annealing step, and repeated O-R cycles were performed. The O-R process is controlled by the interplay between surface oxidation, oxygen and carbon diffusion and our results will be modeled with a simple set of transport equations. We will discuss the role of different bonding environments as we move through the O-R cycle and compare UHV and ambient pressure results up to 800 K. These results clearly illustrate that carbon-rich tungsten carbide materials can be used to achieve a long term use of carbide surfaces in catalysis and fuel cell applications.

supported by NSF-Division of Materials Research (Ceramics) DMR-100580, STINT award.

3:40pm **IS+AS+SA+SS-MoA5 Microscopy, Spectroscopy, and Reactivity of Surfaces in Vacuum and under Ambient Reaction Pressures, Miquel Salmeron, B. Eren**, Lawrence Berkeley National Laboratory **INVITED**

The goal of surface science research is to provide atomic level understanding of the structural and dynamic properties of surfaces, a goal particularly relevant for chemical applications, including catalysis, photochemistry, batteries and fuel cells. With X-ray Photoemission Spectroscopy (XPS) and X-ray absorption Spectroscopy (XAS) we determine composition and electronic structure. With Scanning Tunneling Microscopy (STM) we image atoms and molecules as they adsorb, diffuse and react on single crystal surfaces. To study surfaces in the presence of gases, in the Torr to Atmospheres range, which is relevant to practical catalysis, new instrumentation is needed. Over the last years we developed high pressure STM, XPS and XAS, to study surfaces under high coverage of adsorbates in equilibrium with gases near ambient pressures and temperature. Using a combination of these techniques I will show how under these conditions the structure of surfaces and the adsorbed layers can be very different from that at low coverage, or even at high coverage but at low temperature. Adsorbates can induce dramatic restructuring of the surface, as I will show in the case of CO induced restructuring of Cu surfaces and the reactions with Oxygen.

4:20pm **IS+AS+SA+SS-MoA7 Novel Solutions for Ambient Pressure and In Situ Photoelectron Spectro-Microscopy, Hikmet Sezen, M. Amati, L. Gregoratti**, Elettra-Sincrotrone Trieste, Italy

A technique based on photoelectron spectroscopy (PES) providing simultaneously spectroscopy and microscopy capabilities and being compatible with ambient pressure conditions is still missing. Ambient pressure PES (APPES), based on differential pumping of the electron energy analyzer, offers an optimal spectroscopic solution to overcome

pressure barrier for surface related studies[1]. Unfortunately, APPEs has very limited spatial resolution. On the other hand, a better than 100 nm spatial resolution scanning photoelectron microscope (SPEM), where the X-ray beam is demagnified down to a 130 nm spot by Zone Plate Fresnel optics and the sample scanned under the focused beam, is accessible from a few synchrotrons. A direct adaptation of the APPEs approach to SPEM technique is not possible because of geometric constraints, stabilities and sustainability of the x-ray optics under near ambient pressures, and mechanical stability of the photoelectron detection system under such severe pumping conditions. In this presentation we will introduce two novel solutions for near-ambient pressure SPEM with ~100 nm spatial resolution and compatible with in-situ/operando conditions operated at ESCAmicroscopy beamline at Elettra synchrotron facility.

Dynamic high pressure (DHP) is the one of our near-ambient pressure SPEM solution. The technique is based on generating high pressure pulsed gas packets directed to the sample. Under influence of gas pulses the sample feels a few mbar pressure in a burst instant, then gas packets dilute into the SPEM chamber to yield a 1×10^{-5} mbar background pressure. From the test results a 10^{-3} - 10^{-2} mbar equivalent static pressure was felt by Si and Rh samples during in-situ oxidation reaction.[2] It is available for users.

Effusive cell is another solution for near-ambient pressure SPEM. The sample is encapsulated with a vacuum sealed cell and located just 30-50 μm behind of a 200 μm diameter size pinhole. The focused x-ray beam are scanning the sample through the pinhole. The generated photoelectrons come out from the same pinhole and are able to reach the electron energy analyzer. Due to the geometric orientation of energy analyzer and the pinhole we can achieve ca. a $200 \times 100 \mu\text{m}^2$ aerial point of view on the sample. The pressure inside the cell can be raised up to mbar range while the pressure in the main chamber kept around 1×10^{-5} mbar which is the safety limit for SPEM system. An encapsulated filament is behind the sample for heating, and other electrical connections are ready for biasing of sample, and thermocouple connections.

[1] D. F. Ogletree, et al. Rev. Sci. Instrum. 73, 3872 (2002)

[2] M. Amati, et al. J. Instrum. 8, 05001 (2013)

4:40pm **IS+AS+SA+SS-MoA8 In Situ Studies of Partial Oxidation of Methanol to Hydrogen on Isolated Bimetallic Site Pt₁Zn_n, Shiran Zhang, L. Nguyen, University of Kansas, A. Frenkel, Yeshiva University, J. Liu, Arizona State University, F. Tao, University of Kansas**

Partial oxidation of methanol to hydrogen and carbon dioxide offers a novel route in converting liquid fuel to hydrogen for fuel-cell systems and thus has been widely investigated in the past decade. One important category of heterogeneous catalysts for catalyzing this reaction is bimetallic nanoparticles which consist of continuous bimetallic sites in a metallic state. Isolation of such bimetallic sites through anchoring them on oxide could offer distinctly different catalytic performance in contrast to continuous sites on bimetallic nanoparticles.

Here we reported an isolated bimetallic site Pt₁Zn_n supported on ZnO which offers an extremely high catalytic activity with high selectivity for transformation of methanol to hydrogen with oxygen. It was prepared through a restructuring of singly dispersed Pt atoms on ZnO with reducing treatment. The formed isolated Pt atoms on ZnO was characterized with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along the projected [10-10] of ZnO as well as the corresponding structural model (Figure 1). The bright spots show single dispersion of Pt atoms. The offset of Pt atoms to the Zn atom row suggests Pt atoms are on the column of oxygen atoms, which indicates the bonding of Pt atom to Zn atoms. Photoemission features of Pt4f of the catalyst during catalysis were tracked with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) using monochromated Al K α (Figures 2). The resultant partial reduced state of Pt atoms under reaction conditions is consistent with the electronic state of Pt in Pt₁Zn_n bimetallic site.

Catalytic performance of the formed isolated Pt₁Zn_n bimetallic site in partial oxidation of methanol was evaluated and compared with Pt-Zn bimetallic nanoparticle catalyst (Figure 3). Isolated Pt₁Zn_n bimetallic site catalyst exhibits much higher activity per active site and selectivity to H₂ than Pt-Zn nanoparticle catalyst in transformation of methanol to hydrogen through partial oxidation. The cationic nature of these isolated bimetallic site in contrast to the metallic nature of active sites on a nanoparticle could be responsible for the differences in catalytic performance. This study illustrates that isolation of continuous bimetallic sites on a nonmetallic support is a new opportunity to tune catalytic performance of bimetallic catalysts.

5:00pm **IS+AS+SA+SS-MoA9 New Developments in Small Spot and Imaging Near Ambient Pressure XPS, Andreas Thissen, SPECS Surface Nano Analysis GmbH**

Over the last 15 years, Near Ambient Pressure (NAP-) XPS has demonstrated its promising potential in a wide variety of applications. Starting from the Catalysis and Ice paradigm, the focus has shifted towards solid-liquid interfaces, liquid jets and in-situ electrochemistry. Initially, the experiments had to be carried out using advanced synchrotron sources to reach reasonable count rates. But now, the SPECS PHOIBOS 150 NAP offers optimized transmission for electrons, even at pressures up to and above 100mbar, so researchers can now use it with conventional X-ray and UV sources in their own laboratories. Because of the widened application fields, standard XPS is now also attainable when combined with easily adjustable monochromated X-ray sources that offer stable operation, small excitation spots, and high photon flux densities, even in Near Ambient Pressure conditions. The latest designs and results are presented showing small spot performance for spot sizes < 30 μm , while also showcasing the latest implementations of imaging NAP-XPS that uses a new concept allowing for lateral resolved measurements without a compromise in count rate and usability. Highlighting on how sample environments (in situ cells for gases and liquids, electrochemical cells, gas inlets) and integration are both absolutely essential to obtain relevant results from well-defined samples, the presentation will demonstrate the use of NAP-XPS systems for high throughput-XPS measurements, as well as a variety of applications.

5:20pm **IS+AS+SA+SS-MoA10 In Situ Measurement of the Abundances and Temperatures of the Constituents of Semiconductor Manufacturing Plasmas via Terahertz Absorption Spectroscopy: Comparison with Theoretical Models, Yaser Helal, C.F. Neese, F.C. De Lucia, The Ohio State University, A. Agarwal, B. Craver, P.R. Ewing, P.J. Stout, M.D. Armacost, Applied Materials, Inc.**

Plasmas used by the semiconductor manufacturing industry are similar in pressure, temperature, and electron density to those used for the laboratory study of astrophysical neutrals, ions, and radicals. Thus, methods developed over several decades in the submillimeter/terahertz spectral region are directly applicable. Important attributes of terahertz absorption spectroscopy are that it can provide from first principles, without need for calibration, absolute concentrations and temperatures. Furthermore, since there are no intrusive probes, terahertz observations do not impact or change the plasma under study. Such measurements provide details and insight into the interactions and reactions occurring within the plasma and their implications for semiconductor manufacturing processes. In this work, a continuous wave, 0.5 – 0.75 THz absorption spectrometer was developed and used to study the processes in a commercial inductively coupled plasma (ICP) etch chamber. Because of the relatively long wavelength of the terahertz radiation, diffraction is more serious than in the optical regime. As a result, an important part of this work was the development of optical strategies to couple this spectrometer to the plasma reactor using its existing viewports. Comparisons of the experimental results with predictions from equipment models for ICPs will also be presented for Ar/CF₄/CHF₃ with varying pressures, powers, and gas mixture ratios. Comparisons such as this provide a basis for validating and improving models, whose development is a complex and difficult science in itself. The results presented in this talk show that terahertz rotational spectroscopy can provide unique and easy to interpret information about manufacturing plasmas and is a useful development tool for process, theoretical and physical models, and the improvement of etch methods.

**Novel Trends in Synchrotron and FEL-Based Analysis
Focus Topic**

Room: 112 - Session SA-MoA

**New Insights in Correlated Materials, Organic Materials
and 2D Solids**

**Moderator: Herrmann Dürr, Stanford University, Petra
Rudolf, University of Groningen**

2:20pm **SA-MoA1 Operando Soft X-ray Spectromicroscopy on Electronic States of Graphene Transistors, Hirokazu Fukidome, Tohoku University, Japan**

Graphene, the tiny monolayer honeycomb, is promising for high-speed communication owing to excellent electronic properties, such as carrier mobility and saturation velocity, arising from a linear band dispersion, and vanishment of short-channel effects owing to ultrathinness of graphene. The ultrathinness, on the other hand, deteriorates device performances because the ultrathinness easily induces interface modulation of electronic properties

of the graphene channel in the graphene transistor. This produces a gap between material properties of graphene layers and device performances of graphene transistor.

To bridge the gap, we have developed operando observation, i.e. observation under operation (gate-bias application in this work), of electronic states using soft x-ray spectromicroscopies with spatial resolutions of 20-100 nm, such as photoemission electron microscopy (PEEM) [1] and three-dimensional scanning photoelectron microscopy (3D nano-ESCA) [2]. This operando PEEM reveals gate-bias-dependent modulation of electronic states of the lateral interface between the graphene channel and contact metal. This interface modulation is brought about by the charge transfer between the graphene channel and the metal contact in the lateral direction. The charge transfer region is relatively large owing to a limited density of states near the Dirac point of graphene. In addition, the operando 3D nano-ESCA directly evidences the linear band dispersion of the graphene transistor in operation by doing a pinpoint C 1s core-level spectromicroscopy at the center of graphene channel, followed by analyzing the shift of the graphene peak by the gate bias.

In conclusion, these operando spectromicroscopies provides valuable information on graphene transistors. Further operando spectromicroscopy study is in progress to clarify the reason for degradation of high-frequency performances of the graphene transistor [3].

