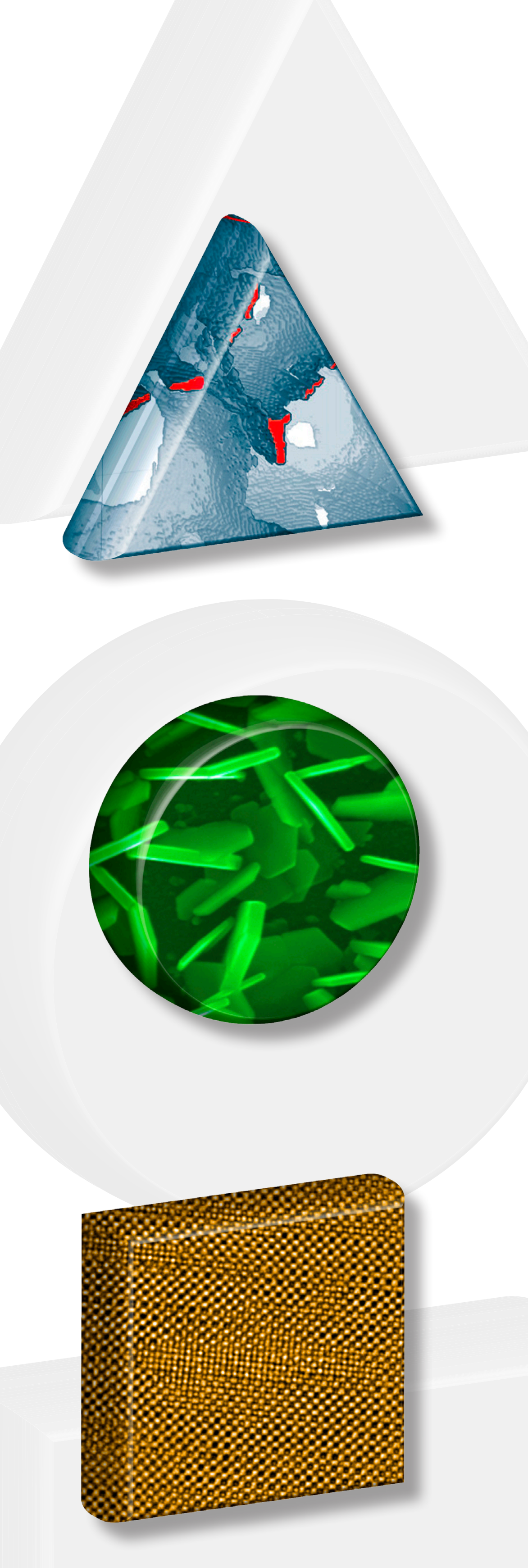
2012 Users Meeting

Argonne National Laboratory
May 7-10, 2012

Program & Abstracts

Our User Science Shapes the Future

Advanced Photon Source • Center for Nanoscale Materials • Electron Microscopy Center



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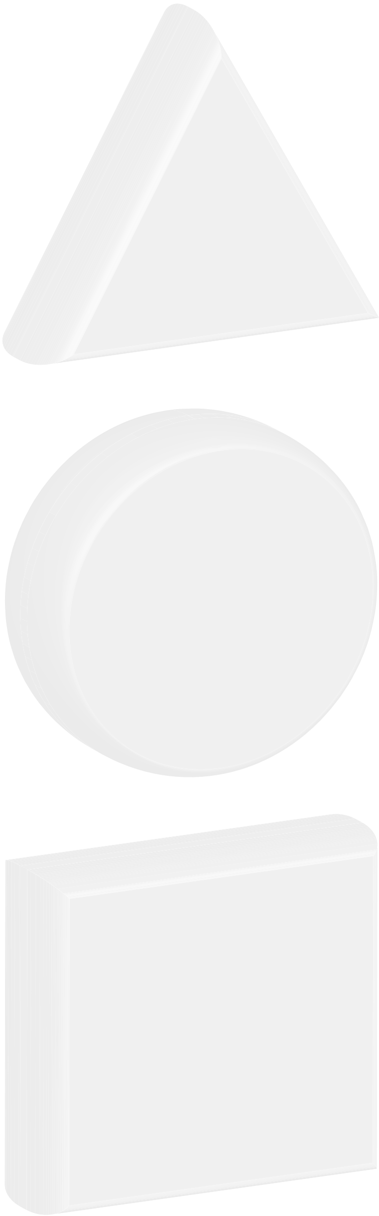
Advanced Photon Source • Center for Nanoscale Materials • Electron Microscopy Center



2012

Users Meeting

PROGRAM & **ABSTRACTS**

May 7-10, 2012

Advanced Photon Source
Center for Nanoscale Materials
Electron Microscopy Center
Argonne National Laboratory
Argonne, Illinois USA

User Facilities at Argonne National Laboratory

User Contacts

Advanced Photon Source
http://www.aps.anl.gov
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apsuser@aps.anl.gov

Argonne Leadership Computing Facility
http://www.alcf.anl.gov
630-252-0929

Argonne Tandem Linac Accelerator System
http://www.phy.anl.gov/atlas
630-252-4044

Center for Nanoscale Materials
http://nano.anl.gov
630-252-6952
cnm_useroffice@anl.gov

Electron Microscopy Center
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Argonne is a U.S. Department of Energy laboratory managed by the UChicago Argonne, LLC under contract number DE-AC02-06CH11357. The Laboratory is located southwest of Chicago at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne, see www.anl.gov.

2012 Rosalind Franklin Award
Damian C. Ekiert

The APS Users Organization has named Damian C. Ekiert as the winner of the 2012 Rosalind Franklin Young Investigator Award. The prize recognizes Ekiert's work on broadly neutralizing antibodies, which holds promise for structure-based design of a universal vaccine for influenza.

Current flu vaccines primarily elicit an immune response against the head region of hemagglutinin, a portion of the influenza virus that changes rapidly. Thus, new vaccines must be developed each year, and unanticipated mutations in the virus may lead to the outbreak of an influenza pandemic. Now, thanks to the work of Ekiert and others on broadly neutralizing antibodies, it may be possible for vaccines to target a region of hemagglutinin that does not change. Thus, one vaccine could protect against most types of flu over a much longer term.

The work focused on two antibodies that neutralize many strains of influenza. Ekiert used beamline 23-ID (GM/CA-CAT) to determine the structure of these antibodies in complex with their target antigen, hemagglutinin. The structural data pinpointed the region on the virus that the antibody targets, and further studies showed that the structure of this region is unchanged, or conserved, across many strains of influenza. One of the antibodies tested is now in initial clinical trials in humans for use as a treatment for acute influenza infection.

Ekiert also collaborated with a group led by David Baker (University of Washington) that developed a computational method for designing novel protein-protein interactions. The method was used to design several proteins to target the conserved region of hemagglutinin, and Ekiert solved the structure of one of these proteins when complexed with hemagglutinin from the 1918 pandemic influenza virus.

According to Ekiert, there were some challenges due to the size, flexibility, and heterogeneity of the sample. Hemagglutinin is heavily glycosylated, which can make crystallization challenging, and large regions of the antibodies were disordered in some of the structures. "Tools developed at GM/CA-CAT were crucial for the collection of high-quality diffraction data," Ekiert said. "Several of the structures would have been difficult or perhaps impossible to obtain at many other beamlines." Critical to the work were the minibeam (an X-ray beam with a 5-20 μm spot size) and a rastering function developed at GM/CA-CAT. "Together, these tools allowed us to find and center on crystals we were unable to visualize in the mounting loop, collect diffraction data from very small crystals, and to zero in on small, high-quality sections of otherwise unusable crystals," Ekiert said.

The X-ray structural studies formed the basis of Ekiert's dissertation work in Ian Wilson's group at the Scripps Research Institute. The antibody project as a whole was a collaboration between Scripps and the biopharmaceutical company Crucell, of the Netherlands.

Ekiert is now a post-doctoral fellow at the University of California, San Francisco, in the laboratory of Jeffery Cox, where he is working on host-pathogen interactions in *M. tuberculosis.*

Publications:

D.C. Ekiert, R.H.E. Friesen, G. Bhabha, T. Kwaks, M. Jongeneelen, W. Yu, C. Ophorst, F. Cox, H.J.W.M. Korse, B. Brandenburg, R. Vogels, J.P.J. Brakenhoff, R. Kompier, M.H. Koldijk, L.A.H.M. Cornelissen, L.L.M. Poon, M. Peiris, W. Koudstaal, I.A. Wilson, J. Goudsmit. "A highly conserved neutralizing epitope on Group 2 influenza A viruses," Science, 333, 843 (2011). DOI: 10.1126/science.1204839.

S.J. Fleishman*, T.A Whitehead*, D.C. Ekiert*, C. Dreyfus, J.E. Corn, E.M. Strauch, I.A. Wilson, D. Baker. "Computational design of proteins targeting the conserved stem region of influenza hemagglutinin." Science, 332, 816 (2011). DOI: 10.1126/science.1202617

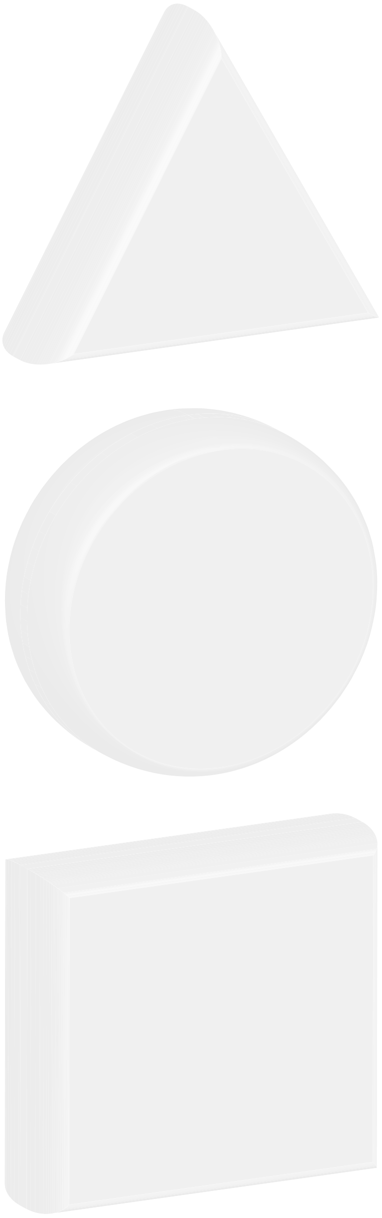
R. Xu*, D.C. Ekiert*, J.C. Krause, R. Hai, J.E. Crowe, Jr., I.A. Wilson. "Structural basis of preexisting immunity to the 2009 H1N1 pandemic influenza virus," Science, 328, 357 (2010). DOI: 10.1126/science.1186430

D.C. Ekiert, G. Bhabha, M.A. Elsliger, R.H. Friesen, M. Jongeneelen, M. Throsby, J. Goudsmit, I.A. Wilson. "Antibody recognition of a highly conserved influenza virus epitope." Science, 324, 246 (2009). DOI: 10.1126/science.1171491

In 2004, in conjunction with the Advanced Photon Source, the APS Users Organization established the APSUO Rosalind Franklin Young Investigator Award to recognize an important scientific or technical accomplishment by a young investigator (senior graduate student or early career Ph.D.) at, or beneficial to, the APS.

Rosalind Franklin was a brilliant chemist who played a critical but largely unacknowledged role in the discovery of the structure of DNA. While working as a research associate for John Randall at King's College in 1951, Franklin was assigned to study the unwieldy DNA molecule with x-ray crystallography—a technique only just beginning to be used for biological molecules. Her results revealed the position of the sugar-phosphate backbone and the basic helical structure of the molecule; when her x-ray photographs filtered unofficially to John Watson at Cambridge, he immediately saw their implications. Franklin went on to work on the tobacco mosaic virus and the polio virus, but her career came to an untimely end when she died of cancer in 1958 at age 37.

Previous award recipients include Alexis Templeton (2004), Wendy Mao (2006), Oleg G. Shpyrko (2008), and Rafael Jaramillo (2010).



2012
Users Meeting

COMPREHENSIVE **PROGRAM**

May 7-10, 2012

Advanced Photon Source
Center for Nanoscale Materials
Electron Microscopy Center
Argonne National Laboratory
Argonne, Illinois USA

Monday May 7

8:00 – 5:00	Exhibits *Bldg. 402, Gallery; Bldg. 401, Atrium*
7:30 – 5:00	Registration *Bldg. 401, Atrium*
12:20 – 1:30	Lunch *Tent*
12:20 – 1:30	Postdoc Luncheon *Bldg. 401, A1100*

A lunchtime talk will focus on postdoctoral opportunities at Argonne National Laboratory.
Please bring a brown bag lunch or purchase lunch ticket. The web page for the Argonne postdoctoral program is http://www.dep.anl.gov/Postdocs/.

Opening Session (Bldg. 402 Lecture Hall)

8:45 – 8:55	Peter Eng, APSUO Chair *Welcome*
8:55 – 9:25	Eric Isaacs, Argonne National Laboratory Director *Welcome from the Laboratory and Introduction of the The Honorable Judy Biggert*
9:25 – 9:45	The Honorable Judy Biggert, U.S. Representative, 13th Congressional District of Illinois *Washington Perspective*
9:45 – 9:50	Peter Eng, APSUO Chair *Introduction of Keynote*
9:50 – 10:30	Keynote Speaker: Richard Harris, Science Desk Correspondent for NPR
10:30 – 11:00	Coffee Break *Gallery and Atrium*
11:00 – 11:20	Brian Stephenson (Associate Laboratory Director for Photon Sciences) *Update on the Advanced Photon Source*
11:20 – 11:40	Amanda Petford–Long (Director, Center for Nanoscale Materials) *Update on the Center for Nanoscale Materials*
11:40 – 12:00	Dean Miller (Director, Electron Microscopy Center) *Update on the Electron Microscopy Center*

12:00 – 12:20	Tony Lanzirotti (The University of Chicago, CARS) *National User Facility Organization (NUFO) Report*
12:20 – 1:30	Lunch *(Tent)* + Postdoc Luncheon *Bldg. 401, A1100*

Parallel Plenary Sessions
APS (Bldg. 402, Lecture Hall)

See abstracts page 11.

1:30 – 2:10	Keynote Speaker: Alexis Templeton (University of Colorado, Boulder) *Iron Mineral Transformations that Drive Subsurface Biospheres*
2:10 – 2:30	2012 APSUO Rosalind Franklin Young Investigator Award Presentation: Damian C. Ekiert (University of California, San Francisco) *From Broadly Neutralizing Antibodies to a Universal Therapy for Influenza*
2:30 – 3:10	Linda Young (X-ray Science Division, Advanced Photon Source) *X-rays in the Fourth Dimension at the Advanced Photon Source*
3:10 – 3:40	Coffee Break *Gallery and Atrium*
3:40 – 4:20	Mike Gillan (London Centre for Nanotechnology & Thomas Young Centre, University College London, UK) *Water on a Knife-edge: The Subtle Balance of Forces in Clusters, Ice, and Liquid*
4:20 – 4:40	Ahmet Uysal (Advanced Photon Source Invited Student Talk) *From Kidney Stones to Gold: Lessons from Biology to Build Better Nanomaterials*
4:40 – 5:30	George Srajer (X-ray Science Division, Advanced Photon Source) *APS Upgrade Presentation*

CNM (E1100-1200)

See abstracts page 13.

1:30 – 2:15	Keynote Speaker: Caroline Ross (Massachusetts Institute of Technology) *Templated Block Copolymers for Nanolithography*
2:15 – 2:45	Horacio Espinosa (Northwestern University) *Recent Advances in Nanoelectromechanical Switches*
2:45 – 3:15	Esmeralda Yitamben (Center for Nanoscale Materials, Argonne National Laboratory) *Tracking Amino Acids inside Chiral Quantum Corrals*
3:15 – 3:40	Coffee Break *Gallery and Atrium*

3:40 – 4:10	Paul Evans (University of Wisconsin at Madison) *Structural Consequences of Ferroelectric Nanolithography*
4:10 – 4:40	Pingshan Wang (Clemson University) *High-frequency Magnetization Dynamics in Patterned Permalloy Thin Films*
4:40 – 4:55	Pongsakorn Kanjanaboos (Center for Nanoscale Materials Invited Student Talk) *Measurement of Resonant Frequencies and Modes of Freestanding Nanoparticle Monolayers*

EMC (A1100)

See abstracts page 15.

1:30 – 2:00	Ted Norris (University of Michigan) *Plasmonic EELS: Towards a Convergence of Optics and Electron Microscopy*
2:00 – 2:30	J. G. Wen (Argonne National Laboratory) *Recent Studies of Chromatic Aberration-corrected Transmission Electron Microscopic Imaging at Argonne National Laboratory*
2:30 – 3:15	Keynote Speaker: David W. McComb (The Ohio State University) *Interfaces in Fuel Cells, Solar Cells and Biomaterials*
3:15 – 3:40	Coffee Break *Gallery and Atrium*
3:40 – 4:00	Yuyuan Lin (Electron Microscopy Center Invited Student Talk) *Atomic Surface Structure of Strontium Titanate Nanocuboids*
4:00 – 4:30	Marquis Kirk (Argonne National Laboratory) *TEM with* In-situ *Ion Irradiation in 4D+*
4:30 – 5:00	Renu Sharma (National Institute of Standards and Technology) *Direct Measurements of Active and Inactive Catalyst Particles under Reaction Conditions Using Environmental TEM*

5:00 – 8:30	Dinner *Tent* The First-ever APS/CNM/EMC Video and Music Event Featuring the “The Big Eddy Springs Blues Band” *Bldg. 402 Auditorium*

Tuesday May 8

8:00 – 5:00	Exhibits *Bldg. 402, Gallery; Bldg. 401, Atrium*
8:00 – 5:00	Registration *Bldg. 401, Atrium*
12:20 – 1:30	Lunch *Tent*

Cross–facility Thematic Workshops

Workshop A *(See page 21 for agenda and abstracts.)*

Operando Characterization of Energy Systems
Bldg. 401, Room A1100

Workshop B *(See page 26 for agenda and abstracts.)*

Probing the Interface between Biological Systems and the Environment
Bldg. 402, Rooms E1100/E1200

Workshop C *(See page 31 for agenda and abstracts.)*

Imaging at All Length and Time Scales
APS 402 Lecture Hall

4:40 – 7:00	Poster Session and Reception *Shuttle bus service provided between APS, Guest House, and TCS Bldg. 240*
7:00 – 9:00	APS Partner User Council Meeting and Dinner *Argonne Guest House Dining Room*

Wednesday May 9

8:00 – 5:00	Exhibits *Bldg. 402, Gallery; Bldg. 401, Atrium*
8:00 – 12:00	Registration *Bldg. 401, Atrium*
12:00 – 2:00	CNM Users Executive Committee Meeting *C4200, Building 401*
12:20 – 1:30	Lunch *Tent*
12:10 – 1:30	APSUO's Steering Committee Lunch *Bldg. 401, Fifth Floor Gallery*

Parallel Facility–specific Workshops (Workshops 1-8)

APS *(See page 36 for agendas and abstracts.)*

Workshop 1—full day:	Spectroscopy of Rare-earth Materials at Extreme Conditions: Structure, Magnetism, and Energy *Bldg. 401, Room A1100*
Workshop 2—full day:	Metal Ion Adsorption at Interface *Bldg. 440, Room A105/106*
Workshop 3—full day:	Energy Materials and Energy Systems Applications of In Situ X-ray Microscopy *APS 402 Lecture Hall*
Workshop 4—full day:	Functional Biomolecular Interfaces *Bldg. 402, Room E1200*
Workshop 5–half day:	Characterization of Materials for Sustainable Energy: Quantitative GIXS for Organic Photovoltaics *Bldg. 460 (Argonne Guest House), Conference Room A*
Workshop 6–half day:	APCF: Crystals, Robots, and X-rays *Bldg. 460 (Argonne Guest House), Conference Room A*

CNM *(See page 68 for agenda and abstracts.)*

Workshop 7—full day:	NanoBio Interfaces: From Materials Design to Complex Systems *Bldg. 401, Room A5000*

EMC *(See page 73 for agenda and abstracts.)*

Workshop 8—full day:	*In situ* and Environmental Science: How Can Electron Microscopy and Spectroscopy Help? *Bldg. 402, Room E1100*

Thursday May 10

CNM Short Courses

CNM Building 440

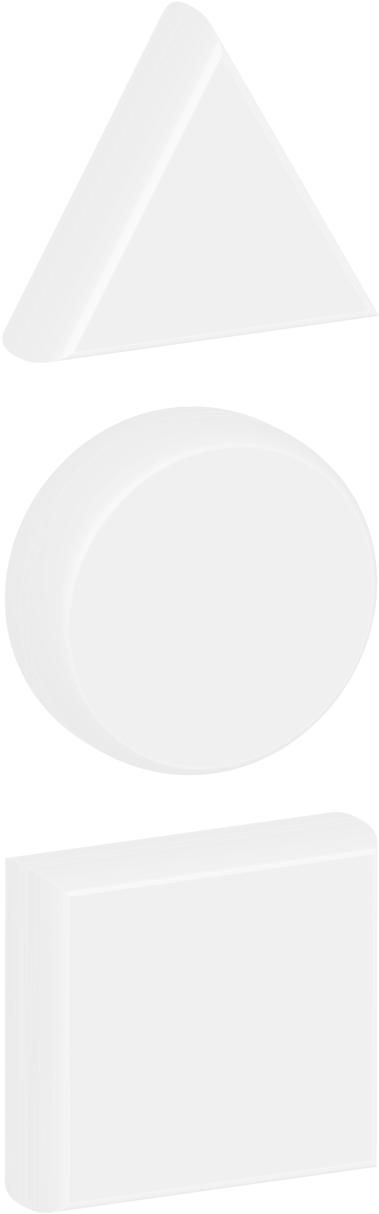
8:30 – 12:00	Morning sessions
1:30 – 5:00	Afternoon sessions

A. Functional Imaging with Ambient Atomic Force Microscopy
(Full Day, Rm. A105/106)
Organizer: Maxim Nikiforov

B. Confocal Raman Microscopy
(Half Day-Morning, Rm. B108)
Organizer: Dave Gosztola

C. Practical Methods for Fabricating Nanostructures and Devices
(Full Day, Upstairs Gallery)
Organizer: Ralu Divan

D. High-performance Computing Techniques for Materials Modeling and Nanophotonics
(Half Day-Morning, Rm. A201)
Organizer: Michael Sternberg



2012
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GENERAL SESSION **ABSTRACTS**

Monday May 7

APS

Iron Mineral Transformations that Drive Subsurface Biospheres

Alexis Templeton

Department of Geological Sciences, University of Colorado, Boulder, CO 80309

Iron is one of the major rock-forming elements on rocky planets such as Earth. Because the majority of iron is far from equilibrium with near-surface environments and is prone to participating in energy releasing redox-reactions, most subsurface geological systems can function as enormous microbial habitats during fluid circulation through fractures and tectonically active regions of the crust. In this talk, we will explore the chemical behavior of Fe during rock alteration processes that produce molecular hydrogen, using a suite of surface sensitive and microscale synchrotron-based x-ray spectroscopic and scattering techniques. We will then discuss the importance of geological hydrogen generation in fueling the activity of modern and ancient extremophile bacteria.