Profs. Oshima, Horiba and Kotsugi and Dr. Nagamura and staff members of BL17SU and BL07LSU of SPrinb-8 are gratefully appreciated for the operando spectromicroscopy. This work has been done partly as the projects of BL07LSU and BL17SU at SPring-8 and also as the academic-industry alliance NEDO project.

[1] H. Fukidome et al., *Sci. Rep.* 4 (2014) 3713.

[2] H. Fukidome et al., *Appl. Phys. Exp.* 7 (2014) 065101

[3] M.-H. Jung, H. Fukidome et al., *Proc. IEEE* 101 (2013) 1603.

2:40pm SA-MoA2 Micro-metric Electronic Patterning of a Topological Band Structure using a Photon Beam, Nick de Jong, E. Frantzeskakis, B. Zwartsenberg, Y. Huang, B.V. Tran, P. Pronk, E. van Heumen, D. Wu, Y. Pan, University of Amsterdam, M. Radovic, Paul Scherrer Institute, N.C. Plumb, N. Xu, Paul Scherrer Institut, M. Shi, Paul Scherrer Institute, A. de Visser, M.S. Golden, University of Amsterdam

We discuss a method of “writing” spatial micro-metric patterns in the electronic surface band structure of the topological insulator (TI) $\text{Bi}_{1.46}\text{Sb}_{0.54}\text{Te}_{1.7}\text{Se}_{1.3}$. Due to fine-tuning of the bulk stoichiometry this material is truly insulating, making it a promising candidate for applications where the special transport properties of the topological protected surfaces states are necessary. However despite the insulating character bulk in transport experiments, the spectroscopic fingerprint of $\text{Bi}_{1.46}\text{Sb}_{0.54}\text{Te}_{1.7}\text{Se}_{1.3}$ is not that of an insulator. Due to band bending, the conduction band is partly occupied at the surface of the material. We present a way to counteract the occupation of the conduction band in both global and local spatial scales. Namely, we make use of an extreme ultra violet photon beam with superband gap energy and a flux exceeding 10^{21} photons/(s m^2) as a “writing tool”. This is a three-step process. First an area of approximately 500 mm x 500 mm is mapped out by angle resolved photoemission spectroscopy (ARPES), taking a spectrum of the topological surface state at each sample location. Secondly, we expose selected sample locations to a higher fluence photon beam. These locations form a pre-defined pattern. Finally, the first map of the area is then again by ARPES. In this way we are able to shift the electronic surface band structure and drive the bulk conduction band to the unoccupied part of the spectrum. This shift is observed to be very local and in our case is only limited by the size of the beam and not by the approach itself.

3:00pm SA-MoA3 Switching 2D Materials Properties with Light, Alessandra Lanzara, University of California, Berkeley INVITED

Understanding how superconductivity emerges from other competing phases and how this balance evolves through the phase diagram is one of the biggest challenges in the field of high Tc superconductors. By using high resolution time- and angle- resolved photoemission spectroscopy (tr-ARPES) we are able to directly probe the effects of optical excitation on the electronic structure of cuprate superconductors, and study the resulting quasiparticles, superconducting gap, and Cooper pair formation dynamics near their natural time- scales. Direct measurements of these and other non-equilibrium spectral phenomena through the phase diagram further illustrate the power of this unique time- and momentum-resolved spectroscopy. These results reveal new windows into the nature of the pairing interaction in high Tc superconductors.

3:40pm SA-MoA5 Science-driven Requirements for Soft X-ray Free Electron Lasers, Fulvio Parmigiani, Elettra-Sincrotrone Trieste, Italy INVITED

Starting from the archetypal FERMI externally seeded FEL, recent theoretical and experimental progress has shown the possibility of producing fully coherent, variable polarization and tunable, soft-X-ray, ultra-short pulses at high repetition rate. This ultimate achievement will unlock the gate for performing X-ray-based experiments that are qualitatively different from those available at any current or planned X-ray source. Here we will review the experiments and the ideas that represent the science frontier in soft X-ray, time-resolved spectroscopy, coherent imaging and scattering experiments. These studies will lead to an understanding of fundamental dynamics, occurring on the ultrafast time and nanometer spatial scales, needed for addressing a broad range of science essential for resolving our complex and long-term energy challenges, environmentally urgent questions and demanding problems in bioscience and novel materials.

4:20pm SA-MoA7 Revealing Spin Texture Dynamics in Complex Materials via Time-resolved Resonant Soft X-ray Scattering, Robert Schoenlein, Lawrence Berkeley National Laboratory INVITED

Self-organized mesoscale spin textures emerge in complex materials due to coupling between charge, spin, and lattice degrees of freedom, and play a significant role in establishing the exotic properties of these materials. Here we focus on two examples: (1) topologically-protected spin vortices (Skyrmions) in the insulating multiferroic Cu_2OSeO_3 which result from a combination of symmetric spin-exchange interactions, and antisymmetric exchange resulting from a Dzyaloshinskii-Moriya (DM) interaction, and (2) helical spin states in the lanthanide metal Dy which result from competition between spin-orbit coupling, magneto-elastic effects, and long-range exchange coupling mediated by the indirect RKKY interaction.

A key scientific challenge is to understand the origin of these ordered spin textures, and the fundamental mechanisms and time-scales for manipulating these phases, in order to develop a knowledge base for potential technology applications. Resonant X-ray scattering (RXS) is a powerful direct probe of charge, spin, and orbital ordering in complex materials. Current synchrotron X-ray sources and new X-ray free-electron lasers enable RXS to be applied in the time domain. This provides an important new route to disentangle the cause-effect interactions that drive the formation and evolution of spin textures in complex materials.

Optical pump and resonant X-ray scattering studies of the skyrmion phase in Cu_2OSeO_3 reveal six-fold symmetric magnetic peaks that appear as satellites around the (001) Bragg peak. Transient optical excitation at 2.3 eV (above band gap) suppresses the spin ordering on a ~40 ps time scale – significantly faster than from excitation below gap at 1.5 eV, indicating an electronically-driven collapse of the skyrmion phase. We will discuss the fluence dependence of the conical and skyrmion phases and the motion of the ordering wavevector in response to excitation above and below the insulating gap.

We also report on recent studies of an epitaxially grown Y/Dy/Y multilayer film to understand the dynamics of the core-level spin helix in response to excitation of the conduction electrons responsible for the exchange interactions. Ultrafast optical excitation at 1.5 eV results in ultrafast injection of unpolarized spins into the 500 nm Dy film via nonequilibrium diffusion. The subsequent dynamics of the helical phase, revealed by time-resolved resonant X-ray scattering, differ significantly from those observed in ferromagnetic materials due to the relationship between the core spins and conduction electron Fermi surface nesting.

5:00pm SA-MoA9 Electronic States of Functional Molecular Materials Probed by Low-energy Excitation, Satoshi Kera, Institute for Molecular Science, Japan INVITED

Understanding the impacts of electron-phonon coupling as well as weak intermolecular interaction on the electronic state is required to discuss the mechanism of charge transport in functional molecular materials. Ultraviolet photoelectron spectroscopy (UPS) is known to be a powerful technique to study the electronic states. However, the experimental study of fine features in the highest occupied molecular orbital (HOMO) state has not been progressed till recently due to difficulty in the sample preparation, damages upon irradiation and so on, though it can offer a variety of key information, that is essential to comprehend charge-hopping transport and small-polaron related transport in the ordered monolayer film [1] as well as to coherent band transport in the molecular single crystal [2,3]. We present recent findings regarding on the precise measurements of electronic states for large aromatic organic molecular materials by using low-energy excitation UPS.

Use of low-energy excitation realizes unique experiments to find out the followings as an advantageous for the organic materials; i) low-kinetic energy of photoelectron may achieve resonance excitation channel to open

eyes for many events accessed, e.g. on a degree of electron cloud localization, inelastic scattering phenomena at the interfaces and a breaking the sudden approximation, and ii) high-photoionization cross section and bulk-sensitive probe may detect a quasi-particle state in very narrow HOMO band. Combining all findings above mentioned, characteristics of an electron in the functional molecular material has been embossed.

[1] S. Kera et al., Prog. Surf. Sci. 84 (2009) 135.

[2] N. Ueno et al., Prog. Surf. Sci. 83 (2008) 490.

[3] S. Ciuchi et al., Phys. Rev. Lett. 106 (2011) 166406.

Tuesday Morning, October 20, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-TuM

In-situ Studies of Solid-liquid Interfaces

Moderator: Anatoly Frenkel, Yeshiva University, Franklin (Feng) Tao, University of Kansas

8:20am **IS+AS+SA+SS-TuM2 Water at Ionic Liquid Interfaces Probed by APXPS, John Newberg, Y. Khalifa, A. Broderick, University of Delaware**

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions. It is therefore critical we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water, its influence on the properties of ILs has been the focus of many bulk studies and, more recently, surface science studies. Here we will highlight the use of a recently commissioned ambient pressure X-ray photoelectron spectroscopy setup in our laboratory and its application in characterizing the interfacial region of hydrophilic and hydrophobic ILs upon interaction with water vapor as a function of increasing pressure.

8:40am **IS+AS+SA+SS-TuM3 Probing the Liquid-Solid Interface of polycrystalline Pt in 1.0 M KOH using Ambient Pressure Photoemission Spectroscopy and "Tender" X-rays, Marco Favaro, B. Jeon, P.N. Ross, Z. Hussain, J. Yano, Z. Liu, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

With the previous success in soft X-ray AP-XPS gas-solid interface^{1a-e} probing, researchers have started to gain insights into the liquid-solid boundaries^{1d}. Taking the cue from these new research frontiers, we have developed on BL 9.3.1 at the Advanced Light Source (LBNL) a new liquid phase AP-XPS system (based on a Scienta R4000 HiPP-2 analyzer) that will shed new light on the understanding of the chemical changes at the electrode surfaces during normal working conditions, leading to a great enhancement of our knowledge on the most important processes in energy conversion and storage^{2a,b}. The combination of this new system with synchrotron radiation in the "tender" X-ray region (between 2 and 7 keV), allows us to probe the interface between thin liquid and solid phases using high kinetic energy photons and then, thanks to the *in operando* approach, directly track the phenomena occurring at the electrode liquid-solid interface during the electrochemical reactions of interest. The technique developed at BL 9.3.1 allows the study of both gas-liquid and liquid-solid interfaces, for pressures up to a hundred of Torr^{2a}.

In order to deeply investigate the possibilities offered by this new technique and, at the same time, to establish a benchmark, a reference material such as polycrystalline Pt has been studied in 1.0 M KOH electrolyte. In this talk we will demonstrate that it is possible to have fine control of the applied potential^{2a,b}, measuring the core level binding energy shift of the oxygen *1s* and potassium *2p* photoemission lines, according to the applied external potential. Moreover we will discuss the observation, under *in operando* conditions, of the changes of the surface oxidation state^{2b} of Pt triggered by the applied potential. Thanks to the innovative experimental approach, we have observed the *in situ* formation of Pt(II) and Pt(IV) species during the oxygen evolution reaction (OER), as well as the reversibility of the surface chemistry passing from anodic to cathodic potentials (up to the hydrogen evolution reaction, HER).

[1] a. Lu et al., *Sci. Rep.* **2**, 715 (2012); b. Zhang et al., *Nat. Mat.* **9**, 944 (2010); c. Axnanda et al., *Nano Lett.* **13**, 6176 (2013); d. Starr et al., *Chem. Soc. Rev.* **42**, 5833 (2013); e. Mudiyansele et al., *Angew. Chem. Int. Ed.* **52**, 5101 (2013).

[2] a. S. Axnanda, E. Crumlin et al., *Sci. Rep.*, accepted; b. E. Crumlin et al., *in preparation*.

9:00am **IS+AS+SA+SS-TuM4 Toward Ambient Pressure Electron Spectroscopy with Conventional XPS Instrumentation, Andrei Kolmakov, National Institute of Standards and Technology (NIST)**

The current state of the art instrumentation for ambient pressure electron spectroscopy requires highly specialized sophisticated laboratory equipment or dedicated synchrotron radiation facilities. The limited access to these equipment impedes *in situ* (*in vivo*) studies under realistic conditions in catalysis, energy, environmental and bio-(medical) fields. We propose a new sample platform which enables ambient pressure XPS to be conducted using conventional XPS instrumentation. The core of the sample platform is

microchannel environmental cells sealed with electron transparent, molecularly impermeable, mechanically and chemically stable graphene layer. The channels can be impregnated with liquids or gases and yet be vacuum compatible. Two major wafer scale fabrication strategies: (i) transferred graphene and (ii) as grown graphene layer were described. The coverage yield, membrane cleanness and leaking rates were comparatively studied. The feasibility tests of the platform included *in situ* XPS and electron microscopy studies of the water radiolysis and electrochemical processes taking place at liquid electrolyte-solid interface.

9:20am **IS+AS+SA+SS-TuM5 Solvation and Chemistry at the Interface: Near Ambient Pressure Electron Spectroscopy Studies of Aqueous Solution Interfaces, John Hemminger, University of California, Irvine**

INVITED
We have combined liquid-jet photoelectron spectroscopy coupled with classical molecular dynamics simulations to study the composition and chemistry of the liquid/vapor interface of aqueous solutions. Our experiments take advantage of the variable x-ray energy capability of synchrotron radiation and the kinetic energy dependence of the electron inelastic mean free path to carry out experiments with different probe depths. At low x-ray energy the low energy photoelectrons are detected primarily from the surface region of the solution. At higher x-ray energy our experiments probe more deeply into the solution. This allows us to directly compare the liquid/vapor interface with the bulk of the aqueous solution. We will present recent results on aqueous solutions of organonitrile compounds (acetonitrile and propionitrile). Our experiments and MD simulations show that both acetonitrile and propionitrile accumulate at the liquid/vapor interface—even though both nitriles are fully miscible with water. We have also studied the salting in and salting out effects for nitriles in water. We also have studied the effect of ion size on the surface propensity of cations in alkali halide aqueous solutions.

11:00am **IS+AS+SA+SS-TuM10 In situ Single-molecule Microscopy of Photoelectrocatalysis for Solar Water Oxidation, Peng Chen, Cornell University**

INVITED
This talk will present our recent results in using single-molecule super-resolution fluorescence microscopy to image photoelectrochemical reactions on single semiconductor nanostructures *in situ* under photoelectrochemical water oxidation conditions. We separately image hole and electron induced reactions, driven by light and electrochemical potential, and map the reactions at single reaction temporal resolution and nanometer spatial resolution. We also correlate the surface hole and electron reactivity with the local water oxidation efficiency using sub-particle level photocurrent measurements. By depositing oxygen evolution catalysts in a spatially controlled manner, we further identify the optimal sites for catalyst deposition for photocurrent enhancement and onset potential reduction.

11:40am **IS+AS+SA+SS-TuM12 In Situ and Operando AP-XPS for the Oxidation State of Pd at Solid/Liquid Interface, Beomgyun Jeong, M. Favaro, P.N. Ross, Z. Hussain, Lawrence Berkeley National Laboratory (LBNL), Z. Liu, Shanghai Institute of Microsystem and Information Technology, China, B.S. Mun, J. Lee, Gwangju Institute of Science and Technology, Republic of Korea, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

A catalyst is defined as a substance that enhances a reaction rate without changing its chemical state. However, often the chemical state of a catalyst surface undergoes changes during the reaction, leading to the degradation of catalyst performance. These phenomena are particularly significant in electrocatalysis in which reaction occurs at solid/liquid interface with electrical potential as an activation energy to drive the reaction. In order to understand the mechanism of catalyst degradation, it is important to have a capability to observe the chemical states of electrode and various chemical species in electrolyte during the reaction taking place at the solid/liquid interface. In order to explore this region, we have developed a new experimental approach [1], using ambient pressure XPS (AP-XPS) coupled with "tender" X-rays (in the range between 2.5 and 7.0 keV) at the Advanced Light Source BL 9.3.1, Lawrence Berkeley National Laboratory. Because of the relatively high kinetic energy of the incoming photons, "tender" X-rays allow probing solid/liquid interfaces through thin electrolyte films characterized by a thickness of 10-30 nm. This unique functionality allows the ability to simultaneously correlate the electrocatalytic activity of electrodes to both the chemical modifications of the electrode surface, and the electrolyte.

This talk will provide details on *in-situ* and *operando* AP-XPS measurements on the chemical modifications of polycrystalline Pd surface studied at different electrochemical potentials. Pd is a cost-effective materials alternative to Pt showing similar electrocatalytic property of Pt in

various reactions, such as oxygen reduction and electrooxidation of hydrogen and formic acid. On the other hand, it is well known that the Pd activity decreases faster than that of Pt especially in formic acid oxidation [2]. This phenomenology could be understood by the direct observation of the Pd surface chemistry evolution at electrified solid/liquid interface. We will discuss the performance of the Pd electrode in two different aqueous electrolytes, in particular in an alkaline medium and in a formic acid solution, an electroactive liquid organic molecule. We believe that our findings represent a step forward in the rationalization of the electrocatalytic behavior of Pd.

[1] S. Axnanda, E.J. Crumlin *et al.*, *Sci. Rep.* 5 (2015) 9788.; b. E.J. Crumlin *et al.*, in preparation.

[2] H. Jeon, S. Uhm, B. Jeong, J. Lee, *Phys. Chem. Chem. Phys.* 13 (2011) 6192.

12:00pm **IS+AS+SA+SS-TuM13 In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVi**, **Juan Yao**, X. Sui, D. Lao, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu, Pacific Northwest National Laboratory

A vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface) was employed for *in situ* chemical imaging of switchable ionic liquids (SWILs) using time-of-flight secondary ion mass spectrometry (ToF-SIMS). A model SWIL system consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with CO₂ gas to change solvent polarity was selected. A series of ionic liquids with different CO₂ loading was analyzed. Spatial chemical differences were observed within the same ionic liquid, indicating inhomogeneity of the ionic liquid. Spectral principal component analysis (PCA) was conducted using both positive and negative ToF-SIMS data. Clear distinctions were observed among SWILs of different CO₂ loadings. The loading plots strongly indicate that fully loaded SWILs share similar spectral components as those of the non-loaded ILs. This finding confirms the hypothesis of the biphasic structure in the fully loaded IL predicated by molecular dynamic simulation and presents the first physical evidence of the liquid microenvironment of IL determined by liquid ToF-SIMS. Various ion pairs were also observed in addition to the known SWIL chemistry of the DBU and 1-hexanol system, indicating the complexity of the ionic liquid previously unknown. The vacuum compatible microchannel in SALVI provides a new way to study ionic liquids in vacuum by sensitive surface techniques. Our approach directly visualized spatial and chemical heterogeneity within the SWILs by dynamic liquid ToF-SIMS for the first time.

Tuesday Afternoon, October 20, 2015

Magnetic Interfaces and Nanostructures

Room: 230A - Session MI+SA-TuA

Spin Currents, Spin Textures and Hybrid Magnetic Structures

Moderator: Greg Szulczewski, The University of Alabama

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

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

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

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

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

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

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

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

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

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

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

* Falicov Student Award Finalist

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

Interfacial magnetolectricity across a multilayer system is known to sometimes result in much larger coupling between electric and magnetism than in single phase systems. The cause has been controversial, but the atomic valence of the magnetic element in these systems is known to change with an applied voltage. We wanted to understand how the interfacial atomic valence was effected as a function of film thickness in thin films of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ on $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$. To separate the Mn valence at the interfacial layer with PZT from the bulk region of LSMO, we took advantage of the drastically different attenuation length of two techniques: x-ray absorption in L-edge total electron yield mode and K-edge fluorescence yield mode. By globally fitting both sets of experimental results, we were able to develop a depth-dependent model to estimate the layer by layer valences in our materials as a function of thickness. This empirical model was developed under the guidance of theoretical work from a two-orbital double exchange model, which also explored the effects of substrate termination and ferroelectric polarization direction. Estimates based on the data and models for surface, interface and bulk valence as well as surface and interface length scales will be discussed.

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

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

6:00pm **MI+SA-TuA12 Substrate Induced Spin-state Locking of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on Au(111)**, *Sumit Beniwal**, *X. Zhang, S. Mu*, University of Nebraska - Lincoln, *A. Naim, P. Rosa, G. Chastanet*, CNRS Universite de Bordeaux, France, *J. Liu*, Northeastern University, *G. Sterbinsky, D. Arena*, Brookhaven National Laboratory, *P.A. Dowben, A. Enders*, University of Nebraska - Lincoln

Spin-crossover (SCO) complexes hold promise for spintronics applications as room-temperature single molecular magnets. Their signature functionality arises from a central transition metal atom, which is in a d^4-d^7 configuration in a (pseudo)octahedral N_6 environment and can be switched between a diamagnetic low-spin ($S=0$) and a paramagnetic high-spin ($S=2$) state by external stimuli such as temperature, pressure, light and electric field. The switching of the molecular spin-state is accompanied by change of other physical and electronic properties of these complexes, such as color, magnetic susceptibility and electrical conductivity. Application in devices requires that the molecules are in contact with metal electrodes, which can significantly alter their electronic and magnetic properties. This study makes use of a comprehensive suite of surface-sensitive spectroscopy and microscopy tools to investigate the electronic properties of SCO complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on Au(111) to identify characteristic signatures of spin-state of the molecules across thermal spin transition temperature. Variable temperature scanning tunneling microscopy, performed as a function of film thickness, revealed that ordering in the molecular layers is established as the films are cooled well below their spin transition temperature, and this ordering is maintained when the films are brought back to room temperature. Temperature and thickness dependent studies of electronic structure using X-ray photoemission (XPS), X-ray absorption spectroscopy (XAS) and inverse photoemission (IPES) on surface supported networks, reveal substrate effects on the spin state.

Satellite features in core level XPS Fe $2p_{3/2}$ peaks are characteristic of the spin transition, whereas angle-resolved XPS (ARXPS) helps to separately determine the electronic structure of interfacial molecules and of molecules away from the interface. Fe L-edge X-ray absorption XAS spectra taken on ultrathin films suggest that the substrate inhibits thermally induced transitions of the molecular spin state, so that both high-spin and low-spin states are preserved far beyond the spin transition temperature of free molecules. These results demonstrate that thin films of the spin crossover complexes studied have distinctively different phase transition behavior as compared to bulk-like samples, which is evidence that interface interactions can considerably affect the molecules' structural conformation, spin state as well as electronic properties. Understanding such interface effects can help establish conditions to control the spin state of molecules and to engineer spin state transitions.

* **Falicov Student Award Finalist**

Wednesday Morning, October 21, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-WeM

In-situ Studies Using X-ray Absorption Spectroscopy and Vibrational Spectroscopy for Catalytic and Energy Materials

Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:00am **IS+AS+SA+SS-WeM1 In Situ X-ray Absorption Spectroscopy Technique for Metal/Water Interface Characterization, Chenghao Wu***, University of California, Berkeley and Lawrence Berkeley National Laboratory, *J.-H. Guo, M.B. Salmeron*, Lawrence Berkeley National Laboratory

Most of the electrochemistry processes occur within the thin layer of electrolyte at the electrolyte/electrode interfaces, commonly denoted as the electrical double layer (EDL). Although some classic continuum theories about EDL have been established and widely accepted over the past century, very little experimental information is available regarding the molecular-level details at such solid/liquid interfaces. We have developed in-situ liquid cells to study such solid/liquid interfaces by means of soft x-ray absorption spectroscopy [1]. Because the fluorescence x-ray photon has much larger mean free path in condensed matters than the secondary electrons, by comparing the total fluorescence yield (TFY) and total electron yield (TEY) spectra, we can extract useful information about the compositional, structural or chemical difference between the bulk and the interfacial electrolyte. Under different bias, by modulating the incident x-ray, the TEY signal current becomes alternating and can be separated from the dominant faradaic current so that we can obtain surface-sensitive TEY signal under electrochemical conditions.

With this *in-situ* and *operando* XAS technique, we investigated the gold/water interface [1] and platinum/sulfuric acid solution interface. It was found that at gold/water interface, the interfacial water layer has significantly different hydrogen-bonding network structure compared to the bulk water. Under different bias, the polar water molecules respond to the external electrical field and reorient at the gold electrode surface, which significantly changes the amount of distorted or broken hydrogen bonds. First-principle simulations were able to corroborate the experimental results and qualitatively reproduce the change in the x-ray absorption spectra at different bias. In the platinum/sulfuric acid system, the charged solute species, such as SO_4^{2-} ions, hydronium ions, introduce extra complexity at the surface under different bias. Using the same *in-situ* technique, we were also able to identify some intermediate surface species in the potential window of OER reaction.