APS

From Broadly Neutralizing Antibodies to a Universal Therapy for Influenza

Damian C. Ekiert[1, 2], Gira Bhabha[1], Robert Friesen[3], Jaap Goudsmit[3], and Ian A. Wilson[1]

[1] Department of Molecular Biology and The Skaggs Institute for Chemical Biology The Scripps Research Institute, La Jolla, CA 92037
[2] Current affiliation: Department of Microbiology and Immunology, The University of California—San Francisco, San Francisco, CA 94122
[3] Crucell Holland BV, Archimedesweg 4-6, 2301 CA Leiden, The Netherlands

Current influenza vaccines provide protection only against viral isolates similar to the vaccine strain, and will likely prove ineffective against an emerging pandemic virus. In contrast, broadly neutralizing antibodies recognizing conserved epitopes in the major surface antigen, hemagglutinin, neutralize across multiple virus subtypes and are protective *in vivo*. In order to advance our understanding of the interplay between influenza virus and the humoral immune response, we are investigating the structural basis of virus neutralization by monoclonal antibodies. We have determined the co-crystal structures of several antibodies in complex with hemagglutinin, including two of the most broadly neutralizing antibodies ever reported against flu: CR6261 and CR8020. These antibodies recognize distinct, highly conserved epitopes on the HA stem, far from the variable regions in the head targeted by most other antibodies, and neutralize infectivity by blocking the fusion of viral and cellular membranes during entry. CR6261 and CR8020 have broad activity against the two major influenza A virus lineages (group 1 and group 2, respectively), and together neutralize the vast majority of viruses causing human disease. Antibodies such as these have immediate therapeutic applications and are being used to guide the design of improved vaccines that elicit similar, broadly neutralizing antibodies.

Ekiert, et al., *Science*, 324:246–251, (2009).

Ekiert, et al., *Science*, 333:843–850, (2011).

APS

X-rays in the Fourth Dimension at the Advanced Photon Source

Linda Young

X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Relative to space, the dimension of time has been underexploited in x-ray science. The advent of new capabilities and x-ray sources promises to change this. X-rays are widely used as powerful probes of elemental, chemical, and orientational degrees of freedom in the bulk and surface of crystalline and non-crystalline systems. These degrees of freedom may be controlled by external inputs and the response monitored by x-rays on multiple timescales ranging from picoseconds to minutes and in sample sizes from millimeters to nanometers at wavelengths short enough to resolve atomic-scale dynamics. Here I will discuss the past, present, and potential for future time-domain studies at the Advanced Photon Source.

APS

Water on a Knife-edge: The Subtle Balance of Forces in Clusters, Ice, and Liquid

Mike Gillan

London Centre for Nanotechnology & Thomas Young Centre, University College London, UK

Water has probably been studied more comprehensively than any other substance, but its molecular-scale energetics remain surprisingly elusive. Parameterized interaction models, including some developed at PNNL, can be remarkably successful. But widely used electronic-structure methods based on conventional density-functional theory (DFT) struggle to reproduce the properties of water clusters, ice structures, and the bulk liquid for reasons that are still controversial. I will summarize some new approaches that we are pursuing at UCL in collaboration with colleagues at Cambridge and Bristol, focusing particularly on our recent work with quantum Monte Carlo (QMC) [1] and Gaussian Approximation Potentials (GAP) [2]. I will show that QMC is much more accurate than DFT for the energetics of clusters [3] and ice structures [4], and that it can also supply useful benchmarks for statistical samples of configurations of the bulk liquid. We are using QMC and correlated quantum chemistry techniques to analyze the sources of error in DFT approximations and to quantify the accuracy of GAP corrections to DFT. It is becoming clear from this work that conventional DFTs have a hard time describing water systems because they misrepresent the subtle balance between 2-body (dispersion) and beyond-2-body (polarization) parts of the energy.

[1] M.J. Gillan, M.D. Towler and D. Alfe, "Petascale computing opens new vistas for quantum Monte Carlo", Scientific Highlight, Psi-k Newsletter No. 103, February 2011: www.psi-k.org/newsletters.shtml.

[2] A.P. Bartók, M.C. Payne, R. Kondor and G. Csányi, "Gaussian Approximation Potentials: The accuracy of quantum mechanics without the electrons", Phys. Rev. Lett., **140,** 136403 (2010).

[3] M.J. Gillan, F.R. Manby, M.D. Towler and D. Alfè, "Energetics of water clusters: assessing the accuracy of quantum Monte Carlo and density functional theory," in preparation.

[4] B. Santra, J. Klimeš, D. Alfè, A. Tkatchenko, B. Slater, A. Michaelides, R. Car and M. Scheffler, "Hydrogen bonds and van der Waals forces in ice at ambient and high pressure," Phys. Rev. Lett., **107,** 185701 (2011).

APS

From Kidney Stones to Gold: Lessons from Biology to Build Better Nanomaterials

Ahmet Uysal[1], Benjamin Stripe[1], Binhua Lin[2], Mati Meron[2], and Pulak Dutta[1]

[1] Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208 [2] Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637

Almost every living organism, from the smallest bacteria to giant whales and elephants, can manufacture highly ordered, organized, and multi-functional hybrid materials, i.e. biominerals. They can control the size, shape, morphology, and orientation of inorganic crystals and deposit them together with organic materials in a multi-level organization from atomic to macroscopic length scales. Moreover this precise assembly of molecules happens in ambient conditions and relatively dirty environments compared to our ultra-high-vacuum techniques and high-temperature treatments for material synthesis. The molecular interactions between the organic and inorganic components of biominerals during nucleation and growth are the underlying basis of this process. However, probing the molecular interactions between the organic matrix and inorganic crystals *in vivo* as real biomineralization occurs is not possible for most biological systems. Therefore it is necessary to develop some *in vitro* models that mimic biomineralization, where *in situ* experiments are doable. We use Langmuir monolayers, floating monolayers of amphiphilic molecules on aqueous subphases, which make it possible to use synchrotron x-ray scattering techniques to study the organic-inorganic interface *in situ* at the molecular level during biomimetic crystallization.

We have studied a wide range of materials to see the effects of organic template in the crystallographic orientation of inorganic crystals. We show that the same organic template can act very differently while growing calcium oxalate monohydrate (kidney stone) or calcium phosphate (bone) minerals. In contrast to assumptions generally made in biomineralization research, our results show directly that both organic monolayer and mineral structures can change during biomineralization and epitaxial interactions are mainly responsible from this change. We also demonstrate how we can utilize what we learn from calcification in biological systems to grow oriented gold nanoparticles in a biomimetic way.

APS

APS Upgrade Presentation

George Srajer

X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

We will present the status of the APS Upgrade project, describe recent R&D activities, and inform you about upcoming reviews. The focus of the talk will be on the current status of the Roadmap and its evolution since it was first shown to the Stakeholders Committee on February 27, 2012. We will also discuss the process of incorporating the Roadmap into the project baseline.

CNM

Templated Block Copolymers for Nanolithography

Caroline A. Ross

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

The self-assembly of block copolymer films produces periodic nanoscale patterns and has been proposed as a method for extending microelectronic fabrication beyond the limits of optical lithography to create features a few nanometers in size, in a process that can be accomplished rapidly and at low cost. This presentation will describe block copolymer lithography, and the thermal and solvent annealing needed to produce a range of microdomain morphologies in the films, which are relevant to nanoscale device fabrication. To make patterns with long range order, as well as patterns with designed aperiodic features, templating strategies based on substrate topography to control the self-assembly will be discussed. The production and templating of more complex patterns, such as arrays of rings or square-symmetry posts from triblock terpolymers and the formation of 3D cross-point structures from bilayer films will be described. Examples of pattern transfer to metals, magnetic films, oxides and polymers and device fabrication will be given.

CNM

Recent Advances in Nanoelectromechanical Switches

Horacio D. Espinosa[1], O. Loh[1], X. Wei[1], J. Sullivan[1], L. Ocola[2], and R. Divan[2]

[1] Northwestern University, Evanston, IL 60208
[2] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

The International Technology Roadmap for Semiconductors (ITRS) identifies emerging technologies with the potential to sustain Moore's Law. A succession from planar CMOS to non-planar/dual-gate CMOS, and ultimately to novel architectures such as carbon nanotube- (CNT)-based nanoelectromechanical systems (NEMS) is envisioned. The ITRS also identifies critical roadblocks currently precluding advances beyond CMOS. Primary among the roadblocks to NEMS are manufacturing challenges and poor reliability. In this presentation, we will report on our investigation of prevalent failure modes in CNT-based NEMS that hamper reliability. An electrostatically actuated switch consisting of a CNT cantilevered over an electrode serves as a platform to study prevalent failure modes in CNT-based NEMS. This architecture is chosen because it shares operating principles (and thus failure modes) with many reported NEM devices.

We will start by discussing CNT-NEM switches using gold electrodes and show that failure (stiction, ablation) can be avoided only in an extremely limited region of the design space. Next, dynamic multiphysics models are discussed and the underlying causes of failure elucidated. Based on this understanding, we show that the CNT-NEM switch operational design space can be expanded dramatically by employing novel electrode materials such as diamond-like carbon (DLC). Finally, we demonstrate the efficiency of this solution through millions of actuation cycles without failure and the system application to volatile memory operations.

CNM

Tracking Amino Acids inside Chiral Quantum Corrals

E.N. Yitamben[1], R.B. Rankin,[1] E.V. Iski,[1] J.P. Greeley,[1] R. Rosenberg[2], and N.P. Guisinger[1]

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Tailoring molecular superstructures on metallic surfaces opens great possibilities for the control and exploration of complex nanosystems for technological applications. Of particular interest is the use of chiral molecules, such as alanine, to build self-assembled nanoscale structures for the trapping of the two-dimensional free electron gas of a metal. In the present work, alanine molecules were deposited on Cu(111). Scanning tunneling microscopy, spectroscopy, and density functional theory calculations revealed the formation of a uniform network of hexagonal chiral pores of average diameter ~ 1.2 nm. Each pore acts as a quantum corral by confining the two-dimensional electron gas of the Cu(111) surface state. Furthermore, time-resolved measurements reveal that each hexagonal pore acts as nanoscale race-track when excess alanine molecules were trapped at the inner perimeter of the pore, and were observed as rotating spatial states periodically moving between the six vertices of the hexagon. This motion could be either electrically or thermally driven within the confined state, and bound by both van der Waals forces and the potential well strength.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

CNM

Structural Consequences of Ferroelectric Nanolithography

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Nanolithographic tools now present the opportunity to control subtle degrees of freedom at unprecedented spatial length scales. Among these magnetic, electronic, and chemical phenomena, the ferroelectric polarization is particularly interesting and challenging. The ferroelectric polarization can be manipulated via scanning-probe nanolithographies based on piezoelectric force microscopy (PFM). Arbitrary ferroelectric domain geometries with spatial resolutions far below 100 nm can be created using this approach. PFM has had an unknown impact on the atomic-scale crystallographic structure of the materials, and as a result questions including the minimum size of domains have remained unanswered.

Synchrotron x-ray nanodiffraction allows nanolithographic ferroelectric domain patterns to be studied using precise crystallographic techniques. Domains written into a thin $Pb(Zr,Ti)O_3$ layer can be imaged using a polarization-dependent intensity contrast and simultaneously studied structurally. The photon-energy dependence of the contrast shows that this effect arises from the crystallographic lack of inversion symmetry in ferroelectrics. The nanodiffraction patterns results from the coherent interference of x-ray beams reflected from several mosaic blocks. A detailed structural analysis shows that strains of up to 0.1% remain following the PFM-based nanolithography, large enough to have important consequences in the stability of written ferroelectric domains. This combination of nanoscale x-ray probes with emerging nanolithographic tools will have further applications in other systems in which nanoscale phenomena lead to significant structural variations. Opportunities in electrochemical systems will be briefly presented.

CNM

High-frequency Magnetization Dynamics in Patterned Permalloy Thin Films

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We focus on high-frequency magnetization dynamics of patterned permalloy thin films, including submicron Permalloy (Py) array structures and single Py wires that are 240-nm wide, 100-nm thick, and 10-μm long. The processes of ferromagnetic resonance (FMR), damping, magnetization reversal, mag-noise, 1/*f* noise, and the effects of DC current and external magnetic field are investigated. In addition to broadband microwave transmission line measurements, a sensitive on-chip microwave interferometer is proposed and fabricated to measure the FMR properties of an individual Py wire.

CNM

Measurement of Resonant Frequencies and Modes of Freestanding Nanoparticle Monolayers

Pongsakorn Kanjanaboos[1], Xiao-Min Lin[2], Heinrich M. Jaeger[1], and Jeffrey Guest[2]

[1] James Franck Institute, Department of Physics, Materials Research Science and Engineering Center (MRSEC), The University of Chicago, Chicago, IL 60637
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We recently showed that freestanding membranes of ligated nanoparticles can be assembled in a one-step drying-mediated process [1]. These 10-nm thin membranes can stretch over holes up to 100 microns in diameter and are supported by a substrate only along their outer edge, thereby freely suspending of the order of 100 million close-packed particles [2]. Previous work has focused on quasi-static mechanical properties [1–3]. Here we present the first investigation of the full dynamic response of freely suspended nanoparticle membranes, utilizing a high-frequency laser interferometer with picometer sensitivity at the CNM. This instrument allows us to rapidly measure the dynamical properties of freestanding nanoparticle monolayers for the first time including resonant frequencies, quality factors, and images of different modes.

[1] Klara E. Mueggenburg et al., "Elastic membranes of close-packed nanoparticle arrays", Nature Materials, **6**, 656–660 (2007).

[2] Jinbo He et al., "Fabrication and Mechanical properties of large-scale freestanding nanoparticle membranes", Small, **6**, 1449–1456 (2010).

(3) Pongsakorn Kanjanaboos et al., "Strain Patterning and Direct Measurement of Poisson's Ratio in Nanoparticle Monolayer Sheets", Nano Letters, **11**, 2567–2571 (2011).

EMC

Plasmonic EELS: Towards a Convergence of Optics and Electron Microscopy

Ted Norris

University of Michigan, AnnArbor, MI 48109

One of the most active frontiers in science today concerns electronic excitations in nanostructures, including plasmonic (metallic), excitonic (semiconducting and organic), and hybrid systems. The field is highly interdisciplinary, where top-down lithographic fabrication methods and bottom-up approaches using chemical self-assembly have enabled entirely new classes of nanostructured materials. The specific classes of materials of concern are electronic nanomaterials with resonances in the optical-frequency range, i.e., with energies on the single-eV scale.

At the eV energy scale, optical spectroscopy provides high spatial and temporal resolution of electronic states and their dynamics. Diffraction, however, limits spatial resolution to a significant fraction of a micron. Transmission electron microscopy (TEM), of course, provides spatial resolution on the single-nm scale governing nanostructure physics; recent advances in TEM/ electron energy loss spectroscopy (EELS) have made it possible to obtain energy loss spectra on the 0.1-eV energy scale, sufficient to resolve optical-frequency nanoplasmonic resonances. Energy filtered images have been shown to correspond closely to the local density of optical states, which is a key property of nanostructured optical materials. High-resolution images enabled detailed tests of calculated modes, well beyond the capability of near-field optical images.

This talk presents TEM/EELS of several important nanostructures, including silver and gold nanorods, coupled nanorods, and nanowires, and comparisons with several optical calculations. I show how plasmon modes are affected by coupling, and determine the dispersion relation for surface plasmons on silver nanowires. I discuss the challenges faced for measurements on hybrid semiconductor (or organic)-metal nanostructures, which are key for active optical or plasmonic devices. I also discuss future directions that may be enabled by the development of TEM systems incorporating optical interactions.

EMC

Recent Studies of Chromatic Aberration-Corrected Transmission Electron Microscopic Imaging at Argonne National Laboratory

J.G. Wen

Electron Microscopy Center and Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Argonne's Electron Microscopy Center (EMC) hosts the world's first chromatic aberration-corrected transmission electron microscope (ACAT). Using this instrument the EMC is exploring the contribution of chromatic aberration correction to transmission electron microscopy (TEM) imaging in three major energy-loss regions: zero-loss, low-loss, and high-loss regions. In the zero-loss region, exploiting sub-angstrom resolution, we have been able to determine surface atomic structure and structural relaxation of the $SrTiO_3$ nanocuboids in combination with the first principle calculations. In the low electron energy loss region, using energy-filtered transmission electron microscopic imaging of plasmon peaks, we have been able to observe three distinct nanodomains with length scales from several hundred nanometers to several nanometers in polymer-fullerene bulk heterojunction solar cells. Finally, in the high electron energy loss region, we found that chromatic aberration correction allows atomic resolution energy-filtered TEM (EFTEM) imaging not only in the low-loss region but also at high-loss regions. Since energy-filtered imaging is accomplished using inelastically scattered electrons, EFTEM offers another method to determine structural and elemental information at atomic resolution. In addition, recent progress in the use of chromatic aberration-correction to *in-situ* TEM imaging using the window-type gas-cell will be discussed.

EMC

Interfaces in Fuel Cells, Solar Cells and Biomaterials

David W. McComb

Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210

Electron energy-loss spectroscopy (EELS) when performed in the scanning transmission electron microscope (STEM) is, arguably, the only technique that can provide information of chemistry and bonding in solid materials with near atomic scale spatial resolution. Recent developments in energy-dispersive x-ray (EDX) analysis have resulted in a paradigm shift—rapid elemental mapping of light elements with atomic-scale spatial resolution is now possible. In this lecture, I will discuss the possibilities and limitations of state-of-the-art analytical electron microscopes with particular emphasis on the potential for study of complex interfaces.

The search for new strategies to enhance the oxide ionic conductivity in oxide materials is an active field of research. Such materials are needed for application in a new generation of more efficient and durable solid-state electrochemical devices such as reduced-temperature solid oxide fuel cells. There have been numerous reports in the literature of significantly enhanced ionic conductivity in multilayer heterostructures formed from ionic conductors and insulators. There have also been a number of reports suggesting that these enhancements are due to electronic rather than ionic conductivity. I will discuss recent results from STEM-EELS-EDX studies where we have probed the structure, composition and bonding with high spatial resolution in order to relate the interfacial structure and chemistry to the observed conductivity.