[1]. J.J. Velasco-Velez, C.H. Wu, T.A. Pascal, L.F. Wan, J.-H. Guo, D. Prendergast, and M. B. Salmeron, *Science*, **346**, 831-834 (2014).

8:20am **IS+AS+SA+SS-WeM2 Tip Enhanced Raman Spectroscopy (TERS) of Graphene Nano-Ribbons and Graphene on Au Surfaces: Imaging and Vibrational Spectroscopy of Surface Reaction Products, Delroy Baugh, S. Liu, T. Kumagai, M. Wolf**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces. TERS could therefore provide unique and heretofore unprecedented insight on adsorbate reactions at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well defined surface sites as well as monitor vibrational spectra to provide bond specific information about the reaction. However, in order to clarify the vibrational structure in TERS, the details of the enhancement mechanism and the issues regarding the plasmonic background that is almost always observed in TER spectra as well the "blinking" that occurs in the SERS part of TERS must be resolved. Towards this end here we will report studies of Graphene and Graphene Nanoribbons (GNR's) on Au surfaces as a model systems because their electronic and vibrational structure are clearly defined. Specifically, Near and Far-field Raman spectra will be reported for

these systems and the above issues will be addressed experimentally and a simple theoretical model will be presented for the TERS observations.

8:40am **IS+AS+SA+SS-WeM3 Isomerization of One Molecule Observed through Tip-Enhanced Raman Spectroscopy: Azobenzene Thiol on Au(111), Joonhee Lee, N. Tallarida, L. Rios, V.A. Apkarian**, University of California, Irvine

The reversible *cis-trans* isomerization of a single azobenzene thiol (ABT) molecule is captured in tip-enhanced Raman trajectories in which the anti-correlated flip-flop between discrete, on and off-states of the two structural isomers is seen. The strongly blue-shifted spectra are recorded from a molecule that appears at the junction plasmon of a scanning tunneling microscope (STM), consisting of an atomically flat Au(111) surface and a silver tip. The variation in frequencies of switching events identifies heterogeneously photocatalyzed chemistry. The chemisorbed ensemble of ABT molecules lie flat on Au(111) surface with azobenzene headgroup strongly coupled to the surface. Nevertheless, we establish through STM imaging that the ABT molecules undergo both current driven and photoinduced *cis-trans* isomerization. Rather than decoupling from the surface, we suggest that strong coupling of the reaction coordinate to a vibrational energy sink is required for *cis-trans* isomerization of azobenzenes on metal surfaces.

9:00am **IS+AS+SA+SS-WeM4 In Situ Characterization and Reaction Studies of MnO_x/Co₃O₄ Catalyst for CO and CO₂ Conversion, Walter Ralston, G. Melaet**, University of California, Berkeley, *S. Alayoglu*, Lawrence Berkeley National Laboratory (LBNL), *G.A. Somorjai*, University of California, Berkeley

As the energy and fuel demands of our growing world continue to increase, non-fossil fuel carbon sources are increasingly attractive – especially if these carbon sources can be easily converted to transportable fuels and higher-value chemicals. Much attention has been focused on carbon dioxide, as capture and storage technology has emerged to mitigate emissions and CO₂ can be used to produce methanol.

Recently, we reported a catalyst for the low-pressure conversion of CO₂ to methanol¹. Manganese oxide nanoparticles supported in mesoporous Co₃O₄ produced methanol in high yields and at significantly lower pressure conditions than typical Cu/ZnO catalysts used industrially. The advantage of this catalyst is in its lower pressure requirement, its high yield of methanol, and its evidence of carbon-carbon bond formation (10% ethylene production).

Catalytic testing of the material has shown the catalyst to be more than the sum of its parts; when each component is tested separately (MnO_x nanoparticles supported in SiO₂; mesoporous Co₃O₄ alone) CH₄ and CO are the major products. Preparation and testing of an inverse catalyst – CoO_x nanoparticles on a mesoporous MnO₂ support – proves the importance of the hybrid architecture in determining the selectivity of the catalyst, as the inverse catalyst is dominated by the selectivity of the support (>80% selective to CO).

Towards understanding this catalyst, in-situ X-ray Absorption Spectroscopy (XAS) utilizing both soft and hard x-ray energies has allowed for a detailed characterization of the catalyst under oxidation, reduction, and reaction conditions. In addition to CO₂, in-situ characterization under CO hydrogenation conditions was used to understand the Fischer-Tropsch activity of the catalyst for making longer chain hydrocarbons. The results of these in-situ studies are correlated with catalytic reaction data to help understand the nature of the active site/interface and guide future catalyst design.

References

(1) C. S. Li, G. Melaet, W. T. Ralston, *et al.* High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis. *Nature Communications*, 6:6538, 2015.

9:20am **IS+AS+SA+SS-WeM5 In Situ and Operando Raman Methodology to Understand the States of Oxide Catalysts and Alkane Oxidative Dehydrogenation and Ammoxidation Reactions, Miguel A. Bañares**, Instituto de Catálisis y Petroleoquímica, Madrid **INVITED**

Operando methodology combines in situ spectroscopy during reaction with simultaneous performance measurement in a cell that behaves like a catalytic reactor. *Operando* methodology connects changes in the performance and in the structure in a simultaneous manner; this is fundamental to assess the structure-performance relationships at a molecular level.

Molecularly dispersed vanadia on oxide carriers is a key component in many catalytic formulations in environmental and selective oxidation and

* ASSD Student Award Finalist

ammoxidation catalysis. The actual state of vanadia catalysts in specific environments depends on its surface density, the nature of the support and the presence of additives. We will summarize our experience on the state of supported vanadia paying particular attention to how the environment and reaction conditions finally shape the structure of vanadia catalysts. *Operando* Raman spectroscopy is an invaluable approach to fully understand the actual state of the catalyst, its transformations during reaction and how these correlate with changes in catalytic performance.

A single technique, may not deliver the complete vista, thus collaboration with complementary talents and techniques is critical. We show the outcome of collaborations with theoretical chemistry approaches to bring the rationale behind structure-activity relationships inferred through *operando* Raman methodology. We also show the interaction with engineering approaches.

11:00am **IS+AS+SA+SS-WeM10 *Operando* Studies of Dynamic Restructuring of Working Catalysts by Correlated Imaging and Spectroscopy Probes, Anatoly Frenkel, Yeshiva University INVITED**

Understanding mechanisms of reactivity is often hindered by complexity of nanoscale supported metal catalysts. In the size range of 1-5nm, they feature a variety of structural motifs, sizes, shapes, compositions, degrees of crystalline order as well as multiple temporal scales. Hence, new experimental methodologies are called for, ones that are capable to capture not only the details of kinetic, dynamic and catalytic properties of metal clusters, but also their statistical distributions over ensemble of such clusters in a particular working catalyst, i.e., in reaction conditions. I will present our recent results obtained at the National Synchrotron Light Source, Advanced Light Source and Center for Functional Nanomaterials, where we combined x-ray absorption spectroscopy, high resolution transmission electron microscopy and micro-IR spectroscopy studies of a complex catalytic system *in operando*, using the same portable micro-reactor. This method will be illustrated on the example of supported Pt and Pd catalysts undergoing dynamic restructuring during ethylene hydrogenation reaction. Our results demonstrate a complexity of structures exhibited in this system and their dynamic, responsive transformations throughout changing reaction conditions. The new method is both general and generalizable to quantitative *operando* studies of complex material systems of broad interest to areas as diverse as catalysis science, applied physics and materials science, using a wide variety of x-ray and electron based experimental probes.

11:40am **IS+AS+SA+SS-WeM12 A Correlation of Raman and Single and Multiple Layer Graphene Conductivity as Detected with a Cryogenic Multiprobe AFM with On-line Raman, NSOM and Other SPM Modalities, Aaron Lewis, The Hebrew University of Jerusalem and Nanonics Imaging Ltd, Israel, O. Zinoviev, A. Komissar, E. Maayan, D. Lewis, Nanonics Imaging Ltd, Jerusalem, Israel**

It is a challenge to study 2D materials, such as Graphene, MoS₂, WSe₂, etc. at temperatures down to 10°K when one considers the wide variety of physical phenomena that have to be applied to get a full picture of the functionality of these materials. This involves questions of structure, nanometric photoconductivity, electrical properties, thermal properties, near-field optical in the apertured and scattering modes, Kelvin probe, and of course Raman. All of these phenomena are common not only to 2D materials but also to carbon nanotubes and related nanomaterials. This presentation will describe both the instrumental development of such a multiprobe cryogenic system that allows for state of the art on-line optical measurements and will also include a review of the probe developments that permit such multifunctional multiprobe operation with on-line full optical access. The system that will be described has a completely free optical axis from above and below that is not obscured by electrical or other probes that have been developed for this system for multiprobe operation. This permits on-line Raman and Tip Enhanced NanoRaman Scattering. With such a system we have investigated graphene and HfO₂ using multiprobe electrical, Kelvin probe, NSOM and on-line Raman. The results have yielded new insights into the chemical changes that are correlated to the electrical conductivity.

12:00pm **IS+AS+SA+SS-WeM13 Surface Structure and Chemistry of Rh(110)-1×2 Under Reaction Condition and During Catalysis explored with AP-XPS and HP-STM, Franklin (Feng) Tao, L. Nguyen, University of Kansas**

High pressure scanning tunneling microscopy (HP-STM), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and computational studies were used to study the surface chemistry and structure of Rh(110)-1×2 and Rh(110)-1×1 at atomic scale in CO at different pressure and different temperature, and during CO oxidation at different pressure and different temperature. In gas of CO at a low pressure of 8×10^{-8} Torr, a Rh(110)-1×2 covered with CO is formed at 25C by replacing the adsorbed oxygen atoms

adsorbed on Rh(110)-1×2 by CO molecules of gas phase. A pressure dependent structure of adsorbate layer of CO on Rh(110)-1×2 was revealed. In gas of CO at a high pressure of 0.08 Torr, the portion of CO molecules bound in atop configuration in the adsorbed layer increases along with the increase of pressure of CO gas though there is no restructuring of Rh(110)-1×2 at 25C in the pressure range of 8×10^{-8} to 0.8 Torr. This is supported by the calculated coverage-dependent binding energy of CO on this surface. At a relatively high temperature of 55C, Rh(110)-1×2 in 0.08 Torr CO is restructured to Rh(110)-1×1 (Figure 1b). This restructuring of surface restructuring is much lower than 153C for Rh(110)-1×2 in UHV. Theoretical simulation suggests that adsorbed CO molecules promote this restructuring compared to the restructuring in UHV since adsorption of CO on the intermediate structures of this restructuring in gas of CO lower the activation barrier of these intermediate structures. Rh(110)-1×2 is restructured to Rh(110)-1×1 during catalysis in the mixture of CO (0.08 Torr) and O₂ (0.02 Torr) even at 25C. Compared to the lack of restructuring in pure CO of 0.08 Torr at 25C, this restructuring during catalysis could result from a local heating of the catalyst surface by the exothermic reaction of CO oxidation. During CO oxidation, certain number of CO molecules are still remained on the catalyst surface. In the temperature range of 50-130C the active phase of catalysis is metallic Rh(110)-1×1. However, at 200C the active phase is surface rhodium oxide. These in-situ studies of surface structure and chemistry integrated with computational studies of Rh(110) in pure CO and in mixture of CO and O₂ clearly demonstrate the complexity of surface structure of a catalyst under reaction condition and during catalysis. The pressure-dependent structure of adsorbate layer, temperature-driven surface restructurings, generation of a new active surface phase of catalyst during catalysis, suggest the significance of in-situ studies of structure and chemistry of surface of a catalyst during catalysis.