Applying STEM-EELS to the study of interfaces in organic, hybrid, and biomaterials system is complicated by many factors. I will discuss the insights that can be gained into the structure-property relationships in mineralised tissue, inorganic wear debris in periprosthetic tissue and organic solar cells. The common aspect in all of these studies is the need to probe hard/soft or soft/soft interfaces between inorganic and organic materials. This presents considerable challenges associated with sample preparation, electron beam damage and achievable spatial resolution. I will show that it is possible in many cases to obtain both qualitative and quantitative chemical information that can significantly enhance our understanding in these complex systems.

EMC

Atomic Surface Structure of Strontium Titanate Nanocuboids

Yuyuan Lin[1], Jianguo Wen[2], Dean Miller[2], Linhua Hu[3], Kenneth Poeppelmeier[3], and Laurence Marks[1]

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[2] Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
[3] Department of Chemistry, Northwestern University, Evanston, IL 60208

Strontium titanate ($SrTiO_3$) nanocuboids are promising catalytic supports for the well-defined shape and small size (~20 nm). The atomic surface structure of $SrTiO_3$ nanocuboids has been solved by using aberration corrected high resolution electron microscopy for the first time in sub-Å resolution. The surface of $SrTiO_3$ nanocuboids is strontium oxide terminated with structural relaxation. The simulated image using a structure model relaxed by first principle calculation matches the experimental image very well.

EMC

TEM with *In-situ* Ion Irradiation in 4D+

M. Kirk

Electron Microscopy Center and Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

With results from our unique IVEM-Tandem Facility, we will highlight recent research, which features dynamic formation of defect structures in materials under *in-situ* ion irradiation in real time at controlled temperature and applied stress, and in three spatial dimensions.

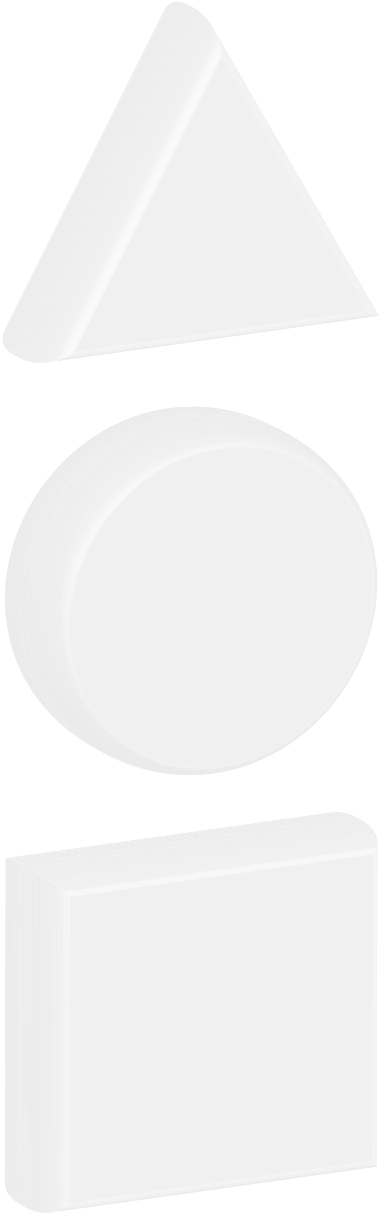
EMC

Direct Measurements of Active and Inactive Catalyst Particles under Reaction Conditions Using Environmental TEM

Renu Sharma

Center for Nanoscale Science and Technology, National Institute of Standards and Technology,
Gaithersburg, MD 20899-6203

Structure, composition, and morphology are some of the major factors that affect the activity of catalyst nanoparticles. Generally a catalyst sample contains both active and inactive nanoparticles. We need to characterize these particles under reaction conditions to differentiate between the two types of particles. Application of in situ dynamic imaging and nano-spectroscopy, using an environmental transmission electron microscope (TEM), to differentiate between the structure and composition of active and inactive nanoparticles will be illustrated using two examples. First, I will describe the role of nanoscale compositional heterogeneity, as determined using electron energy-loss spectroscopy, in zirconia-doped ceria on its redox properties. Second, I will elucidate the structural differences between the Fe nanoparticles that are active and inactive for the nucleation and growth of carbon nanotubes.



2012
Users Meeting

WORKSHOP **AGENDAS** AND **ABSTRACTS**

Tuesday May 8
Cross-facility Workshops

Workshop A
Operando Characterization of Energy Systems

Location: *Bldg. 401, Room A1100*

Organizers: Steve Heald (Advanced Photon Source), Yugang Sun (Center for Nanoscale Materials), and Jianguo Wen (Materials Science Division)

In the study of energy systems such as batteries, fuel cells, photovoltaics, and catalytic processes it is important to simulate their actual operating conditions as close as possible. This workshop brings together researchers engaged in such *operando* studies of energy related systems. It will include experts in x-ray methods, electron microscopy, spectroscopy, and electronic structural theory as applied to energy systems. An important outcome will be to encourage cross-disciplinary discussions of the interactions between these techniques, and to highlight some of the growing capabilities being developed at ANL and elsewhere.

8:50 – 9:00	Welcome & Introductory Remarks
9:00 – 9:40	Dean Miller (Argonne National Laboratory) *Probing Local Behaviour and Microstructural Evolution of Li-ion Battery Cathode Materials through* Operando *Electron Microscopy*
9:40 – 10:20	Thomas Hansen (Denmark Technology University) *Environmental TEM in Energy Research*
10:20 – 10:50	Break
10:50 – 11:30	Haimei Zheng (Lawrence Berkeley National Laboratory) *Real-time TEM Imaging of Nanocrystal Growth in Liquids*
11:30 – 12:10	Shen Dillon (University of Illinois at Urbana-Champaign) In Situ *TEM Characterization of Nanoscale Reactions in Complex Environments*
12:10 – 1:30	Lunch
1:30 – 2:10	Ralph Nuzzo (University of Illinois at Urbana-Champaign) *New Approaches to* In-situ/In-operando *Investigations of Structure and Dynamics in Catalysis*
2:10 – 2:50	John L. Fulton (Pacific Northwest National Laboratory) *Operando XAFS Studies of Homogeneous and Heterogeneous Catalysts in Liquid-phase Hydrogenation Reactions up to 200°C and 50 Bar*
2:50 – 3:20	Break

3:20 – 4:00 Héctor D. Abruña (Cornell University)
X-rays as In-situ *Probes of Energy Systems*

4:00 – 4:40 Mariana Bertoni (Massachusetts Institute of Technology)
Enabling Low-cost Solar Cells: Synchrotron X-ray Investigation of Device-limiting Defects

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WKA

Probing Local Behaviour and Microstructural Evolution of Li-ion Battery Cathode Materials through *Operando* Electron Microscopy

Dean Miller[1], J.G. Wen[1], Christina Proff[1], and D.P. Abraham[2]

[1] Electron Microscopy Center and Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
[2] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

Microstructural changes that take place during electrochemical cycling of Li-ion batteries can influence long-term behavior. It can be challenging to correlate those microstructural changes with battery performance. One approach to this challenge is to carry out electrochemical measurements and microstructural characterization on isolated, individual elements such as a single cathode oxide powder. In the present work we focused on characterization of single powders of $Li(Ni,Co,Al)O_2$ and $Li(Ni,Co,Mn)O_2$ cathode materials. *Operando* electron microscopy studies of single cathode powders during cycling revealed dramatic changes in secondary particle microstructure even during the very first charge cycle that can influence how electrolyte penetrates the powders. Comparing these observations with baseline data from full cells that were subjected to long-term cycling and studied by post-test, *ex situ* characterization using FIB-SEM provides some explanation for the large changes in impedance associated with the positive electrode on full coin cells. The results and insight gained from these experiments will be discussed during this presentation.

Research sponsored by the U.S. DOE, Office of Science – Basic Energy Sciences and by U.S. DOE, EERE – Vehicle Technologies Program, under contract DE-AC02-06CH11357. The Electron Microscopy Center at Argonne is supported by the Office of Science.

WKA

Environmental TEM in Energy Research

Thomas W. Hansen and Jakob B. Wagner

DTU Cen, Fysikvej, Building 307, DK-2800 Kgs. Lyngby, Denmark

The wealth created in the world over the last century is based on easy access to inexpensive fossil fuels. This era is coming to an end. The resources are limited and the demands from everywhere in the world are growing rapidly. At the same time, it is becoming increasingly clear that the emission of CO_2 that follows the use of fossil fuels is threatening the climate of the Earth. Arguably, this makes the development of sustainable energy solutions the most important scientific and technical challenge of our time.

Electron microscopy has played a large role in energy research over the last decades. Particularly, the increasing use of environmental transmission electron microscopy (ETEM) in materials science provides exciting new possibilities for investigating chemical reactions. Careful experimentation can provide input for the development of new generations of catalysts and photocatalysts for e.g., energy production. In order to design experiments with the highest chance of a successful outcome, a detailed understanding of both the interaction of fast electrons with gas molecules, the effect of the presence of gas on high-resolution imaging, and the behavior in this environment is necessary. If data is to be interpreted quantitatively, interaction of the primary electrons with gas molecules must be taken into account. Whereas conventional TEM samples are usually thin (below 10–20 nm), the dilute gas in the environmental cell fills the entire gap between the pole pieces and is thus not spatially localized. Imaging samples with a simple geometry, such as gold particles on a flat graphene substrate, and analyzing the variations in contrast provides a means for understanding the issues involved with imaging in the presence of a gas.

In this work, we have explored the capabilities, possibilities and challenges of using ETEM in catalysis and energy related research exemplified by nanoparticle dynamics, photocatalysis, and alcohol synthesis.

WKA

Real-time TEM Imaging of Nanocrystal Growth in Liquids

Haimei Zheng

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The growth of colloidal nanocrystal architectures by nanoparticle attachment is frequently reported as an alternative to the conventional growth by monomer attachment. However, the underlying mechanism for how nanoparticle attachment proceeds microscopically remains unclear. The recent development in transmission electron microscopy (TEM) on imaging through liquids using a liquid cell provides the opportunity to reveal nanocrystal growth mechanism by real-time observation.

We study single Pt_3Fe nanorod growth trajectories in solution using liquid-cell TEM. About 30 picoliters of growth solution was loaded into the cell and sandwiched between two thin silicon nitride membranes at the window. We observed in real time the evolution from (1) the initial nucleation of Pt_3Fe nanoparticles in a molecular precursor solution to (2) growth into monodisperse nanoparticles, and (3) nanowire formation by shape directed nanoparticle attachment. After nanoparticles attached into a chain, they undergo shape and crystal orientation changes to yield straight single crystalline Pt_3Fe nanorods.

Visualization of Pt_3Fe nanorod growth trajectories strongly suggests the prominence of dipolar nanoparticle-nanoparticle interactions, and allows us to distinguish the force fields exerted by single nanoparticles and chains of nanoparticles. Understanding the mechanism of one-dimensional colloidal nanocrystal growth using nanoparticles as building blocks provides a link between the world of single molecules and hierarchical nanostructures and paves the way to rational design of nanomaterials with controlled properties.

This work was performed using the facility at National Center for Electron Microscopy, Lawrence Berkeley National Laboratory (LBNL), which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Contract #DE-AC02-05CH11231. HZ thanks the support of DOE Early Career Research Program.

[1] H. Liao, L. Cui, S. Whitelam, H. Zheng, "Real time imaging Pt_3Fe nanorod growth in solution" *Science* in review (2012).

WKA

In Situ TEM Characterization of Nanoscale Reactions in Complex Environments

Shen J. Dillon

University of Illinois Urbana-Champaign, 1304 West Green Street, Champaign, IL 61801

The transmission electron microscope provides an ideal platform for performing *in situ* investigations of nanoscale processes due to its high spatial and temporal resolution. Environmental cells enable exciting opportunities to extend these capabilities towards studying materials in their operational environments. For example, lattice imaging has been demonstrated for particles in aqueous solutions and video rate acquisition is common. Such capabilities could enable new insights into dynamic atomic-scale phenomena associated with nucleation and growth, chemical reactions, or response to external stimuli. This talk highlights recent work related to *in situ* TEM characterization of materials reactions in complex environments relevant to their processing and performance. This includes reactions in ionized gases and plasmas, reactions in solution, and electrochemistry. The talk will discuss challenges associated with electron beam effects and emphasize future opportunities in this field.

WKA

New Approaches to *In-situ/In-operando* Investigations of Structure and Dynamics in Catalysis

Ralph G. Nuzzo

University of Illinois at Urbana-Champaign, IL 61820

How the atomic and electronic structural attributes of materials come to underpin the properties of complex heterogeneous catalytic systems remains a frontier challenge for research. Our work has recently come to address the need for tools, and systems of measurement, that can usefully elucidate understandings of this type under the real operating conditions of catalytic processes. In this talk, I will highlight progress made in two exemplary systems. In the first, I will describe new insights into the mechanism(s) of the electrochemical oxygen reduction reaction (ORR). This work exploits a new *in-situ* electrochemical x-ray absorption spectroscopy (XAS) cell that enables high oxygen flux to the working electrode by utilizing a thin diffusion-permissive membrane design. Data from *in-situ* XAS investigations of the ORR (mediated by a supported nanoscale Pt on carbon electrocatalyst at high operating current densities (> 1 mA/cm^2)) reveal a progressive evolution of the electronic structure of the metal clusters that is both potential- and strongly current-dependent. The trends establish a direct correlation to d-state occupancies that directly tracks the character of the Pt–O bonding present. The data further reveal a significant sensitivity of the cluster structure, in terms of complex/evolving forms of bond strain, is also evidenced. The latter attribute appears to be a completely general feature of heterogeneous reaction processes, with the bond strains attending adsorbate bonding harboring significant implications for the energetics and mechanisms of catalysis. Studies in progress to explore this broader set of correlations will be described.

WKA

Operando XAFS Studies of Homogeneous and Heterogeneous Catalysts in Liquid-phase Hydrogenation Reactions up to 200°C and 50 Bar

John L. Fulton[1], Van-Thai Pham[1], Mali Balasubramanian[2], Donald L. Camaioni[1], and John C. Linehan[1]

[1] Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99354
[2] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

The method of *operando* XAFS provides transformational information about the details of the catalyst structure, and thereby the reaction pathways and kinetics. Different types of liquid-phase reactions involving metal ions (Mn^{2+}), metal clusters (homogeneous $Rh(0)_4$), and supported nanoparticles (heterogeneous Pd nanoparticles) are reported at conditions up to 200°C and 50 bar. The reactions include benzene and phenol hydrogenations, and amine borane dehydrocoupling in a variety of different liquid-phase solvents including water, toluene, and iso-propanol. We find in many instances that the chemical state of the catalyst under operating conditions is often dramatically different than the *ex-situ* state. XAFS can provide critical information about the true, kinetically dominant catalytically active species. Further, when XAFS results are combined with other methods such as analysis of reaction kinetics, NMR, or mass spectrometry, then a much clearer picture of the catalyst mechanism emerges. The described reactions are relevant to hydrogen storage, synthesis of transportation fuels, and arene hydrogenation.

1 J.L. Fulton, J.C. Linehan, T. Autrey, M. Balasubramanian, et.al.. J. Am. Chem. Soc., 129(39), 11936-11949, (2007).

2 J.C. Linehan, J.L. Fulton, M. Balasubramanian, Richard Finke, et al. J. Am. Chem. Soc., 133, 18889–18902, (2011).

WKA

X-rays as *In-situ* Probes of Energy Systems

Héctor D. Abruña

Department of Chemistry and Chemical Biology and Energy Materials Center at Cornell University, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301

This presentation will deal with the use of x-ray-based methods (including x-ray diffraction and x-ray absorption spectroscopy) to the *in-situ* (*in-operando*) study of electrochemical interfaces of relevance to energy systems with particular emphasis on elecrocatalysts for fuel cells and materials for battery and supercapacitor applications. Potential dependent changes in surface composition and electrocatalytic activity of ordered intermetallics like PtBi and PtPb, used as fuel cell anodes, will be discussed. Similarly, potential and state-of-charge (SOC) dependent changes in structure and composition in battery and supercapacitor materials will be discussed. The presentation will conclude with future directions.

WKA

Enabling Low-cost Solar Cells: Synchrotron X-ray Investigation of Device-limiting Defects

Mariana Bertoni[1], David Fenning[1], Bonna Newman[1], Steve Hudelson[1], Sirine Fakra[2], Matthew Marcus[2], Barry Lai[3], Volker Rose[3], Jorg Maser[4], and T. Buonassisi[1]

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[2] Advanced Light Source Lawrence Berkeley National Laboratory Berkeley, CA 94720
[3] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439
[4] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

The overall performance of energy devices is often regulated by inhomogeneously distributed nanoscale defects, and multicrystalline silicon is no exception. This talk will exemplify the novel defect science that is enabled by high-resolution synchrotron-based x-ray techniques. X-ray fluorescence microscopy (μ-XRF) and x-ray absorption spectroscopy (μ-XAS) are combined to elucidate the chemical nature, size, and spatial distribution of nanometer-scale impurities while providing orders of magnitude higher bulk sensitivity than electron-based techniques. Coupled with *in-situ* stages (e.g., high-temperature), one can replicate solar cell processing conditions and study the defects kinetics that govern the materials properties during typical industrial processing steps.

Using the state-of-the-art facilities at Argonne National Laboratory (CNM/APS), we exploit sub-100-nm spatial resolution, previously unreachable with standard hard x-ray probe beamlines, to study the elemental makeup of nanoscale defects at intragranular dislocations within commercial multicrystalline silicon. The results distinguish underlying differences between benign and deleterious dislocations in a solar cell device and point the way towards optimization of the industrial solar cell process.

Finally, x-ray techniques in combination with defect-kinetics modeling is discussed in the context of becoming a strong tool for predicting and optimizing solar cell efficiency during device fabrication for a given feedstock quality, cell architecture, and set of processing conditions.

Workshop B
Probing the Interface between Biological Systems and the Environment

Location: *Bldg. 402, Rooms E1100/E1200*

Organizers: Stefan Vogt (Advanced Photon Source), Tijana Rajh (Center for Nanoscale Materials), and Ed O'Loughlin (Biosciences Division)

The diverse and complementary imaging and spectroscopic capabilities at the APS, CNM, and EMC provide unique tools to probe the highly complex interactions between biological systems and their environment. This workshop highlights cutting-edge applications of multiple spectroscopic and imaging approaches to examine biological systems in the context of both environmental processes. This could include, for example, microbial respiration on insoluble electron acceptors, microbial interactions with and transformations of contaminants, biofilm development, and biomineralization processes, among others. The workshop also is expected to feature intrinsic and direct interactions with the environment such as interactions with and uptake of contaminants, phytoremediation, etc.

8:45 – 9:00	Welcome and Introductory Remarks
9:00 – 9:40	Matthew Marshall (Pacific Northwest National Laboratory) *Towards High-resolution Chemical Imaging of Microbial Biofilms: Integration of Synchrotron Imaging and Electron Microscopy*
9:40 – 10:20	Catherine Murphy (University of Illinois at Urbana-Champaign) *Noble Metal Nanoparticles: A Platform For Studying Nano-Bio-Eco Interfaces at the Molecular Level*
10:20 – 10:50	Break
10:50 – 11:30	Jason Unrine (University of Kentucky) *Exploring the Transformations, Bioavailability, Trophic Transfer, and Toxicity of Metal Nanoparticles in Soil*
11:30 – 12:10	Ka Yee Lee (University of Chicago) *Mechanism of Structural Transformations Induced by Antimicrobial Peptides in Lipid Membranes*
12:10 – 1:30	Lunch
1:30 – 2:10	Ryan Tappero (Brookhaven National Laboratory) *Probing the Mechanisms of Metal Tolerance in a Ni/Co Hyperaccumulator Plant*
2:10 – 2:50	Maxim I. Boyanov (Argonne National Laboratory) *Elucidating Bacteria-mineral-contaminant Interactions Using Electron and X-ray Microspectroscopy Approaches*
2:50 – 3:20	Break

3:20 – 4:00 Mark Jensen (Argonne National Laboratory)
Protein-mediated Plutonium Uptake by Living Cells

4:00 – 04:40 Chantel Tester (Northwestern University)
Amorphous Calcium Carbonate in Biomineralization: From Model Systems to Probing Structural Transformation in Cryo-Frozen Sea Urchin Embryos

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WKB

Towards High-resolution Chemical Imaging of Microbial Biofilms: Integration of Synchrotron Imaging and Electron Microscopy

Matthew Marshall[1], Sara Belchik[1], Mathew Thomas[1], Leo Kucek[1], Eric Hill[1], Timothy White[1], Alice Dohnalkova[1], James Carson[1], Erin Miller[1], Xianghui Xiao[2], and Carol Hirschmugl[3]

[1] Pacific Northwest National Laboratory, Richland, WA 99354
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Direct examination of natural and engineered environments has revealed that the majority of microorganisms in these systems live in structured communities termed biofilms. In addition to microbial cells, biofilms are comprised of a poorly characterized organic matrix commonly referred to as extracellular polymeric substance (EPS) that may play roles in facilitating microbial interactions and biogeochemical reactions including extracellular electron transfer. Using synchrotron-based x-ray imaging and high-resolution electron microscopy (EM), we have previously shown copious amounts of highly hydrated bacterial EPS to be produced during microbial metal reduction. The juxtaposition of extracellular electron transfer proteins and nanoparticulate-reduced metal suggested that EPS played a key role in metal capture and precipitation. Here we present a multi-faceted, multi-scale approach using a combination of synchrotron-based x-ray imaging and EM to construct a high-spatial-resolution, complex chemical image of a biofilm community in its nearest-to-native state. Conventional and cryogenic EM capabilities will be correlated with x-ray imaging and nano-secondary ion mass spectroscopy (nano-SIMS) to produce high-sensitivity, element-specific distributions, which correspond to EM images of the biofilm at the nanometer scale. Concurrent with these studies, synchrotron-based infrared imaging will be employed to produce high-spatial-resolution (0.54 μm) images with spectral data showing the localizations of biofilm components (e.g., proteins EPS, nucleic acids, and membrane lipids) to further construct our chemical image of biofilms. For pore-scale and community-scale analysis (100's of nm to 10's of microns), a variety of surface imaging tools (e.g., secondary electrons or helium ions) are available. However, understanding biofilm structure in complex 3D environments is considerably more difficult. X-ray microtomography can reveal biofilm internal structure, but obtaining sufficient contrast to image low-Z biological material against a higher-Z substrate makes detecting biofilms difficult.

Using the x-ray microtomography system at sector 2BM of the Advanced Photon Source, we have imaged *Shewanella* biofilms grown on multiple substrates at energies ranging from 13–18 keV and spatial scales of 0.7 and 1.4 μm/pixel. In some studies, contrasting agents such as Os were added to enhance biofilm visibility. Hard x-ray microtomography data was also obtained using a Talbot interferometer to provide phase and scatter contrast information in addition to absorption. We will evaluate the utility of these different approaches for revealing biofilm structure.

Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

WKB

Noble Metal Nanoparticles: A Platform For Studying Nano-Bio-Eco Interfaces at the Molecular Level

Catherine J. Murphy

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The brilliant colors of gold and silver nanoparticles make them favored substrates for numerous chemical sensing and biological imaging applications. In this talk, I will discuss the importance of surface chemistry in understanding, and possibly predicting, how these metal nanoparticles interact with biological molecules and cells. Experiments in which engineered nanoparticles were exposed to an entire estuarine mesocosm ecosystem suggest that the initial surface charge of the particles influences their partitioning in biological compartments, but in an unpredictable way.

WKB

Exploring the Transformations, Bioavailability, Trophic Transfer, and Toxicity of Metal Nanoparticles in Soil

Jason M. Unrine, William A. Shoults-Wilson, Jonathan Judy, Olga V. Tsyusko, and Paul M. Bertsch

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Our research investigated the transformation, bioavailability, and adverse effects of Au, Ag, CeO_2, and Cu nanoparticles in soils. We exposed earthworms (*Eisenia fetida*) and nematodes (*Caenorhabditis elegans*) to these nanoparticles while varying properties such as particle size and surface coating. Finally we investigated the transfer of Au nanoparticles along simulated terrestrial food chains. Our studies were the first to unequivocally demonstrate the bioavailability and trophic transfer of nanoparticles from soil. X-ray fluorescence microscopy and micro x-ray absorption spectroscopy were essential for establishing the uptake and biodistribution of nanoparticles in tissues as well as their transformations in soils. We observed a variety of adverse effects on earthworms exposed to Ag NPs using endpoints ranging from oxidative damage of proteins and changes in gene expression to changes in behavior and reproduction. These studies have laid a foundation for understanding the bioavailability, trophic transfer, and effects of metal nanoparticles in terrestrial environments.

WKB

Mechanism of Structural Transformations Induced by Antimicrobial Peptides in Lipid Membranes

Ka Yee C. Lee

Department of Chemistry, Institute for Biophysical Dynamics and James Franck Institute, The University of Chicago, Chicago, IL 60637

Antimicrobial peptides are a class of small (<100 residues) host defense peptides that induce selective membrane lytic activity against microbial pathogens. The permeabilizing behavior of these diverse peptides has been commonly attributed to the formation of pores, and such pore formation has been categorized as barrel-stave, toroidal, or carpet-like. Using atomic force microscopy, the disruption of supported lipid bilayer patches by protegrin-1 is studied in a concentration-dependent manner. PG-1 acts to lower the interfacial energy of the bilayer in a way similar to detergents, stabilizing pore formation. The intercalation of PG-1 into the bilayer results in structures beyond that of pore formation, giving rise to worm-like micelles at high peptide concentration. The interaction depends not only on the charge of the peptide, but also on the composition and state of the membrane. Antimicrobial peptides with structural differences, magainin-1 and aurein 1.1, exhibit a mechanistic commonality.

WKB

Probing the Mechanisms of Metal Tolerance in a Ni/Co Hyperaccumulator Plant

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A widespread redistribution of metals in the environment has occurred since the Industrial Revolution, resulting in large areas of the land surface contaminated with heavy metals. Common sources of metal contamination include mining, smelting, electroplating, waste disposal, petroleum refining, intensive agriculture, and combustion of fossil fuels. Costs associated with traditional remediation activities (i.e., dig and haul) are prohibitive when vast areas of land have been contaminated, thus alternative *in situ* remediation strategies are needed. Unique metallophyte plants (i.e., hyperaccumulators) concentrate large quantities of metals in their harvestable biomass, and thereby offer a sustainable method for treatment of metal-contaminated sites (phytoremediation) and an opportunity to mine metal-rich soils (phytomining). Information regarding the distribution and speciation of metals at the micron scale is needed to locate the phenomena of hyperaccumulation in tissues, cells, and organelles in order to understand the mechanism of (hyper)tolerance and ultimately improve phytoextraction efficiency. Laboratory and synchrotron-based techniques were used to study the key mechanisms of metal tolerance in a Ni/Co hyperaccumulator plant, *Alyssum murale*.

WKB

Elucidating Bacteria-mineral-contaminant Interactions Using Electron and X-ray Microspectroscopy Approaches

M. Boyanov[1], D. Latta[1], B. Mishra[1], S. Langley[2], S. Glasauer[2], B. Lai[3], E. O'Loughlin[1], and K. Kemner[1]

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The subsurface is a complex environment in which nutrients, bacteria, and minerals interact and influence contaminant transport. Subsurface systems are often anoxic and have sufficient carbon influx to support bacterial activity. Under oxygen-deficient conditions bacteria use elements other than oxygen as electron acceptors for their respiration (e.g., S, Fe, Mn, U), creating a suite of oxidized and reduced chemical species that can react with dissolved metal and radionuclide contaminants. Understanding such interactions across spatial scales is paramount in predicting contaminant transport and in devising remediation strategies. We will demonstrate how electron microscopy (SEM and TEM) and synchrotron x-ray fluorescence microscopy and spectroscopy (XANES and EXAFS) can be used to obtain unique insights into redox-driven Fe and U transformations related to subsurface processes. As one example, various controls on the secondary mineralization phases (SMPs) produced from biological Fe(III) reduction were identified by the morphology of the resulting micro- and nano-crystallites. However, the formation of small, non-crystalline Fe phases (e.g., ferrihydrite) could only be quantified when electron microscopy methods were used in combination with Fe edge x-ray spectroscopy. We also examined the reactivity and reaction products of dissolved U(VI) with several reduced Fe SMPs, showing dependence on the Fe phase and the solution conditions. Dependence of the U(IV) reaction products on the solution conditions was also observed in studies of U(VI) reduction by *Desulfitobacterium*, *Shewanella*, and *Anaeromyxobacter* spp., allowing conclusions to be made about the electron transfer mechanism from the bacterial cell to U(VI). In a different study, x-ray absorption near-edge spectroscopy (XANES) with a ~0.2 micron beam showed heterogeneity in the valence state of uranium on and away from a single bacterium adhered to a thin iron oxide film, providing insight into the mechanisms of electron transfer. Finally, using TEM and submicron-resolution Fe edge XANES, we determined the valence state of Fe precipitates inside single *Shewanella putrefaciens* CN32 cells and suggested a respiratory function of these internal precipitates. The above studies highlight the utility of combining high-resolution imaging and spectroscopic tools to understand the coupled biological-abiotic mechanisms that control elemental transformations in subsurface environments.

WKB

Protein-mediated Plutonium Uptake by Living Cells

Mark Jensen[1], Drew Gorman-Lewis[1], Baikuntha Aryal[1, 2], Tatjana Paunesku[3], Stefan Vogt[4], Paul Rickert[1], Soenke Seifert[4], Barry Lai[4], Gayle Woloschak[3], and L. Soderholm[1]

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The toxic element plutonium did not exist in biologically relevant amounts on Earth until its synthesis and isolation in 1941. As a consequence, organisms have had no opportunity to develop specific mechanisms for handling Pu poisoning from the environment, and in the body Pu adventitiously follows biochemical pathways dictated by its particular chemistry. Despite years of study, a mechanistic, molecular-level understanding of the pathways that allow transuranium elements such as plutonium to bio-accumulate was never achieved. In an effort to describe and possibly block the pathways of cellular plutonium trafficking, we have been examining the mechanisms of Pu uptake by mammalian cells and the nature of important plutonium-protein complexes using synchrotron x-ray fluorescence microscopy, x-ray absorption near edge structure, and small-angle x-ray scattering measurements. We have identified a particular isomer of a stable Pu-protein complex that is recognized by cells and incorporated by endocytosis just like the naturally occurring metalloprotein. With this specific target, strategies to mitigate Pu toxicity by pre-empting Pu incorporation by cells may be within reach.

WKB

Amorphous Calcium Carbonate in Biomineralization: From Model Systems to Probing Structural Transformation in Cryo-Frozen Sea Urchin Embryos

Chantel Tester[1], Ching-Hsuan Wu[1], Minna Krejci[1], Laura Mueller[1], Alex Park[1], Steven Weigand[2], Barry Lai[2], Si Chen[2], Cheng Jun Sun[2], Mahaling Balasubramanian[2], Stefan Vogt[2], and Derk Joester[1]

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The biological use of amorphous mineral precursors is thought to be directly related to the ability to create single crystalline, yet composite materials with curving, branching shapes that are beyond our synthetic capabilities. Despite considerable effort in recent years, it has not been possible to capture the mechanistic detail of the disorder-to-order transformation that is the key element of this process. This is due to the challenges of characterizing the structure of amorphous precursors, which rapidly crystallize when prepared in solution or upon extraction from the biological tissue. Characterization *in vivo* or in biomimetic systems presents additional obstacles, including low mineral concentrations, small precipitates, and the presence of multiple phases. To overcome these challenges we use a combination of x-ray absorption spectroscopy to determine the local structure, simultaneous small- and wide-angle x-ray scattering to follow the precipitation kinetics, and x-ray imaging to visualize the growth rate. These techniques are applied to characterize the formation and transformation of amorphous calcium carbonate both *in vivo* in sea urchin larval spicules and *in vitro* in liposome models of intracellular biomineralization. We envisage that the strategies and models we have developed can be applied to numerous mineralizing systems to reveal the mechanisms of biological control over crystal growth.

Workshop C
Imaging at All Length and Time Scales

Location: *APS 402 Lecture Hall*

Organizers: Kamel Fezzaa (Advanced Photon Source), Nathan Guisinger (Center for Nanoscale Materials), and Marc De Graef (Carnegie Mellon University)

The ability to understand, modify, and control systems in a variety of environments across multiple time and length scales is central to many fundamental contemporary research and engineering challenges. Success in these efforts hinges on the ability to image not only the structure in systems, but also the electronic, magnetic, optical and chemical properties and behavior associated with this structure. The APS, CNM and EMC possess a diverse and complementary array of imaging, microscopy and spectroscopy platforms to push this frontier of multiscale and time-resolved investigation. Going forward, it will become more important to establish multimodal imaging capabilities focusing on new techniques and the use of novel tool combinations to address the next generation of research challenges.

8:45 – 9:00	Welcome & Introductory Remarks
9:00 – 9:40	Shengnian Luo (Los Alamos National Laboratory) *Temporally and Spatially Resolved Dynamic Phase-contrast Imaging with Individual Synchrotron X-ray Pulses under Shock Loading*
9:40 – 10:20	Xianghui Xiao (Argonne National Laboratory) *Fast Microtromography/Micro-imaging and Applications at APS/2-BM*
10:20 – 10:50	Break
10:50 – 11:30	Wilson K.S. Chiu (University of Conneticut) *Full-field 3D Imaging and Analysis of Heterogeneous Functional Materials (HeteroFoaMs) for Energy Systems*
11:30 – 12:10	Peter Sutter (Brookhaven National Laboratory) In-situ *Microscopy on 2D Materials: Growth, Processing, Properties*
12:10 – 1:30	Lunch
1:30 – 2:10	Phillip First (Georgia Institute of Technology) *Local Measurements of the Electronic Properties of Epitaxial Graphene*
2:10 – 2:50	Paul Kotula (Sandia National Laboratory) *Progress with a Probe-corrected Analytical Electron Microscope with 0.7sr Integral SDD Array*
2:50 – 3:20	Break
3:20 – 4:00	Geoff Campbell (Lawrence Livermore National Laboratory) *Quantifying Transient Dynamics in Materials Using Time-resolved* in situ *TEM*
4:00 – 4:40	Christian Kisielowski (NCEM/LBL, Lawrence Berkeley National Laboratory) *The Ongoing Transformation of Atomic-resolution Transmission Electron Microscopy*

WKC

Temporally and Spatially Resolved Dynamic Phase-contrast Imaging with Individual Synchrotron X-ray Pulses under Shock Loading

S.N. Luo[1], B.J. Jensen[1], D.E. Hooks[1], K. Fezzaa[2], K.J. Ramos[1], J.D. Yeager[1], K. Kwiatkowski[1], and T. Shimada[1]

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The highly transient nature of shock loading and pronounced microstructure effects on dynamic materials response call for *in-situ*, real-time, in-depth, temporally and spatially resolved x-ray-based diagnostics. Third-generation synchrotron x-ray sources provide high photon energy, high photon fluxes, high pulse repetition rates and sufficient coherency, thus advantageous for x-ray phase contrast imaging (PCI) and diffraction under dynamic loading. We investigate the feasibility of bulk-scale gas gun shock experiments with dynamic x-ray PCI and diffraction measurements at the beamline 32ID-B of the Advanced Photon Source. We present the x-ray beam characteristics, experimental setup, x-ray diagnostics, and static and dynamic test results. We demonstrate ultrafast, multiframe, single-pulse PCI measurements with unprecedented temporal (<100 ps) and spatial (2 μm) resolutions for bulk-scale shock experiments, as well as single-pulse dynamic Laue diffraction. The results not only substantiate the potential of synchrotron-based experiments for addressing a variety of shock physics problems, but also allow us to identify the technical challenges related to image detection, x-ray source and dynamic loading.

WKC

Fast Microtromography/Micro-imaging and Applications at APS/2-BM

Xianghui Xiao

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X-ray tomography has become a powerful tool in materials and geoscience research. Utilizing the high photon flux from synchrotron sources, synchrotron-radiation-based fast tomography provides both high-spatial and high-temporal resolution. This combination is particularly suitable for the study of time-dependent processes. In the talk, few examples of dynamic imaging applications in materials science, geoscience, and physics will be presented, and technical concerns in experiments will be discussed. We will also present our workflow for the analysis of large time-resolved tomographic datasets. We will conclude with an outlook on a next generation of *in situ* dynamic imaging station and its potential applications.

WKC

Full-field 3D Imaging and Analysis of Heterogeneous Functional Materials (HeteroFoaMs) for Energy Systems

Wilson K.S. Chiu

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Fuel cells, batteries, electrolyzers, and solar cells all consist of heterogeneous functional materials (HeteroFoaMs) that exhibit functional behavior in a manner that controls their collective performance as an energy system. There is a critical need to understand the role of a HeteroFoaM's structure, morphology, and composition on system performance. This seminar presents a non-destructive approach to image and characterize HeteroFoaMs using synchrotron-based transmission x-ray microscopes at APS, SSRL, and NSLS. Three-dimensional structures within the sample volume are imaged *ex-situ* or *in-situ*, and tomographically reconstructed at up to 20-nm spatial resolution. Multi-component lattice Boltzmann methods are used to analyze mass transfer, heat transfer, ionic/electronic charge transfer, and chemical/electrochemical reaction rates in HeteroFoaMs. To demonstrate this technique, chemical elements, chemical bonding, and phase- and pore-network structures in a solid oxide fuel cell are examined to provide fundamental insight into the origins of transport-related losses during operation.

This work is supported by an Energy Frontier Research Center on Science Based Nano-Structure Design and Synthesis of Heterogeneous Functional Materials for Energy Systems (HeteroFoaM Center) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC000106) and the National Science Foundation (Award CBET-1134052).

WKC

In-situ Microscopy on 2D Materials: Growth, Processing, Properties

P. Sutter

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

Graphene has been used to explore the fascinating properties of two-dimensional sp2 bonded carbon, and shows great promise for applications. Other two-dimensional materials, such as hexagonal boron nitride, are gaining increasing attention as functional materials in their own right, as well as combined in heterostructures with graphene.

Here, we highlight the application of *in-situ* microscopy methods to the discovery of synthesis and processing approaches for two-dimensional materials on transition metal substrates, and to the measurement of their properties. Real-time observations by low-energy electron microscopy (LEEM) provide insight into the fundamental growth mechanisms of graphene [1–3] and boron nitride [2]. Combined *in-situ* microscopy methods, including LEEM imaging, micro-diffraction, and synchrotron-based selected-area angle resolved photoemission spectroscopy (micro-ARPES), have been used to explore the electronic structure and the interaction with transition metal substrates [5, 6], as well as interfacial reactions that can be used for controlled modifications of these characteristics [6]. Scanning tunneling microscopy (STM), finally, is invaluable for atomic-scale studies on complex heterostructures, such as monolayer graphene-boron nitride membranes. Our results show that *in-situ* microscopy provides a powerful tool for achieving and probing a wide range of functionalities in two-dimensional materials.

Work performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences under contract No. DE-AC02 98CH1-886.

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WKC

Local Measurements of the Electronic Properties of Epitaxial Graphene

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An attractive aspect of graphene for nanoelectronic applications is the ability to tailor its electronic properties through chemistry, strain, applied electric fields, or quantum confinement. Characterization of nanostructured graphene requires methods to determine its electronic structure on a few-nanometer scale or smaller. We use scanning tunneling spectroscopy in high magnetic fields to extract the momentum-resolved energy dispersion of graphene [1], and to map atomic-scale variations of the local density of cyclotron states (Landau levels) in multilayer epitaxial graphene [2]. Interesting features of the magneto-electronic structure include the perturbation of Landau levels around defect potentials (in fact, the STM tip itself contributes a local "defect potential"), and a position-dependent valley-splitting energy gap. The observed pattern of valley splitting implies a weak interaction between rotated graphene layers in multilayer epitaxial graphene grown on C-terminated SiC(000 -1). This material has a distinctly non-graphitic layer stacking, with important consequences for its electronic structure [3].

[*] Work done in collaboration with NIST Center for Nanoscale Science and Technology.

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WKC

Progress with a Probe-corrected Analytical Electron Microscope with 0.7sr Integral SDD Array

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The FEI Company Titan G2 80-200 at Sandia consists of a standard Titan column with a 200kV accelerator, high-brightness Shottky emitter (~2 × 10^9 A/cm^2/sr at 200 kV)[1], three condenser lenses, CEOS D-COR hexapole-type probe Cs corrector (corrects out to fourth-order aberrations, fifth-order spherical aberration and six-fold astigmatism) [2] and an analytical objective lens configuration (5-mm gap). In addition the instrument also has an array of four windowless silicon-drift energy-dispersive x-ray detectors integral to the objective pole piece with a combined solid angle of 0.7 sr. This new instrument is both high-resolution STEM imaging system (0.8Å at 200kV) and an analytical electron microscope (AEM) with 50 to 100 times better performance than the previous generation of AEMs. Results of atomic-resolution x-ray microanalysis as well initial work on quantification of these data will be presented.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United Stated Department of Energy's (DOE) National Nuclear Security Administration (NNSA) under contract DE-AC0494AL85000.