Thin Film

Room: 111 - Session TF+AS+NS+SA-ThM

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization I

Moderator: Divine Kumah, North Carolina State University

8:00am **TF+AS+NS+SA-ThM1 Oxynitride Thin Films by Reactive Radiofrequency Magnetron Sputtering - Versatile Materials for Optical Applications**, *Angelique Bousquet, A. Farhaoui, F. Zoubian, C. Taviot-Gueho, J. Cellier, E. Tomasella*, Institut de Chimie de Clermont-Ferrand, France

INVITED

Transition metal oxynitrides are increasingly studied because of their high versatility. Indeed, by tailoring the material composition, their optical, mechanical or electrical properties are tuned. Among thin film deposition processes, reactive sputtering is particularly attractive for this purpose because of its robustness, its wide using in industry and its high versatility. For several years, our research group at ICCF is specialized in control of reactive sputtering process, especially by plasma analysis using Optical Emission Spectroscopy, to deposit thin films for optical applications.

In this presentation, we will show how by tuning the Ar/O₂/N₂ atmosphere during sputtering of elemental target, it is possible to control the film composition in a ternary diagram in metal-rich, oxide, nitride or oxynitride region. The potentiality of this technique will be illustrated by tantalum and silicon oxynitride deposition.

In order to investigate the nature of oxynitride films (Random Bond Model or Random Mixture Model), thin films were characterized by various techniques, such as IR spectroscopy, XPS, XRD/Pair Distribution Function technique and Rutherford Backscattering Spectroscopy. Hence, we obtained an accurate picture of the diversity and the complexity of our material, following the Random Mixture Model, where segregated oxide and nitride phases are randomly distributed at very short scale.

Moreover, the modification of material composition allows controlling their optical properties, characterized by UV-visible spectroscopy and spectroscopic ellipsometry. This latter technique appears as a powerful technique to discriminate metallic, semiconductor and/or insulator contributions into such complex films by using model combining Tauc-Lorentz law and additional Lorentz oscillator. Hence, in a one hand, optical band gap of TaO_xN_y can be changed from 0-4.3 eV. This E_g fine-tuning more particularly in the range of 1.7-2.7 eV is interesting for application in photocatalytic water splitting using visible light. In the other hand, the refractive index variation in the 1.56-3.7 range (at 1.96 eV) of Si_xO_yN_z films is used to realized antireflective multilayer system from only one target. Finally, oxynitride films present promising properties for applications in material for Energy.

8:40am **TF+AS+NS+SA-ThM3 Surface Science in The Wild: Using Synchrotron Radiation and Lab Grown Thin Films to Understand The Behavior Of SiC in Accident Tolerant Nuclear Fuels**, *Jeffery Terry*, Illinois Institute of Technology

INVITED

Out in the "real world," systems are typically much less clean and much more complex than what is seen in the laboratory. This is often the case in the extreme environment of the core of a nuclear reactors. However, complexity often makes it very difficult to understand the dynamics that are occurring in the "real world" systems. Often our understanding can be greatly improved by using measurements on the "real world" system in combination with fundamental surface science measurements on likely components. We have applied these combinations to study the behavior of irradiated accident tolerant nuclear fuels. Development of new accident tolerant nuclear fuels is important because the explosions at Fukushima were the direct result of interactions between water and the Zr cladding on the fuel. The high temperature chemistry of those interactions led to the production of hydrogen gas which eventually ignited. Our research group has looked at potential claddings such as ZrC, ZrN, and SiC. Specifically, we are using synchrotron radiation techniques to collect data on reactor irradiated materials. We compare the results of those measurements with well controlled laboratory grown systems. The data is then provided to modelers to evaluate the performance of reactor components in extreme environments (temperature, neutron flux, chemistry). This talk will focus on the carbides and nitrides that may be used in accident tolerant, TRISO fuel pellets for application in both conventional and advanced nuclear reactors.

9:20am **TF+AS+NS+SA-ThM5 iTF Modulus Solution with xProbe Applications for Ultra-thin Film Systems (<=10nm)**, *Anqi Qiu, A. Romano*, Hysitron, Inc.

Reliable measurements of the Elastic Modulus of thin films is particularly challenging due to substrate effect. The prevalent rule of limiting indentation depth to 10% of the coating thickness to avoid the substrate's influence on the mechanical properties is challenging to assure, especially when the film thickness goes below 200nm. The tip radius can be one of the many factors limiting the application of Oliver-Pharr model on the elastic modulus calculation, just as the surface roughness. With the newly developed ultra-low noise xProbe transducer combined with the **Intrinsic Thin Film Property Solution from Hysitron**, quantitative mechanical properties from nanoindentation tests on 10nm thin film systems become possible. Here a MEMS based transducer with a noise floor similar to that of a contact mode Atomic Force Microscope (AFM). The linear actuation allows for direct and fully quantitative measurements without the need of modeling, which leads to more precise mechanical properties estimation and higher analysis throughput. By combining the ultra-low noise xProbe transducer and analytical intrinsic thin film solution (Itf), we quantitatively estimate elastic properties of the ultra-thin film systems of 10nm or below.

9:40am **TF+AS+NS+SA-ThM6 Real-time Study of Plasma Enhanced Atomic Layer Epitaxy of InN Films by Synchrotron X-ray Methods**, *Neeeraj Nepal, V. Anderson, S.D. Johnson, B. Downey, D. Meyer*, U.S. Naval Research Laboratory, *A. DeMasi, K.F. Ludwig*, Boston University, *C. Eddy*, U.S. Naval Research Laboratory

Atomic layer epitaxy (ALE) is a layer-by-layer materials growth method. Recently, plasma enhanced ALE (PA-ALE) has been used to grow epitaxial III-nitride films at temperatures $\leq 500^\circ\text{C}$ [1-2]. At these growth temperatures, the ad-atom mobility is low and the growth process is significantly influenced by the nature of the substrate surface. Thus, the mechanisms of nucleation and growth kinetics is very important to understand to improve material quality for technological applications. Synchrotron x-ray characterization is one of the best methods for this study.

The temporal evolution of high quality InN growth on a-plane sapphire at 200-250°C were probed by synchrotron x-rays. The growth was carried out in a thin film growth facility installed at beamline X21 of the National Synchrotron Light Source at Brookhaven National Laboratory and at Cornell High Energy Synchrotron Source, Cornell University. Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the x-ray incidence angle of 0.8 degrees show that H₂ plasma cleaning roughens the sapphire substrate surface, but this same surface is recovered completely during subsequent N₂ plasma pretreatment. GISAXS also reveals InN growth steps for each PA-ALE cycle at the optimal growth conditions. During the initial cycles the specular peak broadens and the Yoneda Wing (YW) scattering has a correlated length scale (CLS) of 17.4 nm indicating roughening of the surface during homogenous nucleation. At about 1.3 nm of growth the intensity of YW is increased at the CLS of 10.1 nm indicating a decrease in the surface roughening CLS. Despite this scattering, *ex situ* atomic force microscopy-measured roughness is below instrument sensitivity limits, demonstrating the effectiveness of GISAXS compared to more conventional approaches. *In situ* x-ray reflectivity measurements suggest that the InN growth was self-limited with a growth rate of 0.35 nm/cycle between 200-250°C. Hall measurements show electron sheet carrier density and resistance of $3.5 \times 10^{13} \text{ cm}^{-2}$ and 3.59 kW/sq, respectively. An electron mobility of 50 cm²/V-s is measured for a 5.6 nm thick InN film on a-plane sapphire, which is higher than the reported value of 30 cm²/V-s for a 1300 nm thick InN grown by MBE directly on sapphire [3]. *In situ* synchrotron x-ray study of the epitaxial growth kinetics of InN films is one of the most powerful methods to understand nucleation and growth mechanisms to improve material quality and broaden material applications.

References:

- [1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).
- [2] Nepal et al., Appl. Phys. Lett. **103**, 082110 (2013).
- [3] Kuo et al., Diamond & Related Materials **20**, 1188 (2011).

11:00am **TF+AS+NS+SA-ThM10 Nucleation and Growth of Few-Layer ALD Films on Various Substrates Studied by Low Energy Ion Scattering (LEIS)**, *Malcolm Hathaway*, Harvard University, *T. Grehl, P. Bruener*, ION-TOF GmbH, Germany, *M. Fartmann*, Tascon GmbH, Germany, *H. Brongersma*, ION-TOF GmbH, Germany

Atomic Layer Deposition has found applications in many semiconductor processes due to its several unique characteristics, including high purity, conformality, pin-hole-free character, and atomic level thickness

controllability. It is these last two characteristics which are of particular interest in this present work. The thickness control of ALD films is precise down to the angstrom level, even when depositing layers as thin as a few atomic layers. Ideally, in layers only a few angstroms thick, the ALD process produces material which is completely continuous and free of pinholes. One of the challenges of characterizing ALD processes is the difficulty of directly measuring such thin films and confirming their continuous nature.

Low Energy Ion Scattering (LEIS) spectroscopy is uniquely suited to exploring these questions, due to its extreme surface sensitivity, easy quantification and its ability to yield additional information about the sub-surface composition. Using LEIS, analytical questions like layer closure, surface composition, diffusion processes, or growth modes can be addressed. In this work, we explore the limits of this technique to characterize few-layer ALD films on a variety of substrates, to confirm the capabilities of LEIS in this arena, and to shed new light on the nature of few-layer ALD films.

In the LEIS process, a noble gas ion beam of (1 -10 keV) is directed at the sample, and the fraction of backscattered ions is measured as a function of kinetic energy. Two main mechanisms determine the spectral response: Firstly, scattering in the first monolayer of atoms creates elemental peaks, allowing quantitative determination of the elemental composition of the outermost atomic layer. The intensity of these peaks is directly proportional to the surface coverage. Secondly, scattering processes below the surface (with the ion penetrating the surface, scattering at deeper layers and returning to the surface before leaving it) provide information about sub-surface layers, sometimes as deep as 10 nm, in a non-destructive way. As the additional energy loss is proportional to penetration depth, these data can be evaluated to determine the layer sequence, layer composition and layer thickness in a single measurement and in addition to the top layer composition.

In this study a number of oxide films (e. g. HfO_2 , Al_2O_3) on Si and other substrates like glassy carbon are evaluated. We apply LEIS among other techniques to characterize the films, especially in the early phases of film growth. Using the unique information from LEIS, conclusions on the nucleation behavior and growth are drawn.

11:20am **TF+AS+NS+SA-ThM11 $\text{Ni}_{1-x}\text{Pt}_x\text{Si}$ Film Characterization for sub-32 nm CMOS Fabrication.** *Suraj Patil, R. Rai, S. Beasor, L. Zhou, GLOBALFOUNDRIES, NY, USA*

Aggressive scaling of CMOS devices demands silicide engineering for high performance in the sub-32nm technology node and beyond. Ni-silicide can satisfy many of the integration challenges but it is limited by morphological stability at elevated temperatures. On the other hand, incorporating Pt into Ni-silicide forms a more robust nickel platinum silicide ($\text{Ni}_{1-x}\text{Pt}_x\text{Si}$) and improves morphological stability. Advantages of Pt incorporation include extension of the temperature range over which the NiSi exists, delay in the agglomeration of NiSi phase, suppression of the high resistive NiSi_2 phase formation and retardation of the Ni diffusion at the interface and grain boundaries which could lead to encroachment or piping. This work discusses three important aspects of $\text{Ni}_{1-x}\text{Pt}_x\text{Si}$ formation: (1) understanding NiPt diffusion with two step RTA anneals – formation (RTA1) and transition (RTA2), which is very important for thickness uniformity across structures with varying CDs, encroachment control, device performance and yield; (2) understanding NiSi phase formation for thermal stability, and (3) understanding Pt distribution in the final film with low RTA1 temperatures. For this study $\text{Ni}_{1-x}\text{Pt}_x\text{Si}$ samples were fabricated from a simple n-Si/ $\text{Ni}_{0.85}\text{Pt}_{0.15}$ /TiN stacks, annealed at range of RTA1 temperatures from RTA-20°C to RTA+30°C for 20s followed by a standard RTA2 anneal for 30s. Characterization of final $\text{Ni}_{1-x}\text{Pt}_x\text{Si}$ films obtained at different RTAs based on XRD phase identification and XPS analysis will be presented. Pt distribution in the final silicide films will be discussed.