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WKC

Quantifying Transient Dynamics in Materials Using Time-resolved *in situ* TEM

Geoffrey H. Campbell

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The dynamic transmission electron microscope (DTEM) is a standard TEM that has been modified such that the electron beam can be operated with a single intense pulse of electrons (>10^9 e^-) with a pulse duration of just 15 ns. The short pulse of electrons is created via photoemission at the microscope cathode and enables time resolved observations of *in situ* experiments. However, it can also be operated in thermionic emission mode for normal operation of the microscope for alignment and experiment setup. Additional modifications have also been made to the optical design of the condenser lens system. The *in situ* experiments currently use a second laser to initiate the dynamic response of interest in the specimen. The relative timing of the pulses from the two laser systems sets the time of the observation relative to the initiation of the event under study. The DTEM has been used to investigate a number of rapid phenomena in materials. We have studied the rapid nucleation and growth at the nanoscale of crystalline phases from an initially amorphous metal alloy parent phase and in amorphous Ge. DTEM has also been used to study reactive multilayer films of Ni and Al that sustain a reaction front speed greater than 10 m/s. We have also investigated rapid solidification of nanoscale films of liquid Al-Cu alloys.

WKC

The Ongoing Transformation of Atomic-resolution Transmission Electron Microscopy

Christian Kisielowski

Joint Center for Artificial Photosynthesis and National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, One Cyclotron Rd., Berkeley, CA 94720

In recent years, the TEAM Project (transmission electron aberration-corrected microscope) that was sponsored by the Department of Energy was concluded. As a result a next generation electron microscopes of extraordinary performance is now operated at the National Center for Electron Microscopy (NCEM) with great success. These and other new instruments allow for dynamic studies (<1 kHz) with single atom sensitivity across the Periodic Table of Elements at a resolution limit around 0.5 Å [1–4]. Their unprecedented abilities also reveal that the image formation process is now limited at a fundamental level by the Coulomb scattering process itself and by beam-sample interactions. As a result, efforts to push for higher resolution are coming to an end and there is room for assessing the future of the field. This talk reviews the progress that was made during the last years with aberration-corrected electron microscopy and it highlights recent developments that provide new opportunities. Advancements include the implementation of atomic-resolution, low-dose techniques at variable voltage (20 kV - 300 kV) [5] and atomic-resolution imaging at elevated temperature and pressure. Thus, it becomes feasible to study the functionality of materials and possibly of single molecules in chemically meaningful environments with atomic resolution and single atom sensitivity. Such capabilities are of general interest to material, chemical, and biological sciences. In particular, they can help to improve our understanding of artificial photosynthetic systems that will produce transportation fuels from sunlight.

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Wednesday May 9
Facility-specific Workshops

APS Workshop 1
Spectroscopy of Rare-earth Materials at Extreme Conditions: Structure, Magnetism, and Energy

Location: *Bldg. 401, Room A1100*

Organizers: Kevin Moore (Lawrence Livermore National Laboratory)
and Daniel Haskel (Argonne National Laboratory)

This workshop explores emerging opportunities in the application of synchrotron-based x-ray absorption and inelastic scattering spectroscopies for studying the electronic and magnetic properties of rare-earth materials and their compounds. These materials provide a wonderful playground to explore correlated electron behavior (volume collapse, mixed valency, Kondo physics, superconductivity, magnetism) as well as enable a wide variety of applications in energy and information technologies (magnetocalorics, permanent magnets, spintronics). Particular emphasis will be placed on unraveling the potential of experimentation under extreme conditions, including high-pressure, high magnetic fields and fast timing within the context of the APS upgrade.

Morning I: Historical Perspective, High Pressure (Chair: Guoyin Shen)

8:45 – 9:00 Samuel Bader (Materials Science Division and Center for Nanoscale Materials, Argonne National Laboratory)
Historical Introduction to Rare Earth Research

9:00 – 9:40 James S. Schilling (Washington University in St. Louis)
Interplay between Magnetism and Superconductivity in Elemental Rare-Earth Metals and Related Kondo Alloys at High Pressures

9:40 – 10:20 Joseph A. Bradley (Condensed Matter and Materials Division, Lawrence Livermore National Laboratory)
X-ray Spectroscopy and Rare Earth Volume Collapse: High-fidelity Comparisons to Dynamical Mean Field Theory

10:20 – 10:45 Break

Morning II: Energy (Chair: Jonathan Lang)

10:50 – 11:30 Karl Gschneidner (The Ames Laboratory and Iowa State University)
Magnetic Refrigeration and Cooling – An Energy Efficient and Green Cooling Technology for the 21st Century

11:30 – 12:10 Sam Jiang (Argonne National Laboratory)
Thin Film Exchange-spring Magnets

12:20 – 1:25 Lunch

Afternoon I: Fast Timing, High Magnetic Fields (Chair: Dave Keavney)

1:30 – 2:10	Herman Durr (SLAC National Accelerator Laboratory) *The X-ray View of All Optical Magnetic Switching in FeCoGd*
2:10 – 2:50	Yasuhiro Matsuda (University of Tokyo) *High Magnetic Field X-ray Spectroscopy of Heavy Fermion Systems*
2:50 – 3:15	Break

Afternoon II: High Magnetic Fields, High Pressure (Chair: Zahir Islam)

3:20 – 4:00	Jacob Ruff (Argonne National Laboratory) *Magnetoelastics of a Spin Liquid*
4:00 – 4:40	Mohsen Abd-Elmeguid (University of Cologne) *Study of Quantum Phase Transitions in Rare Earth Compounds Using Mössbauer Spectroscopy*
4:40 – 5:20	Narcizo M. Souza-Neto (Laboratório Nacional de Luz Síncrotron) *Re-entrant Valence Transition in EuO at High Pressures: Beyond the Bond-valence Model*
5:20 – 5:30	Closing Remarks
5:30	Adjourn

WK1

Historical Introduction to Rare Earth Research

S. D. Bader

Materials Science Division and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Around 1920, Woltjer and Kammerlingh Onnes measured the magnetization of a gadolinium compound down to liquid helium temperature. Their work stimulated great interest in the magnetic properties of rare earth materials. It inspired William Giauque, who proposed (in 1926, as did Peter Debye, independently) and demonstrated (in 1933) magnetic refrigeration to temperatures below 1K. Giauque went on to win the 1949 Nobel Prize in Chemistry. It also inspired a graduate student, Franck Spedding, to investigate spectroscopic properties of rare earths. Giauque and Spedding were students of the renowned Berkeley chemist Gilbert Norton Lewis. Spedding was later credited for purifying rare earths, and also for founding Ames as a national laboratory. Ames remains a coveted source of pure rare earths. While at Argonne in the 1960's, Olli Lounasmaa made pioneering low temperature studies of the nuclear hyperfine properties of rare earths, and later in Helsinki, championed the field of nanokelvin exploration. By the 1970's, spin ½ Kondo systems based on cerium dopants entered the stage, as did the first re-entrant Kondo superconductors. SmS under pressure presaged a heavy Fermion era, and Er-based magnetic superconductors opened new vistas beyond the electron-phonon perspective, perhaps portending today's world. By the 1980's, magnetic film research led to the modern era of nanomagnetism and spintronics. Rare earth heterostructures were being pioneered at Urbana and Bell Labs, but the discovery of giant magneto-resistance moved interest to transition metals. Ultrastrong bulk permanent magnets based on NdFeB entered the stage at that time, followed a decade later by the exchange spring principle that utilizes rare earths more sparingly. The present and future will be captured by the great variety of presentations at this workshop

Work supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under contract No. DE-AC02-06CH11357.

WK1

Interplay between Magnetism and Superconductivity in Elemental Rare-Earth Metals and Related Kondo Alloys at High Pressures

James S. Schilling

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In elemental rare-earth (RE) solids, as well as in alloys and compounds containing rare earths, the magnetic state of the RE ion is in general highly localized, i.e. forms a "local magnetic moment". Under progressively higher pressures two scenarios have been proposed whereby the magnetic state of the RE ion morphs from: (1) stable local moment to intermediate valence to another stable local-moment state as an electron jumps from the 4*f* orbital into the conduction band (valence increase), or (2) stable local moment to itinerant magnetism, should the overlap between neighboring 4*f*-orbitals be sufficient. In concentrated RE systems, these dramatic changes in the magnetic state may be accompanied by a volume collapse at a critical pressure, quantum critical behavior and superconductivity. One way to monitor the evolution of the magnetic state in RE ions under pressure is to alloy a dilute concentration of them into a superconducting host metal and study their effect on the pressure dependence of the superconducting transition temperature $T_c(P)$ [1]. Synchrotron-based spectroscopy studies under high pressure provide particularly valuable information. In this talk I will give old and new examples for these phenomena in RE systems under extreme pressure.

[1] M. Brian Maple, *Appl. Phys.* **9**, 179 (1976).

WK1

X-ray Spectroscopy and Rare Earth Volume Collapse: High-fidelity Comparisons to Dynamical Mean Field Theory

Joseph A. Bradley[1], Kevin Moore[1], Magnus Lipp[1], Gerald Seidler[2], Brian Mattern[2], and Joseph Pacold[2]

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[2] Physics Dept., University of Washington, Seattle, WA 98195

Volume collapse in rare earth systems due to delocalization and bonding of 4f electrons at extreme pressures has been a hotly debated topic for several decades because the theory of f-electron correlations is a huge scientific challenge. Advances in x-ray spectroscopy at high pressure allow us to examine the physics underpinning these collapses with unprecedented detail and make for a stringent test of the latest theoretical treatments. In this presentation, we will lay out the x-ray techniques, present our results on rare earth metals, and compare to explicit predictions from dynamical mean field theory.

WK1

Magnetic Refrigeration and Cooling – An Energy Efficient and Green Cooling Technology for the 21st Century

Karl A. Gschneidner, Jr. and Vitalij K. Pecharsky

Ames Laboratory, U.S. DOE and Department of Materials Science and Engineering, Iowa State University,
Ames, IA 50011

Magnetic refrigeration (MR) offers the promise of improved energy efficiencies to be competitive with and eventually replace conventional gas-compression refrigeration technologies. This includes small-scale uses: refrigerators/freezers, air conditioning, automotive and aircraft climate control, wine chillers, etc. Large-scale cooling includes: industrial gas liquefaction, frozen food processing and storage, supermarket chillers, ocean liners and naval vessels, and large building climate control (e.g. schools, auditoriums, department stores, skyscrapers, etc.). In the past 15 years, there have been two significant advances: (1) that MR is a viable technology achieved a cooling power of 20 to 100 times larger than had been attained heretofore, and efficiencies as good as today's best conventional cooling machines; and (2) the discovery of the giant magnetocaloric effect (GMCE) in several families of alloys which should make MR even more competitive. To date, over 50 cooling machines have been built to test various concepts and ideas, including a proof-of-principle device, and several prototypes of near room temperature cooling machines.

Special attention will be given to the GMCE materials because there are a number of serious challenges that need to be addressed before these materials are utilized in magnetic cooling. These include: particle size (~0.3 mm) or plate thickness (~0.3 mm) of the magnetic refrigerant, hysteresis, time for the completion of the transition, adiabatic temperature change, ductility/brittleness, magnetostriction, and friability. Since an operating cooling machine running at 1 to 4 hertz will undergo about a trillion cycles in its lifetime, there are some studies that can be carried out at the Advanced Photon Source and/or Center of Nanoscale Materials and/or Electron Microscopy Center to address some of the obstacles for a reliable magnetocaloric refrigerant.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

WK1

Thin Film Exchange-spring Magnets

Sam Jiang

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Rare-earth-based permanent magnets have become indispensable to clean-energy technologies, as they are widely used in traction motors for hybrid/electric vehicles and in direct-drive turbines for wind power generation, etc. However, the stagnation in permanent magnet performance and the increasing global competition for rare earths are giving impetus for developing better-performing magnet materials with low or no rare earth content. Presently, the most promising approach for reaching this goal is to exploit the "exchange-spring" mechanism, in which a soft magnetic phase is hardened via interfacial exchange coupling to a hard magnetic phase.

We have used thin-film magnetic multilayer structures as model systems for exchange-spring magnets in order to investigate the fundamental magnetization processes and to examine their correlation with nanoscale structural characteristics. The model systems were designed and controlled during synthesis via epitaxial thin-film growth. We have uncovered the origin of the recoil hysteresis in exchange-spring nanocomposite magnets; and have demonstrated that an exchange-spring magnet with an already-ideal interface can be further improved by creating a graded interface. These investigations provide insights for developing ultra-strong permanent magnets and have been aided, in large part, by the use of element- and depth-resolved x-ray resonant magnetic scattering.

Work supported by the U.S. Department of Energy, Office of Science, Basic Energy Siences, under contract No. DE-AC02-06CH11357.

WK1

The X-ray View of all Optical Magnetic Switching in FeCoGd

Hermann A. Durr

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Long-range magnetic order in solids is usually ascribed to the exchange interaction between electron spins. Close to equilibrium this leads to spontaneous magnetization when the system cools below the magnetic ordering temperature. We show that the far from equilibrium flow of angular momentum via spin currents can also achieve long-range ferromagnetic order even above the ordering temperature. To reveal this process, we use ultrafast x-ray diffraction at SLAC's Linac Coherent Light Source to probe the nucleation, growth and transient existence of ferromagnetic order on the nm length and fs timescale after fs optical laser excitation has brought the metallic 3d - 4f alloy system FeCoGd into a highly non-equilibrium chaotic spin state. This provides a microscopic view how the magnetization in this system can be switched by optical excitation.

WK1

High Magnetic Field X-ray Spectroscopy of Heavy Fermion Systems

Yasuhiro H. Matsuda

Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

Correlation between localized and itinerant electrons is one of the most interesting subjects in solid-state physics and manifests itself in the valence state of heavy fermion (HF) systems. One may generally treat the valence state of the rare-earth ions in HF compounds as integer value, e.g., Ce valence in Ce-based HF compounds is regarded to be 3 (Ce^{3+}, f^1 state). However, the valence should be slightly larger than 3 and fluctuating because of the strong hybridization between the *f* and conduction electrons. The deviation from the integer value of the valence reflects the itinerant nature of the *f* electrons and the strength of the correlation. Moreover, there is a great possibility that the magnetic field can weaken the correlation through the Zeeman energy and induce the metamagnetic behavior as a result of localization of the *f* electrons. The purpose of this study is to clarify the change in the nature of the *f* electrons in high magnetic fields by observation of the valance state.

X-ray spectroscopy is a powerful means to investigate the electronic states of matter. The valence state of the rare-earth ions can be directly determined by the x-ray absorption spectra near the L_3 edge. Recent technical developments of the x-ray experiment using a pulsed magnet has enabled us to conduct the x-rays spectroscopy experiments in high fields of up to 40 T. [1, 2] In the present study, we have measured the x-ray absorption spectra of $YbXCu_4$ (X=Ag, In) and CeY_2Si_2 (Y=Ru, Rh) near the L_3 edge of Yb and Ce, respectively, in pulsed magnetic fields of up to 40 T. These compounds exhibit the metamagnetic behavior at high magnetic fields and low temperatures.[3–6] The experiments were carried out at beamline BL22XU and BL39XU in SPring-8. As a result, significant field-induced valence changes were observed in all of the measured samples at low temperatures (1.8–5 K) and it turned out that the magnetic field dependence of the valence corresponded to the metamagnetic transition of the magnetization, suggesting suppression of the itinerant nature of the *f* electrons at the transition.

[1] Y.H. Matsuda, T. Inami, *et al.,* J. Phys. Soc. Jpn. **76,** 034702 1-6, 2007.

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[3] J.L. Sarrao, C.D. Immer *et al.,* Phys. Rev. B **59,** 6855-6866, 1999.

[4] K. Yoshimura, T. Nitta *et al.,* Phys. Rev. Lett. **60,** 851-854, 1988.

[5] P. Haen, J. Flouquet *et al.,* J. Low Temp. Phys. **67,** 391-419, 1987.

[6] R. Settai, *et al.,* J. Phys. Soc. Jpn. **66,** 2260-2263, 1997 ; H. Abe *et al.* J. Phys. Soc. Jpn. **66,** 2525-2526, 1997.

WK1

Magnetoelastics of a Spin Liquid

Jacob Ruff

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Recently, the rare-earth titanate pyrochlores have been extensively studied as model magnetic materials. These materials present pristine cubic pyrochlore lattices, and variation of the rare-earth ion allows for tuning of interactions and anisotropy, realizing a wide range of canonical frustrated systems including both the classical and quantum spin ices. One member of this family, $Tb_2Ti_2O_7$, has long been known to manifest a collectively paramagnetic or “spin-liquid” ground state, although a satisfactory explanation for this phenomenon has not been achieved. In this talk, I will report extensive x-ray diffraction measurements at low temperatures and in high magnetic fields, which reveal strong spin-lattice coupling in the low-temperature phase of $Tb_2Ti_2O_7$. I will argue that a compound frustration that occurs for the coupled spin and lattice degrees of freedom is responsible for the unusual low-temperature phase, which I identify as a magnetoelastic spin liquid.

WK1

Study of Quantum Phase Transitions in Rare Earth Compounds Using Mössbauer Spectroscopy

Mohsen M. Abd-Elmeguid

II. Institute of Physics, University of Cologne, Germany

Quantum phase transitions (QPT) are phase transitions at zero temperature that can be triggered by a non-thermal parameter such as pressure, chemical substitution, or magnetic field. They are driven by a corresponding change of quantum fluctuations between phases across a quantum critical point (QCP). Particularly interesting is the fact that these fluctuations strongly affect the physical properties of the system at finite temperature, resulting an unusual low-temperature behavior and the formation of new ground states including unconventional superconductivity.

In this talk, I first will give a brief and simple introduction to quantum phase transitions and the associated novel phenomena near a quantum critical point. I will then focus on how external pressure can be used to tune the properties of selected rare earth compounds across a QPT and show how ^{151}Eu high-pressure Mössbauer spectroscopy and ^{149}Sm nuclear forward scattering can be used to obtain at a microscopic level valuable information about the nature of novel ground states at/ near a QCP.

WK1

Re-entrant Valence Transition in EuO at High Pressures: Beyond the Bond-valence Model

N.M. Souza-Neto[1, 2], J. Zhao[1], E.E. Alp[1], G. Shen[3], S.V. Sinogeikin[3], G. Lapertot[4], and D. Haskel[1]

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[2] Laboratório Nacional de Luz Síncrotron, Campinas, SP 13083-970, Brazil
[3] HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20005
[4] SPSMS, UMR-E 9001, CEA-INAC/UJF-Grenoble 1, 17 rue des martyrs, 38054 Grenoble, France

X-ray synchrotron-based spectroscopies and x-ray diffraction are used to describe the pressure-dependent valence of Eu ions in model compound europium oxide. It is shown that a novel re-entrant valence transition happens concomitantly with the pressure induced structural phase transition. This highlights the need for probing both structure and electronic states directly when valence information is sought in mixed-valent systems. Most importantly we show that widely used bond-valence methods fail to capture essential features of the complex electronic valence behavior of EuO under pressure.

APS Workshop 2
Metal Ion Adsorption at Interfaces

Location: *Bldg. 440, Room A105/106*

Organizers: Lynne Soderholm and Paul Fenter (CSE Division, Argonne National Laboratory)

Driven by such diverse motivations as improving separations science and predicting environmental contaminant fate and transport, recent interests have focused on developing a molecular level understanding of multivalent metal ions at interfaces. Whether solid-liquid, solid-gas, liquid-liquid, or liquid-gas, recent experiments (primarily x-ray and photon-based probes) are providing new insights into interfacial structures and the interactions that define them. Information quantifying molecular concentrations, coordination environments and interatomic distances as well as molecular organization and orientation with surfaces are providing new and unexpected results that are quickly revolutionizing some of the long-held beliefs about metal-surface interactions. This workshop will focus on recent advances in experimental synchrotron techniques together with some novel results and how they are providing information about how to build predictive models for metal interactions at an interface.

8:45 – 9:00	Welcome and Introductory Remarks
9:00 – 9:45	Mark L. Schlossman (University of Illinois at Chicago) *The Role of Molecular Ordering in Solvent Extraction of Metal Ions*
9:45 – 10:20	Mark Antonio (CSE, Argonne National Laboratory) *Erbium(III) Coordination At The Surface Of An Aqueous* $ErCl_3$*-HCl-*H_2O *Solution*
10:20 – 10:50	Break
10:50 – 11:30	Ilan Benjamin (University of California, Santa Cruz) *Hydration Shell Water Molecules and the Adsorption of Ions at Interfaces*
11:30 – 12:10	David Vaknin (Ames Laboratory/Iowa State University) *X-ray Spectroscopy and Diffraction from Ions at Charged Aqueous Interfacial Templates*
12:10 – 1:30	Lunch
1:30 – 2:10	Franz M. Geiger (Northwestern University) *Metal Ion Adsorption to Oxide/Aqueous Interfaces Studied by Second Harmonic Generation*
2:10 – 2:50	Ian C. Bourg (Lawrence Berkeley National Laboratory) *Molecular Dynamics Simulations of the Electrical Double Layer on Smectite Clay Surfaces*
2:50 – 3:20	Break
3:20 – 4:00	Moritz Schmidt (Karlsruhe Institute of Technology) *Interfacial Reactivity Of Actinides On The Muscovite (001) Basal Plane*
4:00 – 4:40	Joanne Stubbs (The University of Chicago) *Oxidative Corrosion of the Uraninite (111) Surface*

WK2

The Role of Molecular Ordering in Solvent Extraction of Metal Ions

Mark L. Schlossman

Department of Physics, University of Illinois at Chicago, Chicago, IL 60607

The separations process known as solvent extraction relies upon the extractant-mediated transfer of ions from an aqueous to an organic phase. Other than the knowledge that this transfer takes place at the oil/water (liquid/liquid) interface, there is little known about this interfacial process on the nanoscale. A model extraction system was developed whose behavior can be tuned from that of a typical oil-water-surfactant system that displays amphiphilic adsorption at the water/oil interface to an extractant system in which the amphiphile selectively binds to the targeted metal ion (Er^{3+}) at the water-oil interface and extracts it from the aqueous phase into the organic phase. This model system allowed us to capture and investigate the structure of an intermediate state in the extraction process by x-ray reflectivity and x-ray fluorescence near total reflection measurements (carried out at APS 9-ID and 15-ID). The intermediate state consists of an inverted bilayer at the interface, which provides a sensible pathway for the conversion of a hydrated metal ion in the aqueous phase to an inverted micelle encapsulated ion in the organic phase.

WK2

Erbium(III) Coordination At The Surface Of An Aqueous $ErCl_3$-HCl-H_2O Solution

Mark R. Antonio

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The coordination environments of metal ions in bulk solutions (both aqueous and organic) and at their surfaces play critical roles in the molecular reactions at play in solvent extraction (SX) processes widely used for metal purification, notably of the rare-earth (RE) family of elements, which are of contemporary interest, not the least of which includes national security.[1] The SX process involves the contact of an aqueous liquid, containing the aquated RE cations to be separated (here, we focus on erbium), with an oily and water-immiscible organic solvent containing one (or more) extractant molecule(s) that are tailor-made to facilitate the targeted extraction of one (or more) RE element(s). We chose to study Er (Z = 68) because it is a small lanthanide with a well-known coordination environment in aqueous solutions.[2] Although the knowledge of its bulk coordination is an important aspect of the overall energetics that influence its SX, its speciation at the liquid-liquid interface, where the phase transfer occurs, is as yet unknown. In our first step to probe this complicated, multicomponent system, and to simplify the experiment, we chose to examine the water-helium interface of an aqueous, acidic $ErCl_3$ solution by use of x-ray absorption spectroscopy, including a comparison of the bulk speciation, using fluorescence detection, with that at the surface, using electron-yield detection at grazing incidence conditions. With this approach, we find significant differences in the speciation of Er in the bulk and at the surface of the 1 M $ErCl_3$ solution. The research advances our understanding of the atomic-level, surface-speciation of Er(III). In particular, details of the electron-yield experiments provided unexpected results, namely evidence for significant Er-Cl and Er-Er correlations within about 16 Å of the solution-helium interface.

This work and the use of the Advanced Photon Source are supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357.

[1] Rare earths for national security, *C&E News,* 5 December 2011, Vol 88, No 49, 33.

[2] Soderholm, L.; Skanthakumar, S.; Wilson, R.E. *J. Phys. Chem. A* **2009,** *113*, 6391-6397.

WK2

Hydration Shell Water Molecules and the Adsorption of Ions at Interfaces

Ilan Benjamin

University of California, Santa Cruz, CA 95064

Molecular dynamics computer simulations are used to gain insight into the role of hydration shell water molecules in the adsorption and transfer of ions across the water/oil interface. The ability of the ion to keep all or part of the first-shell water molecules has a profound effect on the free energy of transfer, the dynamics of the ion and its reactivity, and is strongly coupled with local surface fluctuations. The role of co-transferred counter ions is also briefly discussed.

WK2

X-ray Spectroscopy and Diffraction from Ions at Charged Aqueous Interfacial Templates

David Vaknin

Ames Laboratory and Physics and Astronomy Department, Iowa State University, Ames, IA 50011

Combining surface sensitive x-ray diffraction and spectroscopic techniques we determine ion distributions at charged bio-mimetic membranes. We have extended standard methods, such as, anomalous x-ray reflectivity, fluorescence spectroscopy, and x-ray absorption near-edge structure to monitor ion-specific surface enrichment at charged liquid/vapor interfaces, and verified the applicability of a modified interfacial Poisson-Boltzmann model to monolvalent ion solutions. Energy scans at constant Q_z are used to monitor the ionic coordination and subtle behavior of Fe^{2+} and Fe^{3+} upon binding to a charged lipid or protein template. Applying these methods to same charge multivalent ions, such as Ca^{2+}/Ba^{2+} or La^{3+}/Fe^{3+} show remarkable ionic specificity demonstrating the inadequacy of standard statistical/electrostatic models in capturing the binding phenomena of multivalent ions to charged interfaces.

WK2

Metal Ion Adsorption to Oxide/Aqueous Interfaces Studied by Second Harmonic Generation

Franz M. Geiger

Irving M. Klotz Professor of Physical Chemistry, Northwestern University, Evanston, IL 60208

Aqueous/oxide interfaces are notoriously difficult to study, as most surface-selective methods require vacuum or temperature conditions that prevent such investigations. Here, we discuss how second harmonic generation (SHG) is used to access surfaces of fused silica, alpha alumina, and hematite in contact with aqueous bulk solutions containing various di- (Mg, Ca, Sr, Ba, Cd, Mn) and trivalent (Al, Sc, Y, La, Gd, Lu) metal cations held at various electrolyte and pH conditions. We show how interfacial charge densities and interfacial potentials are obtained from the SHG measurements, and how this information is used to determine the interfacial speciation of the metal cations at the interface vs. the bulk.

WK2

Molecular Dynamics Simulations of the Electrical Double Layer on Smectite Clay Surfaces

Ian C. Bourg and Garrison Sposito

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

We report molecular dynamics results elucidating the structure of the electrical double layer (EDL) on smectite surfaces contacting mixed NaCl-$CaCl_2$ electrolytes. Our results consist of two datasets, the first investigating a range of concentrations relevant to ocean sediments and brine aquifers [0.34 to 1.83 $mol_c\ dm^{-3}$ (Bourg and Sposito, 2011)] and the second investigating a Na-Ca ion exchange isotherm at 0.1 $mol_c\ dm^{-3}$. Our results confirm the

existence of three distinct adsorption planes (0-, β-, and d-planes), often assumed in EDL models, but with two important qualifications: (1) the location of the β- and d-planes are independent of ionic strength or ion type and (2) "indifferent electrolyte" ions can occupy all three planes. We discuss the implications of our results for the parameterization of surface complexation and ion exchange models (capacitance parameters of the triple layer model, ion exchange selectivity coefficients, activity coefficients of adsorbed species, and adsorption selectivity of $CaCl^+$ ion pairs).

Bourg, I.C. and Sposito, G., (2011) *J. Colloid Interface Sci.* 360, 701–715.

WK2

Interfacial Reactivity of Actinides on the Muscovite (001) Basal Plane

Moritz Schmidt[1], Sang Soo Lee[2], Richard E. Wilson[2], Karah E. Knope[2], L. Soderholm[2], and Paul Fenter[2]

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The actinides' interaction with mineral phases is of foremost importance for the safety assessment of nuclear waste disposal sites as well as remediation efforts in legacy contamination sites [1, 2]. Actinide-mineral interactions will control the mobility and transport behavior of the actinides and thus there hazard potential in the biosphere. The complex nature of the aqueous-mineral interface system in conjunction with the multifaceted aqueous chemistry of plutonium requires techniques that are capable of selectively probing the complete near-interface regime while yielding molecular-level information of the structures and reactions in this system.

Recent results on the interaction of actinides (Th and Pu) with the (001) basal plane of muscovite from *in situ* surface x-ray diffraction experiments (crystal truncation rods, CTR, and resonant anomalous x-ray reflectivity, RAXR) will be presented. The interaction of "simple" aqueous ions, such as Pu(III) and Th(IV), with the charged interface, as well as the sorption of Pu(IV)-oxo-nanoparticles will be presented. The results will be discussed with respect to the actinides aqueous chemistry, in particular, redox states, hydration, hydrolysis, and polymerization reactions. Additional discussion will focus on experimental procedures for surface diffraction experiments with radioactive materials at the APS.

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[2] H. Geckeis and T. Rabung, *Actinide geochemistry: From the molecular level to the real system*. Journal of Contaminant Hydrology, 2008. 102(3–4): p. 187–195.

WK2

Oxidative Corrosion of the Uraninite (111) Surface

Joanne E. Stubbs[1], Peter J.Eng[1], Craig A. Biwer[1], Anne M. Chaka[2], Glenn A. Waychunas[3], and John R. Bargar[4]

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[3] Lawrence Berkeley National Laboratory, Berkeley, CA 94720
[4] Chemistry and Catalysis Division, Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025

Uraninite (UO_2) is the most abundant uranium ore mineral, the product of proposed bioremediation strategies for uranium-contaminated soils and aquifers, and its synthetic analog is the primary constituent of most nuclear fuels [1–3]. This material is known to incorporate interstitial oxygen up to a stoichiometry of $UO_{2.25}$ without disruption of the uranium lattice, but the structural details of the process are the subject of ongoing study and debate [e.g., 4–6]. Because the solubility and dissolution kinetics of uraninite depend heavily on the oxidation state of uranium, understanding the mechanims of UO_2 surface oxidation and corrosion is essential to predicting its stability in the environment throughout the nuclear fuel cycle. To date, however, no study has addressed this process at the molecular scale at atmospheric pressure and room temperature.

We present results of a crystal truncation rod (CTR) x-ray diffraction study of the UO_2 (111) surface. This hard x-ray technique is ideally suited to such studies because it can probe the structures of interfaces at atmospheric conditions and buried below liquids and solids. The single-crystal surface was prepared under anoxic conditions, measured under dry helium, then exposed to dry O_2 gas and measured at several time points over the course of two weeks. The pristine surface is characterized by minimal contraction of the uppermost atomic layers and the addition of an oxygen layer above the vacuum-terminated surface. Following exposure to dry O_2, an oxidation front proceeds into the crystal, intersitial oxygen atoms penetrate to depths of 30 Å or more, U-U layer distances contract (consistent with bulk uraninite oxidation), and an ordered superlattice, which is commensurate with the underlying bulk, forms. These results demonstrate that the solid state diffusion of oxygen into UO_2 and UO_{2+x} surfaces is facile and that ordering kinetics are relatively rapid, even at room temperature.

Ab initio thermodynamics, which combines density-functional theory calculations with macroscopic thermodynamics, provides insight into the energetics, bonding, and oxidation processes that occur as oxygen reacts with the surface and diffuses into the solid. Surface oxidation results in formation of a U^{+6} cation triply bonded to single oxygen adatoms. Subsurface oxidation is predicted to contract U-U layers consistent with experimental observations.

[1] Finch & Murakami (1999) *Rev. Mineral. Geochem.* **38,** 91-180.

[2] Bargar et al. (2008) *Elements* **4,** 407-412.

[3] Wilson (1996) *The nuclear fuel cycle,* Oxford University Press

[4] Cooper and Willis (2004) *Acta Cryst. A.* **60,** 322-325.

[5] Conradson et al. (2004) *Inorg. Chem.* **43,** 6922-6935.

[6] Andersson et al. (2009) *Phys. Rev. B.* **79,** 060101.

APS Workshop 3
Energy Materials and Energy Systems Applications of *In Situ* X-ray Microscopy

Location: *APS 402 Lecture Hall*

Organizers: Barry Lai and Jörg Maser (X-ray Science Division, APS)

The aim of the workshop is to explore applications in energy science that may be addressed by *in situ* x-ray microscopy. It will encompass the study of advanced energy harvesting, conversion and storage systems, approaches to sustainable energy, and platforms for advanced electronics. All these systems have in common complex, hierarchical structures with nanoscale features, often in nonplanar geometries, where small quantities of inhomogeneously distributed dopants, precipitates, contaminants, and second-phase particles play an increasingly important role in overall system performance. In many cases, we seek to understand and control material properties that determine system performance, system efficiency and environmental impact. Examples of materials systems and devices to be studied are solar cells, fuel cell components, and advanced battery concepts. The science of nanoelectronics will include the study of CMOS devices designed for 22-nm node technologies and below, with a view to increase performance, speed, and power efficiency. Approaches to sustainable energy will include the study of advanced building materials that reduce CO_2 emissions, research on understanding natural carbon sinks and development of artificial carbon sinks, and biogeochemical cycling of metal contaminants. In most cases, high-spatial-resolution imaging with trace-level sensitivities in complex 2D or 3D geometries and under real operation conditions is required, which is the focus of the *In Situ* Nanoprobe beamline that will be built as part of the APS Upgrade. The workshop will explore high-impact questions within the scientific thrust of the beamline, discuss the capabilities and complementary roles of alternative approaches such as scanning probe microscopies and electron microscopies, and inform the design of the *In Situ* Nanoprobe instrument and the envelope of its *in situ* capabilities.

8:50 – 9:10	Welcome/Introduction
9:10 – 9:40	John Mitchell (MSD, Argonne National Laboratory) *Opening Talk: Grand Challenges in Energy Science*
9:40 – 10:10	Chris Johnson (CSE, Argonne National Laboratory) In Situ *Evaluation of Batteries Using the CNM/APS Hard X-ray Nanoprobe*
10:10 – 10:40	Break
10:40 – 11:10	Tonio Buonassisi (Massachusetts Institute of Technology) *Advancing Inorganic Photovoltaics Via High-throughput* In-situ *X-ray Microscopy*
11:10 – 11:40	Wilson Chiu (University of Connecticut) In situ *Hard X-ray Microscopy of Fuel Cells: Progress, Challenges and Opportunities*
11:40 – 12:10	Tijana Rajh (CNM, Argonne National Laboratory) *Nanoscience for Energy*
12:10 – 1:30	Lunch

1:30 – 2:00	Simon Bare (UOP) *Adventures in Catalyst Characterization using X-ray Micro- and Nano-tomography*
2:00 – 2:30	Paulo Monteiro (University of California, Berkeley) *Carbon Sequestration and Sustainable Construction Materials: Multiscale Studies of Complex Hierarchical Materials*
2:30 – 3:00	Conal E. Murray (IBM) *Interesting Defects: Assessing the Role of Impurities in Nano-electronics*
3:00 – 3:30	Break
3:30 – 4:00	J. G. Wen (MSC, Argonne National Laboratory) *Increase Resolution to Atomic Level for* in-situ *Environmental TEM with Enclosed Gas or Liquid Cell*
4:00 – 4:30	Tolek Tyliszczak (Lawrence Berkeley National Laboratory) *Soft X-ray* In-situ *Spectromicroscopy Measurements at the ALS*
4:30 – 5:00	Tonio Buonassisi (Massachusetts Institute of Technology) *Closeout: Future*

WK3

Grand Challenges in Energy Science

John Mitchell

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

New materials are the gateway to future technologies. Examples from the past century—the transistor, magnetoresistive read-heads, LEDs, lithium-ion batteries—attest to this point and foreshadow that the breakthrough technology needs of the 21st century—energy, high-density memory, ultra selective catalysts, etc.—depend on the discovery of new materials and chemistries. And in today's globally competitive environment a rapid, efficient discovery process is paramount to vital U.S. national interests. Unfortunately, the pace of functional materials and chemical synthesis discoveries in the U.S. markedly lags that of our highly advanced characterization tools. This 'synthesis gap' can be recognized then as the rate-limiting step in the advance of materials and molecular science and ultimately the deployment of new technologies based on these discoveries. This talk will focus on our need to create novel materials and molecules and how it pushes us beyond 'materials by design' toward 'synthesis by design,' characterized by predictable, controllable mechanistic frameworks of materials formation pathways and chemical transformations—knowing where to put the atoms and how to put them there.

WK3

In Situ Evaluation of Batteries Using the CNM/APS Hard x-ray Nanoprobe

Christopher S. Johnson[1], Lynn Trahey[1], Benjamin J. Blaiszik[2], Fulya Dogan[1], Fikile R. Brushett[1], Volker Rose[2, 3], and Robert P. Winarski[2]

[1] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439
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[3] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

The first *in situ* lithium-ion battery experiment at the Advanced Photon Source (APS) was conducted in 1997 using a cathode of $LiNi_{0.8}Co_{0.2}O_2$ coupled with a Li anode operating inside an aluminized pouch cell. The evaluation of the charge compensation and the average changes in bond lengths during insertion and removal of lithium in this material were revealed for the first time [1]. These results led to the broad realization that synchrotron x-rays were a powerful tool for battery research and development. Since that first demonstration, numerous groups and researchers worldwide have used the x-ray facilities at the APS to conduct experiments on a variety of battery active materials, including graphites, silicon-composites, transition metal oxides and sulfides, intermetallics, alloys, and carbons. The Center of Nanoscale Materials CNM/APS Hard X-ray Nanoprobe is the next user facility to be utilized to understand batteries. The combination of 360° tomography and 2D or 3D x-ray fluorescence imaging at the nanoscale is being developed for both *in situ* and *ex situ* interrogation of battery materials and their electrochemical lithiation/de-lithiation reactions. The real-time visualization of material morphological changes in an operating capillary battery is currently being developed. The science chosen for the initial demonstration addresses the question of strain and pulverization that occurs when Si nanoparticles react electrochemically with Li. These results and a discussion of the capabilities of the CNM/APS nanoprobe to study batteries will be the focus of the presentation.

[1] C.S. Johnson and A.J. Kropf, "*In situ* XAFS Analysis of the $Li_xNi_{0.8}Co_{0.2}O_2$ Cathode During Cycling in Lithium Batteries," *Electrochim. Acta.,* **47,** 3187–3194 (2002).

WK3

Advancing Inorganic Photovoltaics Via High-throughput *In-situ* X-ray Microscopy

Tonio Buonassisi

Massachusetts Institute of Technology, Cambridge, MA 02139

Throughout the development history of inorganic photovoltaics (PV), industrial technology advances have been driven by basic science breakthroughs. We begin by reviewing the impact of synchrotron-based x-ray micrprobe to identify performance-limiting defects in commercial solar cells, leading to the development of new solar cell manufacturing technologies. We then preview the coming challenges in crystalline silicon and thin-film solar cell development, including the emergence of kerfless silicon and Earth-abundant chalcogenide absorbers, highlighting the opportunities enabled by the next generation of *high-throughput*, *in-situ* x-ray microprobes.

WK3

In Situ Hard X-ray Microscopy of Fuel Cells: Progress, Challenges, and Opportunities

Wilson K.S. Chiu

Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139

Substantial losses can arise in the solid oxide fuel cell (SOFC) due to degradation during operation. This presentation will focus on the development of *in situ* x-ray imaging and spectroscopy techniques that will allow the direct observation of the SOFC under operational conditions and provide a scientific and engineering understanding of degradation. Progress on x-ray fluorescence spectroscopy mapping of sulfur-treated SOFC Ni-YSZ anodes using the Hard X-ray Nanoprobe at beamline 2-ID-D at the Advanced Photon Source will be presented. *In situ* x-ray imaging of 3D microstructural and chemical changes in SOFC materials using the transmission x-ray microscope at APS beamline 32-ID-C will also be presented. Challenges and opportunities of *in situ* hard x-ray microscopy using nanoprobe and full-field x-ray microscopy techniques will be discussed. The long-term goal of this work will be to develop hard x-ray *in situ* techniques to further the understanding and enhance SOFC long term performance and reliability to enable SOFCs as a viable technology for efficient and sustainable energy conversion.

This work is supported by the National Science Foundation (Award CBET-1134052) and an Energy Frontier Research Center on Science Based Nano-Structure Design and Synthesis of Heterogeneous Functional Materials for Energy Systems (HeteroFoaM Center) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC000106).

WK3

Nanomaterials for Energy

Tijana Rajh, Elena Shevchenko, Elena Rozhkova, Chris Fry, Yuzi Liu, and Ralu Divan

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Important elementary steps in energy-relevant processes such as energy conversion, electronics and catalysis, as well as in their biological analogs, occur on the nanoscale and require electron exchange within energy gradient structures. The energy and electron flow in these multiphase systems, designed and arranged to direct a specific process, delineates the desired function of a system. In our work we are trying to understand how deliberate tailoring and assembling of materials on the nanoscale can lead to gradient nanoarchitectures with targeted functionalities. We employ directed synthesis and assembly of nanoparticles with the objective of perfecting electron transfer, charge conversion and energy storage.