11:40am **TF+AS+NS+SA-ThM12 Growth of β -Tungsten Films Towards a Giant Spin Hall Effect Logic Device.** *Ayaya Narasimham, University at Albany-SUNY, R.J. Matyi, State University of New York, A. Green, University at Albany-SUNY, A.C. Diebold, V. LaBella, State University of New York*

Spin-orbit coupling in metastable β -W generates spin transfer torques strong enough to flip magnetic moment of an adjacent magnetic layer. In a MTJ stack these torques can be used to switch between high and low resistive states. This technique can be used in designing efficient magnetic memory and non-volatile spin logic devices. Deposition conditions selective to β -W need to be understood for the large scale fabrication of such devices. The transition from β to α phase of Tungsten is strongly governed by thickness of W layer, base pressure and oxygen availability for example, above 5 nm β film relaxes and forms an α phase. Resistivity measurements as well as x-ray photoelectron spectroscopy and x-ray diffraction and reflectivity analysis are performed to determine the phase and thickness of tungsten

films. We show that β phase is influenced by ultrathin thermal oxide of Si layer and the amount of oxygen flow during the growth. These results demonstrate a reliable technique to fabricate β W films up to 20 nm on bare Si and silicon dioxide, while providing insight to growing it anywhere in the device stack.

12:00pm **TF+AS+NS+SA-ThM13 Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering.** *Virginia Anderson, N. Nepal, S.D. Johnson, US Naval Research Laboratory, A. DeMasi, Boston University, J.K. Hite, US Naval Research Laboratory, K.F. Ludwig, Boston University, C.R. Eddy, Jr, US Naval Research Laboratory*

Aluminum nitride, gallium nitride, and indium nitride have desirable qualities for many semiconductor applications, and have recently been studied intensely.¹ Because of their direct, tunable band gaps and capacity for high current density they are attractive for photovoltaics and high power transistors. The current methods of depositing high-quality III-nitride films, are metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The temperatures for the depositions make ternaries challenging. Indium nitride, for example, is difficult to mix with aluminum nitride, as typical MOCVD temperatures for AlN and for InN are 1000°C and 450°C respectively. Aluminum nitride deposition with atomic layer epitaxy (ALE) is currently being explored by some groups as a fabrication friendly technique for thin films at lower temperatures.²

Crystalline AlN deposited with plasma assisted ALE (PA-ALE) in a Fiji reactor from Ultratech/Cambridge Nanotech at 500°C currently has lower material purity than the AlN deposited by MBE and MOCVD, and understanding the film deposition mechanism in order to improve quality is the subject of ongoing research.³ There is a need for a better understanding about the film evolution during nucleation. Grazing incidence small angle x-ray scattering (GISAXS) is sensitive to changing surface features and can be conducted at a wide range of pressures, making it useful for real time monitoring of deposition.⁴

AlN deposited by PA-ALE was grown using trimethylaluminum and hydrogen/nitrogen plasma pulses in a custom reactor at the Brookhaven National Synchrotron Light Source and the Cornell High Energy Synchrotron Source. In both instances, GISAXS was used to examine surface changes during the deposition.

GISAXS information collected during AlN growth at nominally 400°C, 450°C, and 500°C suggested that temperature influenced nucleation, with changes in roughening behavior observed. Post-growth examination of the AlN films with x-ray photoelectron spectroscopy and atomic force microscopy gave important information on the final film elemental composition and morphology. The GISAXS data also show that the surface continued to evolve during the cooling after growth completion while still in the reactor. This information only adds to the necessity of *in situ* growth monitoring to fully understand the mechanisms involved in the ALE growth process.

References:

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² M. Bosund et al., *Appl. Surf. Sci.* **17** 7827 (2011)

³ N. Nepal et al., *Appl. Phys. Lett.* **103** 0 82110 (2013)

⁴ K. Devloo-Casier et al., *Appl Phys. Lett.* **98** 231905 (2011)

Thursday Afternoon, October 22, 2015

Thin Film

Room: 111 - Session TF+AS+NS+SA-ThA

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization II

Moderator: Jay Hendricks, National Institute of Standards and Technology

2:20pm **TF+AS+NS+SA-ThA1 Dynamic and Structural Stability of Cubic Vanadium Nitride**, *Antonio Mei**, University of Illinois at Urbana-Champaign, *O. Hellman*, California Institute of Technology, *N. Wireklint*, Chalmers University of Technology, Sweden, *C.M. Schlepütz*, Argonne National Laboratory, *D.G. Sangiovanni*, *B. Alling*, Linköping University, Sweden, *A. Rockett*, University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden, *I. Petrov*, *J.E. Greene*, University of Illinois at Urbana-Champaign

Structural phase transitions in epitaxial stoichiometric VN/MgO(011) thin films are investigated using temperature-dependent synchrotron x-ray diffraction (XRD), selected-area electron diffraction (SAED), and resistivity measurements combined with high-resolution cross-sectional transmission electron microscopy (HR-XTEM) and *ab-initio* molecular dynamics (AIMD). At room temperature, VN has the B1 NaCl structure. However, at temperatures below $T_c = 250$ K, XRD and SAED results reveal forbidden (00 l) reflections of mixed parity associated with a non-centrosymmetric tetragonal structure. At $T \leq T_c$, forbidden reflections intensify continuously following the scaling behavior $I \propto (T_c - T)^{1/2}$. This suggests a transition of second-order character, but the incompatible symmetries of the parent cubic VN (space group) and product tetragonal VN (I) phases ultimately requires that the structural transition be first order. Resistivity $\rho(T)$ plots between 300 and 4 K consist of two linear regimes resulting from different electron/phonon coupling strengths in cubic and tetragonal VN.

The VN transport Eliashberg spectral function $\alpha^2_{\nu}F(\hbar\omega)$, the product of the phonon density-of-states $F(\hbar\omega)$ and the transport electron/phonon coupling strength $\alpha^2_{\nu}(\hbar\omega)$, is determined and used in combination with room-temperature inelastic neutron scattering results to establish that while entropy favors the higher-temperature cubic phase, as T is lowered below T_c , tetragonal VN becomes the thermodynamic ground state due to its lower enthalpy. AIMD renormalized phonon dispersion relations are in agreement, showing that the energy of (00 l) X-point phonons in NaCl-structure VN decreases and eventually becomes imaginary at $T \leq 250$ K. We demonstrate that free energy contributions due to vibrational entropy, often-neglected in theoretical modeling, are essential in understanding the room-temperature stability of NaCl-structure VN, and of strongly anharmonic systems in general.

2:40pm **TF+AS+NS+SA-ThA2 Comparison of Solution Based Aluminum Oxide Phosphate Thin Films Deposited via Spin Coating vs. a Novel Mist Deposition System**, *Nishit Murari*, *R.H. Mansergh*, *Y. Huang*, *G. Westerfield*, *D. Kesler*, *J.F. Conley*, Oregon State University

Solution based spin coating techniques are well known for producing high quality organic as well as inorganic metal oxide thin films. However, spin coating is primarily suitable for planar substrates and lacks the ability to form uniform ultrathin films over large surface areas. In recent years, several alternative mist based deposition techniques have been introduced to enable solution based deposition over large areas and non-planar substrates. Mist deposition involves the creation of a precursor mist and its subsequent condensation on the substrate. Mist deposition techniques to date have been limited by disadvantages such as the requirement for highly volatile precursors and the non-homogeneous distribution of the mist, both of which lead to inferior film thickness uniformity. To address these limitations, we employ a new mist deposition system with a novel mist creation technique consisting of an atomizer with two opposing precursor jets. The unique opposing configuration of the atomizer enables the formation of a highly uniform mist even from low volatility precursors. In this work, we address the question of whether this new mist deposition technique can produce film quality comparable to spin coating technique.

Amorphous aluminum phosphate (AlPO) thin films were deposited via mist deposition using a BENEQ ACS 200-101 as well as standard spin coating. All films were deposited at room temperature and pressure using precursors based on aqueous suspensions of aluminum phosphate inorganic clusters. The inorganic ligands decompose at low temperature with minimal volume

change presenting a route to high density films at low temperature. Both mist and spin coating achieve thickness uniformity of 5% across a 150 mm Si substrate. Both techniques result in ultra-smooth films with average surface roughness of less than 1 nm RMS. Variation in film density and roughness as a function of annealing temperature was identical for both techniques. Finally, similar charge transport behavior and dielectric constant were exhibited as a function of anneal temperature.

An aqueous precursor was used in a side by side comparison of spin coating and a novel mist deposition technique. High quality AlPO thin films of similar uniformity, density, roughness, and electrical properties were obtained using both techniques. Based on these results, this novel mist based deposition technique appears to be a promising candidate for the next generation of thin film deposition techniques for large area electronics.

3:00pm **TF+AS+NS+SA-ThA3 Electro-Optic Studies of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ Thin Films Deposited by Chemical Solution Deposition Method**, *Vaishali Batra*, *S. Kotru*, *V.N. Harshan*, The University of Alabama, *M. Varagas*, *C.V. Ramana*, University of Texas at El Paso

Lanthanum doped lead zirconate titanate (PLZT) of perovskite type crystalline structure is an interesting transparent ferroelectric material due to its large remnant polarization and electro-optic effects, near the morphotropic phase boundary. The excellent optical and electrical properties make it material of choice for applications in MEMS, optical modulators/transducers and smart sensors. Recent studies reveal that this material possesses great potential for use in future photovoltaic (PV) devices which involves combination of optical transparency and ferroelectric properties. The advantage of using this material for PV applications is that the effect can be realized without a need of p-n junction as in semiconductor devices. Additionally the material exhibits bulk PV effect due to internal electric field originating from electric polarization. However, the optimization of processing conditions of deposited films is important to design efficient devices, which require understanding of the structure, its behavior with light, and response to electric field.

Lanthanum-modified lead zirconate titanate (PLZT) thin films with a composition of $(\text{Pb}_{0.95}\text{La}_{0.05})(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ were deposited on Pt/TiO₂/SiO₂/Si substrates. The films were rapidly annealed in the temperature range of 550 to 750 °C in oxygen ambient to study the effect of crystallization on the electric and optical properties. X-ray diffraction revealed that the post deposition temperature changes the preferential orientation of the films. Optical band gap values determined from UV-visible spectroscopy and spectroscopic ellipsometry for PLZT films were found to be in the range of 3.42-4.00 eV. The optical constants and their dispersion profiles for PLZT films were also determined from SE analyses. PLZT films exhibit an index of refraction ~ 2.5 ($\lambda=630$ nm). The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Au electrodes. High remnant polarization (41.85 $\mu\text{C}/\text{cm}^2$), low coercive voltage (1.19 V) and high free carrier concentration ($\sim 1.1 \times 10^{18} \text{ cm}^{-3}$) were obtained from films annealed at 750 °C. Thus post deposition annealing temperature plays a major role in deciding the electrical and optical properties.

3:20pm **TF+AS+NS+SA-ThA4 Electron Scattering at Surfaces of Epitaxial Metal Layers**, *Pengyuan Zheng*, *D. Gall*, Rensselaer Polytechnic Institute

Epitaxial Cu(001) is grown on MgO(001) with different overlayers to demonstrate that electron surface/interface scattering can be engineered by surface doping, causing a decrease in the resistivity. For instance, the resistivity of 9.3-nm-thick epitaxial and polycrystalline Cu layers is reduced by 11-13% when coated with 0.75 nm Ni. This is due to partially specular surface scattering with specularly parameters $p = 0.3$ and 0.15 for the Ni-coated Cu in vacuum and air, respectively, while scattering is completely diffuse ($p = 0$) for a pure Cu surface in air. This is attributed to the suppression of Cu₂O formation, leading to a lower localized density of states (LDOS) at the surface, and therefore less diffuse electron scattering. The change of surface scattering by controlling the LDOS is further confirmed: the sheet resistance of 9.5-nm-thick epitaxial Cu(001) increases by 4-43% if a 0.1-4 monolayer thick Ti coating is added, but subsequent exposure to 37 Pa of O₂ causes a resistivity reduction of 3-24%. This reduction is due to a recovery of specular interface scattering associated with a reduction of the LDOS during Ti oxidation from 15-27.4 to 2.4-6.5 eV⁻¹nm⁻², as quantified by *ab initio* calculations. Furthermore the surface scattering effect is found to be orientation dependent. For example, the resistivity of 5-nm-thick epitaxial tungsten layers is two times higher for 001 vs 110 orientated layers. This is due to the anisotropy in the Fermi surface, as indicated by transport simulations based on first-principles band structure calculations, which suggest a 1.5 times smaller size effect for the

* TFD James Harper Award Finalist

110 orientation. These epitaxial films were sputter deposited onto Al₂O₃(11-20) and MgO(001) at 1050 °C and 900 °C, respectively, followed by in situ annealing at 1050 °C for 2 hrs. X-ray diffraction θ -2 θ , ω , and ϕ -scans confirm epitaxy and X-ray reflectivity indicates atomically smooth film-substrate interfaces and smooth film surfaces with a root-mean-square roughness that increases from 0.32±0.05 to 0.81±0.05 nm for W(110) with $t = 5.7$ -39.2 nm, and from 0.21±0.05 to 0.40±0.05 nm for W(001) with $t = 4.8$ -50 nm. In summary, we have systematically shown that (1) surface scattering can be altered by carefully controlling the surface LDOS at the Cu surface or interface with the barrier and (2) the crystalline orientation of interconnect wires with non-spherical Fermi surfaces is a major factor when considering alternative metals to replace Cu interconnects.