Nanocrystalline structures offer unique opportunities for tailoring the electronic, mechanical and chemical properties of materials. Large surface area and different coordination sphere of the surface atoms causes the change in the local crystalline environment facilitating enhanced coupling with neighboring molecules. This, in turn, enables formation of hybrid materials in which the exchange interaction of two materials in close proximity affects their electron density and is critically dependent on individual size and mutual geometry of the constituents. In order to understand electronic coupling in hybrid materials we are developing scalable multi-component architectures of nanoparticles. These multi-component nanoarchitectures are built from the molecular level in order to achieve (1) detailed control over morphology that enables energy gradient optimization (2) small diffusion length of charges and (3) improved conductivity obtained by tailored binding of conductive molecular bridges to different nanoarchitecture components.

External stimuli on multiple time and length scales are utilized to perturb the electronic structure of the hybrid nanoparticle architectures. Integration of hybrid nanoparticles with biological entities such as single cells are also utilized to achieve redox-sensitive cellular labeling as well as photocatalytically triggered enzymatic reactions. An understanding of light absorption, carrier dynamics, energy and charge transfer, and electric and magnetic field effects in these engineered nanostructures are employed to guide their use in applications in the areas such as catalysis, energy conversion and storage, as well as advanced medical therapies.

WK3

Adventures in Catalyst Characterization using X-ray Micro- and Nano-tomography

Simon R. Bare and Shelly D. Kelly

UOP LLC, a Honeywell Company, Des Plaines, IL 60017

The development of an industrial catalyst is a complex problem and can benefit from the use of synchrotron-based techniques to provide multi-dimensional characterization to obtain information on the distribution and speciation of both catalytically active and tramp metals, and catalyst support properties such as meso-porosity and strength. Utilizing beamlines at the APS, NSLS, and SSRL, we have investigated the internal structure of catalyst extrudates, beads, and pills using micro- and nanoscale tomography, the distribution and speciation of metals using microprobe x-ray fluorescence and x-ray absorption near-edge structure and the speciation of supported metal clusters using *in situ* x-ray absorption spectroscopy. Each of these techniques is under continuous development, and when combined with the exciting and active area of scientific discovery in catalysis, they promise new and unique understanding.

WK3

Carbon Sequestration and Sustainable Construction Materials: Multiscale Studies of Complex Hierarchical Materials

Paulo J. M. Monteiro

Department of Civil and Environmental Engineering, University of California at Berkeley, CA 94720

The National Research Council recently articulated an urgent national need to invest in and modernize the country's aging civic infrastructure to maintain global competitiveness. The present status of the cement and concrete industry is not sustainable. The production of Portland cement is responsible for 7% of the CO_2 emission in the world and existing reinforced concrete infrastructure is deteriorating at a fast pace. In conjunction with this ever-increasing need for enlarging the built environment is the bleak future facing our aging civil infrastructure. Corrosion, frost action, sulfate attack, and cracking due to alkali silica reaction have significantly reduced the life cycle of buildings, bridges, dams, roads, and marine structures. For instance, of the 597,340 bridges in this country, 73,784 or about 12.4 percent are structurally deficient. To change existing technology requires new developments in the understanding of nanostructure of the hydration products and of the complex deterioration reactions.

Our research group has been developing new materials and using synchrotron radiation to characterize the nano- and microstructure of cement paste and concrete exposed to aggressive environments. In addition to fly-ash, blast furnace slag, volcanic ash, or activated-clay-substituted Portland cement and geopolymers, we are beginning to systematically evaluate a series of low-carbon-emission cementitious materials. This approach will allow CO_2 from the flue gas to be concentrated before reacting with the source of cations (i.e. seawater). Our specific research goals are to: a) demonstrate a process combining carbon capture and sequestration b) investigate the impact of crystalline and amorphous carbonates on the structure, flow and performance of cement pastes; b) optimize concrete mixtures that maximize incorporation of CO_2; and c) evaluate long-term performance. In parallel, we are also optimizing the dissolution of fly ash (a waste product) to increase it reactivity and minimize or even reduce the use of Portland cement.

WK3

Interesting Defects: Assessing the Role of Impurities in Nano-electronics

Conal E. Murray

IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

The drive to increase performance within CMOS technology while improving power efficiency towards exascale computing platforms requires the use of new strategies beyond traditional scaling of device dimensions. A key element in this endeavor involves the determination of trace elements and their chemical state within current and future technology nodes at a very high-spatial resolution. The distribution and activity of dopants within the current-carrying regions of silicon-based devices clearly represent important aspects to mitigate short-channel effects and increase carrier mobility. But the incorporation of novel materials within nearly every level of ultra-large scale integration underscores the importance of ascertaining impurity information *in-situ* and nondestructively within complex, three-dimensional architectures. Examples will be presented, from gate insulation to metallization, where impurities that are deliberately introduced to extend or enhance performance must be quantified as well as localized. Cases where dopant species can lead to a reduction in device behavior or be deleterious to overall reliability will also be shown.

WK3

Increase Resolution to Atomic Level for *in-situ* Environmental TEM with Enclosed Gas or Liquid Cell

J.G. Wen, Dean Miller, Nestor Zaluzec, and Russell Cook

Materials Science Division and Electron Microscopy Center, Argonne National Laboratory, Argonne, IL 60439

In-situ environmental TEM using a window-type environmental cell with two O-ring sealed window membranes has become popular because it can enclose both liquid and atmospheric-pressure gas in the microscope. The drawback of this technique is that atomic-level resolution becomes very difficult to achieve due to the large total thickness of the sample, two window membranes, and the liquid or gas in the path. Chromatic aberration-correction is expected to improve TEM imaging resolution for thick samples. Using the Argonne aberration-corrected TEM (ACAT), we explored the contribution of chromatic aberration to the resolution improvement for the window-type gas cell. Both resolution and signal-to-noise ratio were found improved with chromatic aberration. Experimental results indicate that whether nanoparticles are on top or bottom of membranes along electron beam direction (also called top-bottom-effect) affects the imaging resolution. In the case of liquid cell, methods to reduce total thickness such as reducing the gap between two membranes by avoiding cleave-induced Si fragments using etching guideline on Si wafer and reducing membrane thickness using rectangular windows will be discussed. Several examples of *in-situ* TEM experiments with reduced total thickness will also be presented.

WK3

Soft X-ray *In-situ* Spectromicroscopy Measurements at the ALS

Tolek Tyliszczak

Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Soft x-ray spectroscopy is a powerful method to characterize the chemical and physical properties of many systems. When combined with a microscope, it has many unique applications. Photon-in/photon-out principle allows the use of this technique in a relatively easy way to study *in situ* reactions on the nanoscale.

At the ALS there are three scanning transmission x-ray microscopes used for *in-situ* measurements down to 20-nm resolution. There are many types of environmental cells available for use with those microscopes. They allow the control of temperature, humidity, or gas environment. There is also an ambient pressure scanning photoelectron emission microscope, which makes it possible to obtain information of surface interaction with gases and vapors with pressures up to 20 Torr and spatial resolution of 100 nm.

APS Workshop 4
Functional Biomolecular Interfaces

Location: *Bldg. 402, Room E1200*

Organizers: Laurence Lurio (Northern Illinois University) and Mark Schlossman (University of Illinois at Chicago)

Numerous electronic and catalytic processes take place on the molecular scale at interfaces in biological systems. The physical constraints of the interfacial geometry and the multi-molecular chemical interactions available at interfaces act to promote the aggregation of specific biomolecules in response to biological signaling. Subsequent membrane-induced ordering of the aggregated biomolecules results in enhanced biological functionality. High-resolution x-ray scattering probes the molecular organization that underlies such functionality. Lipids, peptides, and proteins form the basic building blocks of functional biomembranes. Model membrane systems studied with x-ray scattering include Langmuir and Gibbs layers at liquid surfaces and interfaces, supported membranes at solid-liquid interfaces, and complex bulk structures such as vesicles in suspension. While early work focused on neat lipid membranes, recent investigations have addressed complex phenomena such as raft formation, lipid-protein binding, and virus-membrane interactions. Membranes are also a dynamic platform for biological activity, continually re-organizing and re-forming themselves for specialized processes. New activities in x-ray photon correlation spectroscopy are starting to probe these dynamics. The goal of the present workshop is to provide an opportunity to present the variety of work on biomolecular interfaces and opportunities for using scattering techniques to determine their static and dynamic structure.

8:50 – 9:00	Laurence Lurio *Welcome & Introductory Remarks*
9:00 – 9:40	Ka Yee Lee (The University of Chicago) *Pushing the Boundaries of Structural Immunology: Utilizing X-ray Surface Scattering to Explore Lipid Membrane Recognition in Immune Response*
9:40 – 10:20	Liat Rosenfeld (Stanford University) *Molecular Structure of Interfacial Human Meibum Film*
10:20 – 10:40	Break
10:40 – 11:20	Tonya Kuhl (Department of Chemical Engineering and Materials Science and Department of Biomedical Engineering, UC Davis) *Lipid Membranes from the Molecular- to Macro-scale*
11:20 – 12:00	Ting Xu (University of California, Berkeley) *Structural Characterization of Peptide-Polymer Conjugates toward Hybrid Biomolecular Materials*
12:00 – 1:30	Lunch
1:30 – 2:10	Masafumi Fukuto (Brookhaven National Laboratory) *Lipid-mediated Assembly of Biomolecular Nano Objects at Liquid Interfaces*
2:10 – 2:50	J. K. Blasie (Department of Chemistry, University of Pennsylvania) *High-energy X-ray vs. Neutron Reflectivity Probes of Structure and Dynamics of Single Lipid:Protein Membranes at the Solid:Liquid Interface: A Progress Report*

2:50 – 3:10 Break

3:10 – 3:50 John F. Nagle (Carnegie Mellon University)
Diffuse X-ray Scattering Provides More and Better Information for Fluctuating, Fully Hydrated Membranes than Traditional Diffraction Methods

3:50 – 4:30 David Gidalevitz (Illinois Institute of Technology)
Cholesterol Mediates Membrane Curvature during Fusion Events

WK4

Pushing the Boundaries of Structural Immunology: Utilizing X-ray Surface Scattering to Explore Lipid Membrane Recognition in Immune Response

Greg Tietjen[1], Chiu-Hao Chen[1], Kathleen Cao[1], Charles Heffern[1], Ernesto Vargas[1], James Crooks[1], Benoit Roux[1], Mati Meron[1], Mark Schlossman[2], Binhua Lin[1], Erin Adams[1], and Ka Yee C. Lee[1]

[1] University of Chicago, Chicago, IL 60637
[2] University of Illinois at Chicago, Chicago, IL 60607

The immune system recognizes a vast array of chemical signatures as antigens although historically most research has focused almost exclusively on protein/ protein recognition. More recently it has been appreciated that lipids can also be a potent stimulus for an immune response, as with phosphatidylserine recognition in apoptotic cell clearance. We are studying the molecular mechanisms by which a family of three unique phosphatidylserine receptors (Tim family) can directly recognize "out of context" components of the lipid membrane and how this recognition process then stimulates an appropriate immune response. The Tim proteins have been shown to play an integral role in both apoptotic cell recognition and immune regulation. However, despite the demonstrated immunological significance, little is known about the molecular basis for protein/membrane interaction in immune recognition. In large part this is due to the fact that the standard tools of structural immunology, such as x-ray crystallography, are not amenable to protein/lipid interactions. Utilizing x-ray surface scattering and advanced modeling techniques, we endeavor to unveil the structural basis for the recognition of phosphatidylserine containing membranes by each of the three Tim proteins. By comparing the molecular details of the membrane interaction for each of these three structurally similar but functionally diverse immune receptors, we can elucidate fundamental properties of immunogenic lipid membrane recognition. Do the Tims recognize the same PS exposing membrane but affect differing immune responses by binding with different affinities? Or are the Tims individually tuned to bind to 'different' types of PS exposing membranes? Answering these basic, but as yet unexplored questions regarding the nature of PS membrane recognition has the potential to significantly shift the paradigm with respect to our understanding of the protective strategies employed by our immune system.

WK4

Molecular Structure of Interfacial Human Meibum Film

Liat Rosenfeld[1], Danielle L. Leiske[1], Binhua Lin[2], Mati Meron[2], Michael F. Toney[3], and Gerald G. Fuller[1]

[1] Chemical Engineering Department, Stanford University, Stanford, CA 94305
[2] CARS, University of Chicago, IL 60637
[3] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Meibum is the primary component of the tear film lipid layer. Thought to play a role in tear film stabilization, understanding the physical properties of meibum and how they change with disease may be valuable in identifying dry eye treatment targets. Grazing incidence x-ray diffraction and x-ray reflectivity were applied to meibum films at an air-water interface to identify molecular organization. At room temperature, meibum films formed two coexisting phases with rectangular lattices and next-nearest neighbor tilts, similar to the Ov phase previously identified in fatty acids. The intensity of the diffraction peaks increased with compression, although the lattice spacing and molecular tilt did not change. Reflectivity measurements at surface pressures of 18 mN/m and above revealed multilayers with d-spacings of 50 Å, suggesting that vertical organization rather than lateral was predominantly affected by meibum-film compression.

WK4

Lipid Membranes from the Molecular- to Macro-scale

Erik Watkins[2], Jarek Majewski[3], and Chad Miller[4], and Tonya Kuhl[1]

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[2] Current address - LSS Group, Institut Laue-Langevin, Grenoble, 38042 France
[3] Manual Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, NM 87545
[4] Current address - Center for Advanced Molecular Photovoltaics, Stanford University and SLAC National Laboratory, Menlo Park, CA 94025

Over the past several decades, supported lipid bilayers have been used as model systems of cellular membranes, to investigate various membrane interactions, and as platforms for development of bio-sensors. Precise structural characterization by neutron and x-ray scattering offers a wealth of insight into membrane organization, self-assembly, and domain formation as well as how membranes respond to changes in their environment, e.g. temperature, protein binding, etc. In this talk, I will discuss some recent advances in our understanding of supported membranes, lateral domain formation, and a novel lipid phase due to specific-multivalent protein binding from grazing incidence diffraction measurements. There is great potential to expand these studies to follow dynamic rearrangements due to specific environmental cues.

1 Watkins, E.B., Miller, C.E., Majewski, J., and Kuhl T.L. "Membrane texture induced by specific protein binding and receptor clustering: active roles for lipids in cellular function" Proceedings of the National Academy of Science, 108 (17) 6975-6980 (2011).

2 Watkins, E.B., Miller, C.E., Mulder, D.J., Kuhl, T.L., and Majewski, J. "Structure and orientational texture of self-organizing lipid bilayers," Phys. Rev. Lett. 102(23) 4 pgs (2009).

WK4

Structural Characterization of Peptide-Polymer Conjugates toward Hybrid Biomolecular Materials

Ting Xu

Department of Materials Science and Engineering & Department of Chemistry, University of California, Berkeley, CA 94720

Peptides and proteins are hierarchically structured nanoscale assemblies with well-defined atomic-level structures. As materials, they possess structural and catalytic functionalities that are unmatched by any synthetic counterparts to date. Hybrid biomaterials based on synthetic polymers and natural building blocks have the potential to combine the advantages of both components and overcome the inherent limitations, such as the ease of degradation, loss of functionality, and difficulty in processing for biomolecules. With recent advances in our fundamental understanding of protein science, especially in designing peptide/protein sequences to achieve properties similar or superior to their natural counterparts and in developing synthetic methods to modify proteins in a controlled manner, these building blocks present numerous opportunities to create soft materials to meet current challenges in life science, energy, and environment.

To effectively combine these two families of disparate building blocks, careful structural control over multiple length scales is required. We synthesized a family of peptide-polymer conjugates based on a common protein tertiary structure, coiled-coil helix bundle to investigate the effect of architecture of peptide-polymer conjugate, the hydrophobicity of covalently linked polymers and the surrounding solvent media on the protein structure and binding pocket in the interior of coiled-coil. The phase behavior of peptide-polymer conjugates reflects a delicate balance between the protein-polymer-solvent interactions and conformational entropy of polymer chains. We also carried out structural characterization study of water soluble coiled-coil peptide-polymer conjugates in solution to experimentally determine the conformation of PEG around the helix bundle. The peptide-polymer conjugates were found to retain helix bundle structure, with the polymer slightly compressed in comparison to the conformation of free polymers in solution. Such detailed structural characterization of the peptide-polymer conjugates will help elucidate the effect of PEG on peptide structure and the conformation of PEG around the peptide. Present studies provide useful guidelines to design peptide-polymer conjugates and to direct their macroscopic assemblies toward functional biomaterial.

WK4

Lipid-mediated Assembly of Biomolecular Nano Objects at Liquid Interfaces

Masafumi Fukuto

Brookhaven National Laboratory, Upton, NY 11973

Key challenges in self-assembly of nanoscale objects include controlling the long-range order, exploiting the effects of anisotropy, and understanding the complex interplay between various types of interactions in aqueous media. To address these challenges, we investigate the 2D assembly of proteins and viruses on lipid monolayers at planar aqueous interfaces. Proteins and viruses are used as model particles, characterized by well-defined size, shape, and surface heterogeneities. The ability to tune their interactions through the lipid composition in the monolayer and the aqueous solution properties provides means to impose a specific particle orientation and control the 2D particle density. Taking advantages of these, we have recently carried out *in situ* x-ray reflectivity and grazing-incidence small-angle x-ray scattering studies to elucidate the mechanism of 2D crystallization for two types of particle-interface interactions, one based on specific protein-ligand binding and the other based on electrostatic interactions. Our results show that this assembly approach not only facilitates crystallization but also provides insights on the roles of particle orientations, density, and complex anisotropic interactions in generating long-range order.

WK4

High-energy X-ray vs. Neutron Reflectivity Probes of Structure an. Dynamics of Single Lipid:Protein Membranes at the Solid:Liquid Interface: A Progress Report

J.K. Blasie

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

High-energy x-ray and neutron reflectivity techniques, enhanced by interferometry, are capable of probing the structure and dynamics of ultrathin biomolecular films at the solid:liquid and liquid:liquid interfaces. Each has their distinct advantages as well as limitations. I will describe our work on voltage-gated ion channel proteins that can be vectorially-oriented within a single reconstituted phospholipid membrane at the solid:liquid interface with high in-plane density. Much of the structural and electrical characterization of these membranes has been accomplished, the most extensive concerning a prototypical voltage-sensor domain of a prokaryotic Kv-channel. Progress toward the investigation of the structural response of such proteins to step-wise changes in the transmembrane electrical potential directly related to their mechanism of voltage gating will be described.

Support: NIH P01-GM86685

WK4

Diffuse X-ray Scattering Provides More and Better Information for Fluctuating, Fully Hydrated Membranes than Traditional Diffraction Methods

John F. Nagle

Carnegie Mellon University, Pittsburgh, PA 15213

Conventional x-ray methods fail for the most biologically relevant, fluid, liquid-crystalline samples because interlamellar fluctuations of the second kind smear out the higher order diffraction peaks. However, the fluctuations produce copious diffuse scattering that contains much more information than in conventional diffraction peaks. Although much weaker than peak scattering, diffuse scattering intensity is easily measured using CCDs and synchrotron sources. By using oriented samples, we first obtain the membrane bending modulus K_C, the compression modulus B, and the stacking interference factor $S(\mathbf{q})$. Structure along the normal to the membranes is obtained from $I(\mathbf{q})/qS(\mathbf{q})=|F(q_z)|^2$, where data are obtained as a function of continuous q_z in the range 0.2–0.9Å^{-1} so the phases of the membrane form factor $F(q_z)$ are trivially obtained. These data are supplemented at smaller q_z with scattering from unilamellar vesicles and also by volumetric data and modeling that help to set the otherwise arbitrary scale factor.

Results have been published (see http://lipid.phys.cmu.edu) for pure lipid bilayers (DOPC, DMPC, DLPC, POPC, SOPC, DiC22PC, DPhyPC, DHPC) and for bilayers with additives (cholesterol, alamethicin, HIV fusion peptide, CRAC peptides, and, most recently, bioflavinoids [*J. Phys. Chem. B,* 116, #13]); a few of these results will be shown. When combined with simulations and neutron scattering, our x-ray results provide an in depth view of membrane structure. If time permits, a result will also be presented from a different type of x-ray study that improves the phase diagram of the canonical raft mixture DOPC/DPPC/Cholesterol (*Langmuir,* 26, 17363, 2010).

Research supported by Grant GM44976 from the U.S. National Institutes of Health.

WK4

Cholesterol Mediates Membrane Curvature during Fusion Events

David Gidalevitz

Department of Physics and Center for Molecular Study of Condensed Soft Matter (μCoSM), Illinois Institute of Technology, Chicago, IL 60616

Cellular membranes exhibit a broad spectrum of curvatures depending on the function they perform. Constituent and peripheral molecules can define membrane curvature in several ways: lipids of different molecular shape can distribute inhomogeneously within the bilayer, peripheral proteins with curved shapes can scaffold the membrane, or proteins can embed amphipathic domains shallowly into the lipid matrix. At the same time, the distribution of membrane constituent molecules and activity of bending proteins depend on curvature. The mechanism of this mechano-chemical interplay between lipids and proteins remains unclear.