4:00pm **TF+AS+NS+SA-ThA6 Lattice Relaxation in Multilayered Si_{1-x}Ge_x/Si (001) Metamorphic Heterostructures**, *Tedi Kujofsa, J.E. Ayers*, University of Connecticut

The inclusion of compositionally-graded metamorphic buffer layers in multilayered heterostructures allows tremendous flexibility designing novel SiGe/Si microelectronic and optical semiconductor devices. For example, advanced CMOS transistors can be fabricated on strain relaxed buffers to obtain enhanced mobility in n-channel and p-channel devices using tensile and compressive strain, respectively. While it is necessary to control the strain in the device layers, it is also desirable to fabricate these structures with low threading dislocation densities and minimum buffer thickness. Thus, understanding lattice relaxation in multilayered and compositionally-graded heterostructures is desirable to provide guidance in designing SiGe/Si devices. This work focuses on the design of the multilayered heterostructures comprising a uniform layer of Si_{1-x}Ge_x (device layer) deposited on a Si (001) substrate with an intermediate compositionally-graded buffer layer of Si_{1-x}Ge_x. The objective of this work is to study the relaxation dynamics and misfit dislocations in the device and buffer layer. We present minimum energy calculations and show that for a given device layer with fixed germanium composition and layer thickness, there exists a combination of the buffer layer thickness and compositional grading to provide tight control of the strain in the device layer. Furthermore, we give a simple model describing the strain in the device layer.

4:40pm **TF+AS+NS+SA-ThA8 Growth Stress Evolution in Low Adatom Mobility Fe(Cr) Thin Films**, *Xuyang Zhou*, The University of Alabama, *T. Kaub, R.L. Martens*, The University of Alabama, *G.B. Thompson*, The University of Alabama

During the post coalescence portion of thin film deposition, thin film stress is related to the grain size and adatom mobility of the depositing material. This stress state can be regulated by the mobility of atoms into or out of these grain boundaries. Using Fe(Cr) alloy thin films as a case study, the stress evolution during growth was investigated as a function of Cr content up to 8 at.%. During the deposition of the elemental films, each film grew with a tensile stress state on a Si wafer because of their low adatom mobility. Upon alloying 4 at.% Cr to the Fe film, the as-deposited grains grew from ~40 nm (pure Fe) to ~65 nm (Fe-04Cr), resulting in a stress relaxation from ~200 GPa*nm to 50 GPa*nm at a thickness of 300 nm. As the Cr content increased further, the grains refined back towards ~50 nm in size resulting in a recovery of the higher tensile stress condition. The reduction of the grain size is contributed to Cr solute segregation to the grain boundaries, clustering, and ultimately precipitation at the boundaries. The real-time stress evolution during growth will be discussed in terms of the inferred microstructural evolution of the film using post-mortem atom probe tomography and transmission electron microscopy characterization. The results of which address how segregating behavior can be used as a means of thin film stress engineering.

5:00pm **TF+AS+NS+SA-ThA9 Development of an Analytical Model for Langmuir-Blodgett Silica Microsphere Assembly and Investigation of Ge Back Filling of the Opal Template by Polymer-Assisted Deposition**, *Sarun Atiganyanun, M. Zhou, S.E. Han, S.M. Han*, University of New Mexico

Self-assembled photonic crystals find a wide variety of applications, including low-loss waveguides, high-efficiency solar cells, and thermal emission control. Here, we investigate a low-cost scalable fabrication of an opal structure via self-assembly of colloidal silica microspheres and propose a model describing a relationship between assembly parameters. To fabricate an opal structure, silica microspheres with a diameter of ~900 nm are first functionalized with allyltrimethoxysilane. Langmuir-Blodgett (LB) method is then used to self-assemble silica microspheres onto Si(100) substrates. By optimally adjusting the pulling speed of the substrate and surface pressure within the trough, a hexagonally closed-packed structure is achieved. By repeating LB coating processes for n number of times, an n -multilayer assembly is formed, creating an opal template structure. Scanning electron microscopy and light diffraction experiment are used to identify assembly parameters that give the largest domain size. An

analytical model is also derived from material flux balance and a 2D van der Waals equation of state of silica spheres on water surface to describe the relationship between pulling speed, surface pressure, barrier speed, number of layers, and sphere's diameter for optimal assembly. In this presentation, we will also discuss a facile approach to back-fill opal templates via polymer-assisted deposition of Ge. After forming the template structure, a solution of polyethylenimine, ethylenediaminetetraacetic acid and germanium dioxide is used to back-fill the voids between microspheres. The sample is then annealed in a forming gas environment, forming Ge films around the microspheres. After the microspheres are removed, the Ge structure is characterized with SEM, XRD, and light transmission.

5:20pm **TF+AS+NS+SA-ThA10 The Determination of Porosity and Pore Size Distribution of The Al₂O₃ Antireflection Coating Deposited By Atomic Layer Deposition**, *Chao Li, M. Goorsky*, University of California at Los Angeles

The porosity and pore size distribution of coatings prepared by atomic layer deposition and by other deposition techniques is important to understand their optical and mechanical properties. Specular X-ray reflectivity (SXRR) is capable of extracting layer thickness with angstrom resolution as well as determining the layer density. This makes it a good candidate for the porosity characterization of the antireflection coatings. On the other hand, advances in the development of X-ray generators and optics have made in-house glancing incidence small angle X-ray scattering (GISAXS) experimentation suitable for the determination of the size and shape of pores (in the scale of sub-nanometer to 100 nm) existing in thin films. It can be realized through the simulation of pore scattering based on distorted wave Born approximation (DWBA). Unfortunately, previous GISAXS studies failed to exclude the scattering from the rough surface and interfaces of thin films from the total scattering that was used for the simulation. In this study, we propose a refined GISAXS method characterizing the pore size distribution with the scattering from the rough surface and interfaces excluded. The scattering from the surface and interfaces was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with the parameters of the surface roughness σ , the lateral correlation length ξ and the Hurst parameter h extracted from the atomic force microscopy measurement, and layer thicknesses, densities and compositional grading determined by the specular XRR simulation. This refined GISAXS method, together the SXRR technique, was applied to utilized to reveal the effect of deposition techniques on the nanostructures of single-layer Al₂O₃-based antireflection coatings. They were deposited using atomic layer deposition (ALD) which is a good candidate for multilayer antireflection coatings, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Each of them has two amorphous structures on a Si substrate grown with different deposition parameters. It is indicated by the refined GISAXS method that the first Al₂O₃ single layer is porous with a mean pore (spherical shape) radius of 7.2 nm while there are no pores in the second Al₂O₃ single layer. This agrees well with the SXRR showing a lower density of the first Al₂O₃ single layer (2.93 g/cm³) than that of the second Al₂O₃ single layer (3.04 g/cm³).

5:40pm **TF+AS+NS+SA-ThA11 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Composites**, *Colin Rementer, Q. Xu, K. Fitzell, Z. Yao, P. Nordeen, G. Carman, Y. Wang, J.P. Chang*, University of California at Los Angeles

Traditionally, the use of magnetic materials in high frequency applications has been limited to oxides. This is because the materials' high resistivity, which reduces the formation of eddy currents by the incident electromagnetic waves. However, these oxides have limited applications in multiferroics, which are materials that possess more than one ferroic ordering in a single phase or strain-coupled composite systems, due to their low magnetomechanical coupling. Metallic materials are more desirable to this end, but their magnetic hardness and conductive losses have limited their use.

Rare-earth-free iron-gallium (FeGa) is one of the most promising magnetostrictive materials for use in composite multiferroics, due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in the MHz range or below¹. This is due to the fact that the material has a large ferromagnetic resonance (FMR) linewidth (>300 Oe) at X band (9.6 GHz), which will result in incident energy being converted to heat. Metalloid dopants have been used to soften magnetic materials and to tune frequency dependent properties, such as permeability and piezomagnetic behavior, but at the cost of saturation magnetization as well as magnetostriction². In this work, multilayer laminates containing alternating hard and soft ferromagnetic layers were fabricated to reduce loss at high frequencies.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets into multilayers on Si [100] and piezoelectric substrates with total thicknesses ranging from 40-500 nm. The compositions of the films were verified via X-ray photoelectron spectroscopy (XPS) and were found to be Fe_xGa_{1-y} (78≤y≤85

at%) and $\text{Ni}_x\text{Fe}_{1-x}$ ($79 \leq x \leq 83$ at%). Static magnetic properties were evaluated via superconducting quantum interference device (SQUID) magnetometry, and it was found that the incorporation of NiFe layers was found to reduce the coercivity by up to 80%, while only reducing the saturation magnetization by 20%. FMR measurements revealed a narrowing of the linewidth by up to 90% at X band. Permeability extracted from the reflection coefficient (S11) obtained via stripline measurement was found to be affected by layer thickness and number of layers. FeGa showed strong magnetoelastic behavior and the multilayers are expected to exhibit an enhanced piezomagnetic effect due their reduced coercivity.

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Authors Index

Bold page numbers indicate the presenter

— A —

Agarwal, A.: IS+AS+SA+SS-MoA10, 4
Alayoglu, S.: IS+AS+SA+SS-WeM4, 11
Albertini, O.R.: MI+SA-TuA11, 10
Alling, B.: TF+AS+NS+SA-ThA1, 15
Amati, M.: IS+AS+SA+SS-MoA7, 3
Anderson, V.: TF+AS+NS+SA-ThM13, **14**;
TF+AS+NS+SA-ThM6, 13
Apkarian, V.A.: IS+AS+SA+SS-WeM3, 11
Arena, D.: MI+SA-TuA12, 10
Armocost, M.D.: IS+AS+SA+SS-MoA10, 4
Atiganyanun, S.: TF+AS+NS+SA-ThA9, **16**
Ayers, J.E.: TF+AS+NS+SA-ThA6, 16

— B —

Back, C.H.: MI+SA-TuA1, 9
Bañares, M.A.: IS+AS+SA+SS-WeM5, **11**
Batra, V.: TF+AS+NS+SA-ThA3, **15**
Baugh, D.: IS+AS+SA+SS-WeM2, **11**
Beach, G.S.D.: MI+SA-TuA3, **9**
Beasor, S.: TF+AS+NS+SA-ThM11, 14
Beniwal, S.: MI+SA-TuA12, **10**
Bousquet, A.: TF+AS+NS+SA-ThM1, **13**
Broderick, A.: IS+AS+SA+SS-TuM2, 7
Brongersma, H.: TF+AS+NS+SA-ThM10, 13
Bruener, P.: TF+AS+NS+SA-ThM10, 13

— C —

Carman, G.: TF+AS+NS+SA-ThA11, 16
Cellier, J.: TF+AS+NS+SA-ThM1, 13
Chang, J.P.: TF+AS+NS+SA-ThA11, 16
Chastanet, G.: MI+SA-TuA12, 10
Chen, P.: IS+AS+SA+SS-TuM10, 7
Chu, Y-H.: MI+SA-TuA10, 10
Conley, J.F.: TF+AS+NS+SA-ThA2, 15
Corbett, J.P.: MI+SA-TuA9, 9
Craver, B.: IS+AS+SA+SS-MoA10, 4
Crumlin, E.J.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-TuM3, 7

— D —

de Jong, N.: SA-MoA2, **5**
De Lucia, F.C.: IS+AS+SA+SS-MoA10, 4
de Visser, A.: SA-MoA2, 5
Decker, M.: MI+SA-TuA1, 9
DeMasi, A.: TF+AS+NS+SA-ThM13, 14;
TF+AS+NS+SA-ThM6, 13
Diebold, A.C.: TF+AS+NS+SA-ThM12, 14
Dong, S.: MI+SA-TuA10, 10
Dougherty, D.B.: MI+SA-TuA7, **9**
Downben, P.A.: MI+SA-TuA12, 10
Downey, B.: TF+AS+NS+SA-ThM6, 13

— E —

Eddy, C.: TF+AS+NS+SA-ThM6, 13
Eddy, Jr, C.R.: TF+AS+NS+SA-ThM13, 14
Enders, A.: MI+SA-TuA12, 10
Eren, B.: IS+AS+SA+SS-MoA5, 3
Ewing, P.R.: IS+AS+SA+SS-MoA10, 4

— F —

Farhaoui, A.: TF+AS+NS+SA-ThM1, 13
Fartmann, M.: TF+AS+NS+SA-ThM10, 13
Favaro, M.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-TuM3, 7
Fitzell, K.: TF+AS+NS+SA-ThA11, 16
Frantzeskakis, E.: SA-MoA2, 5
Frenkel, A.: IS+AS+SA+SS-MoA3, 3;
IS+AS+SA+SS-MoA8, 4;
IS+AS+SA+SS-WeM10, **12**
Fukidome, H.: SA-MoA1, 4

— G —

Gall, D.: TF+AS+NS+SA-ThA4, 15
Gangopadhyay, S.: MI+SA-TuA11, 10
Golden, M.S.: SA-MoA2, 5
Goorsky, M.: TF+AS+NS+SA-ThA10, 16

Green, A.: TF+AS+NS+SA-ThM12, 14
Greene, J.E.: TF+AS+NS+SA-ThA1, 15
Gregoratti, L.: IS+AS+SA+SS-MoA7, 3
Grehl, T.: TF+AS+NS+SA-ThM10, 13
Gruebel, G.: SA-MoM10, **1**
Guo, J.-H.: IS+AS+SA+SS-WeM1, 11

— H —

Han, S.E.: TF+AS+NS+SA-ThA9, 16
Han, S.M.: TF+AS+NS+SA-ThA9, 16
Harshan, V.N.: TF+AS+NS+SA-ThA3, 15
Hathaway, M.: TF+AS+NS+SA-ThM10, **13**
Helal, Y.H.: IS+AS+SA+SS-MoA10, **4**
Heldebrant, D.: IS+AS+SA+SS-TuM13, 8
Hellman, O.: TF+AS+NS+SA-ThA1, 15
Hemminger, J.C.: IS+AS+SA+SS-TuM5, 7
Hitchcock, A.P.: SA-MoM1, **1**
Hite, J.K.: TF+AS+NS+SA-ThM13, 14
Holcomb, M.: MI+SA-TuA10, **10**
Huang, Y.: SA-MoA2, 5; TF+AS+NS+SA-ThA2, 15
Hultman, L.: TF+AS+NS+SA-ThA1, 15
Hussain, Z.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-TuM3, 7

— I —

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

— J —

Jeon, B.: IS+AS+SA+SS-TuM3, 7
Jeong, B.: IS+AS+SA+SS-TuM12, 7
Johansson, N.: IS+AS+SA+SS-MoA4, 3
Johnson, S.D.: TF+AS+NS+SA-ThM13, 14;
TF+AS+NS+SA-ThM6, 13
Jones, B.A.: MI+SA-TuA11, **10**

— K —

Kaub, T.: TF+AS+NS+SA-ThA8, 16
Kera, S.: SA-MoA9, **5**
Keszler, D.: TF+AS+NS+SA-ThA2, 15
Khalifa, Y.: IS+AS+SA+SS-TuM2, 7
Kolmakov, A.: IS+AS+SA+SS-TuM4, 7
Komissar, A.: IS+AS+SA+SS-WeM12, 12
Kotru, S.: TF+AS+NS+SA-ThA3, 15
Kujofsa, T.: TF+AS+NS+SA-ThA6, **16**
Kumagai, T.: IS+AS+SA+SS-WeM2, 11

— L —

LaBella, V.: TF+AS+NS+SA-ThM12, 14
Lanzara, A.: SA-MoA3, **5**
Lao, D.: IS+AS+SA+SS-TuM13, 8
Lee, J.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-WeM3, **11**
Lewis, A.: IS+AS+SA+SS-WeM12, **12**
Lewis, D.: IS+AS+SA+SS-WeM12, 12
Li, C.: TF+AS+NS+SA-ThA10, **16**
Li, J.: IS+AS+SA+SS-MoA3, 3
Liu, A.Y.: MI+SA-TuA11, 10
Liu, J.: IS+AS+SA+SS-MoA8, 4; MI+SA-TuA12, 10
Liu, S.: IS+AS+SA+SS-WeM2, 11
Liu, Z.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-TuM3, 7
Lucy, J.M.: MI+SA-TuA9, 9
Ludwig, K.F.: TF+AS+NS+SA-ThM13, 14;
TF+AS+NS+SA-ThM6, 13

— M —

Maayan, E.: IS+AS+SA+SS-WeM12, 12
Mandru, A.-O.: MI+SA-TuA9, **9**
Mansergh, R.H.: TF+AS+NS+SA-ThA2, 15
Martens, R.L.: TF+AS+NS+SA-ThA8, 16
Matyi, R.J.: TF+AS+NS+SA-ThM12, 14
McClimon, J.B.: IS+AS+SA+SS-MoA4, 3
Mei, A.B.: TF+AS+NS+SA-ThA1, **15**
Melaet, G.: IS+AS+SA+SS-WeM4, 11
Meyer, D.: TF+AS+NS+SA-ThM6, 13
Monazami, E.: IS+AS+SA+SS-MoA4, 3

Mu, S.: MI+SA-TuA12, 10
Mun, B.S.: IS+AS+SA+SS-TuM12, 7
Murari, N.: TF+AS+NS+SA-ThA2, **15**

— N —

Naim, A.: MI+SA-TuA12, 10
Narasimham, A.J.: TF+AS+NS+SA-ThM12, **14**
Neese, C.F.: IS+AS+SA+SS-MoA10, 4
Nepal, N.: TF+AS+NS+SA-ThM13, 14;
TF+AS+NS+SA-ThM6, **13**
Newberg, J.: IS+AS+SA+SS-TuM2, 7
Nguyen, L.: IS+AS+SA+SS-MoA3, **3**;
IS+AS+SA+SS-MoA8, 4;
IS+AS+SA+SS-WeM13, 12
Nordeen, P.: TF+AS+NS+SA-ThA11, 16
Nune, S.: IS+AS+SA+SS-TuM13, 8

— O —

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

— P —

Pan, Y.: SA-MoA2, 5
Parmigiani, F.: SA-MoA5, **5**
Patil, S.K.: TF+AS+NS+SA-ThM11, **14**
Petrov, I.: TF+AS+NS+SA-ThA1, 15
Plumb, N.C.: SA-MoA2, 5
Pronk, P.: SA-MoA2, 5

— Q —

Qiu, A.: TF+AS+NS+SA-ThM5, **13**

— R —

Radovic, M.: SA-MoA2, 5
Rai, R.: TF+AS+NS+SA-ThM11, 14
Ralston, W.: IS+AS+SA+SS-WeM4, **11**
Ramana, C.V.: TF+AS+NS+SA-ThA3, 15
Reid, A.H.: SA-MoM8, **1**
Reinke, P.: IS+AS+SA+SS-MoA4, **3**
Rementer, C.: TF+AS+NS+SA-ThA11, **16**
Richard, A.L.: MI+SA-TuA9, 9
Rios, L.: IS+AS+SA+SS-WeM3, 11
Rockett, A.: TF+AS+NS+SA-ThA1, 15
Romano, A.: TF+AS+NS+SA-ThM5, 13
Rosa, P.: MI+SA-TuA12, 10
Ross, P.N.: IS+AS+SA+SS-TuM12, 7;
IS+AS+SA+SS-TuM3, 7

— S —

Salmeron, M.B.: IS+AS+SA+SS-MoA5, **3**;
IS+AS+SA+SS-WeM1, 11
Sangiovanni, D.G.: TF+AS+NS+SA-ThA1, 15
Schleppütz, C.M.: TF+AS+NS+SA-ThA1, 15
Schlögl, R.: IS+AS+SA+SS-MoA1, **3**
Schnadt, J.: IS+AS+SA+SS-MoA4, 3
Schneider, G.: SA-MoM6, **1**
Schoenlein, R.: SA-MoA7, **5**
Sezen, H.: IS+AS+SA+SS-MoA7, **3**
Shapiro, D.: SA-MoM1, 1
Shayesteh, P.: IS+AS+SA+SS-MoA4, 3
Shi, M.: SA-MoA2, 5
Smith, A.R.: MI+SA-TuA9, 9
Somorjai, G.A.: IS+AS+SA+SS-WeM4, 11
Sterbinsky, G.: MI+SA-TuA12, 10
Stout, P.J.: IS+AS+SA+SS-MoA10, 4
Sui, X.: IS+AS+SA+SS-TuM13, 8

— T —

Tallarida, N.: IS+AS+SA+SS-WeM3, 11
Tao, F.: IS+AS+SA+SS-MoA3, 3;
IS+AS+SA+SS-MoA8, 4;
IS+AS+SA+SS-WeM13, **12**
Taviot-Gueho, C.: TF+AS+NS+SA-ThM1, 13
Terry, J.: TF+AS+NS+SA-ThM3, **13**
Thissen, A.: IS+AS+SA+SS-MoA9, **4**
Thompson, G.B.: TF+AS+NS+SA-ThA8, 16
Tomasella, E.: TF+AS+NS+SA-ThM1, 13

Tran, B.V.: SA-MoA2, 5
Trappen, R.: MI+SA-TuA10, 10
Tyliszczak, T.: SA-MoM1, 1

— **U** —

Urpelainen, S.: IS+AS+SA+SS-MoA4, 3

— **V** —

van der Schot, G.: SA-MoM3, 1
van Heumen, E.: SA-MoA2, 5
Varagas, M.: TF+AS+NS+SA-ThA3, 15

— **W** —

Wang, J.: MI+SA-TuA7, 9
Wang, Y.: TF+AS+NS+SA-ThA11, 16
Wei, D.: MI+SA-TuA1, 9
Westerfield, G.: TF+AS+NS+SA-ThA2, 15

Wireklint, N.: TF+AS+NS+SA-ThA1, 15
Wolf, M.: IS+AS+SA+SS-WeM2, 11
Woltersdorf, G.: MI+SA-TuA1, 9
Wu, C.H.: IS+AS+SA+SS-WeM1, 11
Wu, D.: SA-MoA2, 5
Wu, J.: SA-MoM1, 1

— **X** —

Xu, N.: SA-MoA2, 5
Xu, Q.: TF+AS+NS+SA-ThA11, 16

— **Y** —

Yang, F.: MI+SA-TuA9, 9
Yano, J.: IS+AS+SA+SS-TuM3, 7
Yao, J.: IS+AS+SA+SS-TuM13, 8
Yao, Z.: TF+AS+NS+SA-ThA11, 16
Yu, X.-Y.: IS+AS+SA+SS-TuM13, 8

— **Z** —

Zhang, S.: IS+AS+SA+SS-MoA8, 4
Zhang, X.: MI+SA-TuA12, 10
Zheng, P.Y.: TF+AS+NS+SA-ThA4, 15
Zhou, J.: MI+SA-TuA10, 10
Zhou, L.: TF+AS+NS+SA-ThM11, 14
Zhou, M.: TF+AS+NS+SA-ThA9, 16
Zhou, X.: TF+AS+NS+SA-ThA8, 16
Zhou, Y.: IS+AS+SA+SS-TuM13, 8
Zhu, X.H.: SA-MoM1, 1
Zhu, Z.: IS+AS+SA+SS-TuM13, 8
Zinoviev, O.: IS+AS+SA+SS-WeM12, 12
Zoubian, F.: TF+AS+NS+SA-ThM1, 13
Zwartsenberg, B.: SA-MoA2, 5