The N-terminal fusion domain of glycoprotein gp41 is the only player of HIV-1 virus that directly interacts with the lipid bilayer of the host cell membrane and bends it via the insertion mechanism during virus entry. Membrane bending rigidity depends on cholesterol, i.e. membranes with higher cholesterol content require more energy to bend. Cholesterol affects the conformation of the gp41 fusion domain favoring a β-sheet structure over α-helix. In this talk, I will demonstrate, based on x-ray data, that cholesterol also regulates membrane penetration depth and occupied surface area of the gp41 fusion domain in model Langmuir monolayer systems and thus can control curvature in biological membranes. Altogether, our present and previous studies suggest a new mechanism of how lipids and proteins could regulate membrane curvature.

APS Workshop 5
Characterization of Materials for Sustainable Energy: Quantitative GIXS for Organic Photovoltaics

Location: *Bldg. 460 (Argonne Guest House), Conference Room A*

Organizers: Zhang Jiang, Joseph Strzalka, and Jin Wang (X-ray Science Division, APS)

Recent improvements in power conversion efficiency have brought organic photovoltaics (OPVs) nearly to the threshold for commercialization. Accelerating the progress in OPV technology requires an understanding of the interplay between morphology, processing conditions, and performance. Grazing-incidence x-ray scattering (GIXS), which can non-destructively probe the range of length scales required for OPVs, has provided much insight into the morphology of the organic photoactive materials. However, significant challenges remain including the application of GIXS to working devices, *in situ* characterization during processing, and extracting the most information possible from GIXS data. This workshop will focus on advances in sample preparation, sample environments, the application of appropriate complementary techniques, and, especially, GIXS analysis for the complete characterization of OPVs.

8:30 – 8:35	Welcome
8:35 – 9:10	Luping Yu (The University of Chicago) *Elucidating Structural Effect of Donor Polymers on Photovoltaic Solar Cells*
9:10 – 9:45	Michael F. Toney (SLAC National Accelerator Laboratory) *The Effect of Solvent and Thermal Annealing on the Nanoscale Morphology in Organic Photvoltaic Bulk Heterojunction Blends*
9:45 – 10:20	Jodi M. Szarko (Northwestern University) *Film Morphology Optimization in Copolymer Organic Photovoltaics*
10:20 – 10:40	Break
10:40 – 11:15	Edward J. Kramer (University of California, Santa Barbara) *Probing the Effects of Additives in Solvent Processing of Bulk Heterojunction Films with Grazing Incidence X-ray Scattering*
11:15 – 11:50	Seth B. Darling (Center for Nanoscale Materials, Argonne National Laboratory) *Rethinking the Idealized Morphology in Organic Photovoltaics*
11:50 – 12:25	Anna M. Hiszpanski (Princeton University) *Post-deposition Processing Methods to Tune Texture and Crystal Structure of Contorted Hexabenzocoronene for Field-effect Transistors*

WK5

Elucidating Structural Effect of Donor Polymers on Photovoltaic Solar Cells

Luping Yu

Department of Chemistry and The James Franck Institute, The University of Chicago, 929 E 57th St.,
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In this presentation, we will discuss the effect of molecular structural and solid structure of donor polymers on organic photovoltaic solar cells. Our recent results on investigation of low-bandgap polymers lead us to conclude that not only the energetics but also the internal dipole moment along the polymer chain is critical in facilitating charge transfer to PCBM, which were shown to be partially responsible for the high-PCE device made from these low-bandgap copolymers. Furthermore, solid state of the polymers plays a crucial role in facilitating solar cell conversion efficiency. The grazing-incidence small-angle x-ray scattering technique at ANL helped us to probe their detailed structural of bulk heterojunction polymer thin films.

WK5

The Effect of Solvent and Thermal Annealing on the Nanoscale Morphology in Organic Photvoltaic Bulk Heterojunction Blends

Michael F. Toney, Eric Verploegen, Chad Miller, Alex Ayzner, Kristin Schmidt, and Chris Tassone

Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

“Plastic” solar cells based on interpenetrating blends of a semiconducting polymer and a fullerene are becoming a viable technology for sustainable energy generation due to the promise of low-cost solution-based manufacturing. Both the nanoscale morphology of the two-phase film and the molecular packing within the polymer and fullerene are tremendously important to device performance. We have used grazing incidence x-ray scattering to probe the nanometer length scale microstructure and the molecular packing in organic solar cells. In this talk, I will describe *in-situ* results on how thermal and solvent annealing quantitatively affect the morphology and resulting device performance in blends of high performance polymers (including the widely studied poly(3-hexylthiophene or P3HT) and phenyl-butyric acid methyl ester (PCBM).

WK5

Film Morphology Optimization in Copolymer Organic Photovoltaics

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Our research focuses on correlations of nanoscale morphologies in organic photovoltaic (OPV) materials with fundamental processes relevant to photovoltaic functions such as light harvesting, exciton splitting, exciton diffusion, and charge separation (CS) and diffusion. Photovoltaic functions in organic materials are intimately connected to interfacial morphologies of molecular packing in films on the nanometer scale and molecular levels. Using grazing incidence x-ray scattering (GIXS) methods, we have investigated the domain size and orientation of several polymer and oligomer species. Using improvements made on beamline 8-ID-E, we could measure both the small- and wide-angle x-ray scattering of these materials in order to obtain the long- and short-range order in these films. The highest efficiency polymer we have investigated, **PTB7,** has domain sizes of less than 3 nm. These domain sizes were smaller than expected and required us to rethink the optimization parameters for such systems. The π–π stacking arrangement also shows a “side-on” orientation of the polymer chains, which is favorable for OPV function. These structural results suggest that there is an interplay between optimal π–π stacking for exciton diffusion and optimal PCBM intercalation for optimal electronhole separation. The degree of intercalation for the **PTB7** species is higher compared to benchmark homocyclic polymer materials such as **P3HT.**

WK5

Probing the Effects of Additives in Solvent Processing of Bulk Heterojunction Films with Grazing Incidence X-ray Scattering

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Solution processable, highly efficient organic photovoltaics typically consist of a two-component donor-acceptor type system composed of a low bandgap conjugated polymer donor blended with a fullerene acceptor. Efficient charge extraction from these blends demands that donor and acceptor components form nanoscale phase separated percolating pathways to their respective electrodes. Although post deposition thermal annealing has been shown to degrade device performance in low bandgap polymer systems, the incorporation of a small concentration of solvent additive (e.g., octanedithiol) into the solution from which a bulk heterojunction solar cell is cast has been shown to nearly double device efficiency without the need for subsequent thermal annealing. *In situ* grazing incidence wide-angle x-ray scattering measurements as a function of time after spin coating for films with and without additives suggest that the primary role of additives is to induce nucleation of polymer crystals during the film drying process. The overall morphology of polymer and fullerene in the optimized films can be probed in real space using energy filtered tomographic transmission electron microscopy and in reciprocal space using grazing incidence small-angle x-ray scattering. We show results for two different polymer/additive/fullerene systems and attempt to use these results to understand differences in device efficiency.

WK5

Rethinking the Idealized Morphology in Organic Photovoltaics

Seth Darling

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Traditionally, the ideal morphology for organic photovoltaic (OPV) active layers is viewed as a bicontinuous network of pure donors and acceptors with a periodicity comparable to the exciton diffusion length. We find that the active layer of high-performance OPV devices, in fact, involves hierarchical nanomorphologies ranging from several nanometers to hundreds of nanometers in size. These hierarchical nanomorphologies are coupled to significantly enhanced exciton dissociation indicating that the nanostructural characteristics at multiple length scales is one of the key factors determining the performance of polymer:fullerene systems.

WK5

Post-deposition Processing Methods to Tune Texture and Crystal Structure of Contorted Hexabenzocoronene for Field-effect Transistors

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The structure of organic electrically active thin films is known as a critical parameter in influencing the performance of devices comprising them. Controlling film structure, however, remains challenging, and generally requires stringent deposition conditions. To this end, we have developed post-deposition processing methods that induce different molecular orientations in contorted hexabenzocoronene (HBC) thin films. As-deposited, HBC thin films are amorphous; subjecting them to post-deposition processing, such as hexanes-vapor annealing, thermal annealing, and physical contact with elastomeric polydimethylsiloxane (PDMS), induces crystallization with increasing extents of preferential out-of-plane molecular orientation. Not surprisingly, field-effect transistors comprising post-deposition processed HBC films exhibit hole mobilities that vary depending on post-deposition treatment. With increasing extents of out-of-plane orientation, corresponding to greater degrees of π-stacking in the plane of the substrate, the mobilities derived from the field-effect transistors increase correspondingly. PDMS-crystallized HBC exhibit the greatest extent of in-plane π-stacking; mobilities of devices comprising such films are as high as $2*10^{-2}$ cm^2/Vs and are thus two orders of magnitude higher than the mobilities of devices comprising as-deposited HBC.

In addition to tuning the extent of out-of-plane molecular orientation with post-deposition processing methods, we can also access different polymorphs of HBC by tuning the solvent-molecule interactions during solvent-vapor annealing. Generally, HBC adopts a slip-stack packing motif. Annealing with more polar solvent vapors, however, decreases the slip-stack packing motif and instead increases the herringbone packing motif in HBC thin films. Interestingly, we can gain an additional level of tunability through fluorination of the peripheral aromatic rings of the parent HBC. With compounds having increased extents of fluorination, we retain the slip-stack packing motif even when these thin films are annealed with polar solvent vapors. The ability to tune both texture and crystal structure of HBC films independently and after film formation has yielded processing structure-function relationships that will guide the fabrication of field-effect transistors with improved device performance.

APS Workshop 6
APCF: Crystals, Robots, and X-rays

Location: *Bldg. 460 (Argonne Guest House), Conference Room A*

Organizers: Stephan Ginell and Andrzej Joachimiak (BIO Division, Argonne National Laboratory)

The workshop will review the most recent advances in structural biology, robotics, automation, and structure determination and their application to the Advanced Protein Crystallization Facility (APCF). The APCF will be a premier facility for research directed toward understanding the structure and function of proteins found in diverse biological systems. Synchrotron facilities, such as the Advanced Photon Source, with dedicated MX beamlines, robotics and automation, sophisticated software and computing resources have expanded our competence in determining protein structures. World-wide structural genomics efforts have contributed an array of rapid, integrated, cost effective methods in bioinformatics, molecular biology, proteomics and crystallization, and created efficient structure determination pipelines. The human genome sequencing efforts of a decade ago gave rise to the technology that currently allows genome sequences to be determined in days rather than years. Each genome sequence describes the predicted primary structure of thousands of proteins for each organism. Genome sequencing of environmental samples (referred to as "microbiomes" and "metagenomics") that contain hundreds or thousands of organisms allied in complex consortia is expanding rapidly and provide sequence information about these complex communities. Through such efforts millions of new proteins and protein complexes are being identified each year. Proteins are the molecular machines, working parts of all biological systems responsible for virtually everything cells do. In order to understand how biological systems perform, it is essential to understand how each protein works and how it interacts with other cellular components under normal and disease states. Structural genomics uses the ever-growing body of genome sequence knowledge that infers protein primary structure from genomic data, together with a novel and integrated set of molecular biology and chemistry technologies, to determine the three-dimensional structure of gene products with the aspiration of characterizing all possible protein structures.

Major bottlenecks in the structure determination process are: the production of high quality proteins and diffraction quality single crystals. The APCF will address these bottlenecks by combining highly automated laboratories together with computational support. The APCF will include the bioinformatics, molecular and structural biology capabilities to:

1. Analyze a genomic sequence and other data to identify proteins for structural studies,
2. Clone and express proteins and protein/protein complexes of microbial and eukaryotic origin,
3. Purify, characterize and crystallize proteins,
4. Deliver crystals to X-ray beams robots and novel techniques,
5. Collect data and solve structures,
6. Analyze structures for fold and function assignment,
7. Confirm function experimentally, and
8. Engineer proteins for new applications.

The APCF will automate the whole process from cloning of protein-encoding genes, production and purification of proteins, protein crystallization, crystal harvesting and delivery, rapid identification of diffraction quality crystals, collection and analysis of crystallographic data, and interpretation of the X-ray patterns collected there to the validation of protein function using both structural and biochemical data. The co-location of all of these capabilities will be a unique feature of the APCF. By taking full advantage of X-ray diffraction capabilities of the highly productive MX beamlines at the APS, the APCF will increase the overall efficiency of protein crystallography. The challenges, the possible solutions and potential future advances will be presented and discussed during the Workshop.

The APCF will provide Illinois with unique capabilities in biological, biomedical, bioenvironmental and biotechnology research and will advance the education through the user facility component of the APCF which will provide training in advanced protein chemistry methods in collaboration.

1:30 – 2:00	Victor Cardona (SmithGroupJJR) *Creating Research-centered Environments for the National Laboratories...Over Three Decades and One Building at a Time!*
2:00 – 2:30	Andrzej Joachimiak (Argonne National Laboratory) *From Genes to Structures Using Synchrotron Radiation*
2:30 – 3:00	Conn Mallett (Rigaku Automation, Inc.) *Developments in High-throughput Crystallization*
3:00 – 3:30	Break
3:30 – 4:00	Petra Fromme (Arizona State University) *Femtosecond Nanocrystallography Opens New Era for Structure Determination*
4:00 – 4:30	Bernhard Rupp (k-k. Hofkristallamt) *Making Robotic Protein Crystal Harvesting Work: Improvements in Cryo-protection and Controlled Hyper-quenching*
4:30 – 5:00	Garth Simpson (Purdue University) *Towards Automated Protein Crystal Detection and Centering by Nonlinear Optical Imaging*

WK6

Creating Research-centered Environments for the National Laboratories… Over Two Decades and One Building at a Time!

Victor J. Cardona

AIA NCARB, Vice President SmithGroupJJR

SmithGroupJJR has been planning and designing research environments for the national laboratories for the last three decades. We have seen the planning and design of these facilities evolve. What lessons can we take from this evolution and what can we apply for the future? Before we can answer that, we need to look at the following questions:

- Is the planning and design of research buildings in the national laboratories keeping pace with the trends that we observe in academic and corporate lab environments?
- How have research-centered environments evolved in the last decade? Which ones are valid today?
- What research-centered concepts have we applied to the planning and design in buildings at the national laboratories over the last few decades and which ones are valid today?

In this presentation, I will explore the following laboratory planning concepts:

- *Planning Concepts* – modular, flexible, adaptable, expandable, serviceable, sustainable, energy efficient…
- *Cultural / Community Ideas* – multidisciplinary, interdisciplinary, collaborative, interactive, integrated, sociable…
- *Scientific Needs* – technological requirements (air, temperature, humidity, vibration, power, data, redundancy, etc). , space requirements (low bay, high bay, etc.), process flow, efficiency, safety, demonstration, showcase…

Utilizing eight, selected examples of projects designed for the national laboratories during the last two decades, we will explore the evolution of these concepts and culminate with the planning and design of Argonne's Advanced Protein Crystallization Facility.

Examples of national laboratory projects to be studied include:

- Los Alamos National Laboratory, Materials Science Laboratory, 1993.
- Sandia National Laboratories, Technology Support Center, 1995.
- National Renewable Energy Laboratory, Science + Technology Facility, 2006.
- Lawrence Berkley National Laboratory, Molecular Foundry, 2006.
- National Renewable Energy Laboratory, Energy Systems Integration Facility, 2012.
- National Institutes of Science and Technology, Boulder's Radio Building Renovation, 2012+.
- Argonne National Laboratory, Advanced Protein Crystallization Facility, 2014 (est.).

Takeaways from this session will be:

- Evolution of laboratory planning and design.
- Lesson learned from the past – what can we apply for the future.
- Beyond the lab space – what other spaces are included in research-centered environments.
- Showcasing your lab – advantages and pitfalls.

WK6

From Genes to Structures Using Synchrotron Radiation

Andrzej Joachimiak

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The Center for Structural Genomics of Infectious Diseases, Computational Institute,
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Advances in structural biology, including new synchrotron facilities with dedicated PX beamlines and sophisticated software and computing resources, have expanded our competence in determining protein structures. Genome sequencing projects rapidly enlarge the protein sequence families and allow for comprehensive approaches to the studies of entire complex cellular systems. Worldwide structural genomics efforts have contributed a complementary array of rapid, integrated, cost-effective methods in bioinformatics, molecular biology, proteomics, and crystallization, and have created efficient structure determination pipelines. The semi-automated pipelines of the Midwest Center for Structural Genomics (MCSG) and Center for Structural Genomics of Infectious Diseases (CSGID) comprise all components needed for rapid structure solution (i. analyzing a genomic sequence to establish a prioritized protein target set, ii. cloning and expressing proteins and protein/protein complexes of microbial and eukaryotic origin, iii. purifying and crystallizing proteins, iv. collecting data using synchrotron radiation and solving structures,

v. analyzing structures for fold and function assignment, and vi. homology modeling of related proteins). These pipelines have allowed these structural genomics centers to determine nearly 2,000 protein structures, most of which are annotated for function and ligand binding, and many are known or potential drug targets. Homology models are generated and will ultimately provide good structural coverage of major protein families. Results, data, and materials are made available to the scientific community. Important trends have emerged from this research: very distant protein sequence families share the same fold, and proteins with similar structural scaffolds have evolved many different functions. Structural genomics continues to contribute to an understanding of molecular mechanisms and plays a significant role in the discovery of the evolutionary and functional relationships among protein families that are often not apparent from their sequences. This research provides a wealth of ideas, concepts and understanding of the mechanisms for the acquisition of novel biological functions and the evolution of biological systems. The impact of synchrotron radiation and co-localization of structural genomics pipelines with synchrotron facilities on structural biology and potential future advances will be discussed.

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WK6

Developments in High-throughput Crystallization

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The field of macromolecular structural biology has witnessed major technological advances in x-ray crystallography over the past decade. These developments have significantly increased the resolution, speed, and quality of data collection and structure determination. Many of these technologies specifically address bottlenecks in the complex process of protein crystallography, such as the development of automated high-throughput crystallization platforms that greatly increase the efficiency of the screening process. In combination with the increased availability and automation level of synchrotron and other x-ray home sources, these advances have dramatically increased the likelihood of success and are facilitating explorations into more complex and challenging structural biology projects. Rigaku Automation continues to be a major player in addressing these technological challenges as world leader in automation technology that facilitates the crystallization process and serves the protein crystallography community. In this presentation, we will review each step of the crystallization process and how Rigaku products were developed to match the needs, increase productivity, and enhance throughput. In particular, we will cover crystallization data management, ease-of-use in crystallization optimization, UV technology to detect protein crystals, and the fully integrated crystallization platform for high throughput crystallization. Scientific validation data will be presented for each technology that we developed over the years. The ongoing strategic partnership with the Joint Center of Structural Genomics (JCSG) at The Scripps Research Institute has enabled us to develop and fully test our systems in a high throughput "real world" environment. Our flagship CrystalMation system, a fully integrated high throughput crystallization platform, has been in production for over five years at JCSG. The results and benefits of CrystalMation system to the research at JCSG will be discussed.

WK6

Femtosecond Nanocrystallography Opens New Era for Structure Determination

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Femtosecond nanocrystallography provides a novel concept for structure determination, where x-ray diffraction "snapshots" are collected from a fully hydrated stream of nanocrystals using femtosecond pulses from the world's first high-energy x-ray free-electron laser, the Linac Coherent Light Source. Photosystem I, which is the most complex membrane that has been crystallized to date, consisting of 36 proteins and 381 cofactors, was used as the model system. The experiments show the proof of concept that diffraction of nanocrystals that contain only 100–10,000 Photosytem I molecules can be observed using femtosecond pulses that are 10^{12} stronger than 3rd generation synchrotron sources and destroy any material that is placed in its focus. Over three million diffraction patterns from individual nanocrystals (100 nm–2 μm in size) were collected and evaluated [1]. By using femtosecond pulses briefer than the time scale of most damage processes, femtosecond nanocrystallography overcomes the problem of x -ray damage in crystallography. Data collected at the new CXI LCLS beamline at higher energy (8 keV) showed that the concept of femtosecond crystallography extends to atomic resolution. Data will be presented that show that nanocrystals of membrane proteins, which are notoriously difficult to crystallize, have extremely low mosaicity. Femtosecond crystallography also opens a new avenue for determination of protein dynamics. First experiments on time-resolved x-ray crystallography have been performed on Photosystem I-ferredoxin and Photosystem II nanocrystals. The first results are very promising and pave the way for a new avenue in x-ray crystallography that may allow the determination of molecular movies of the dynamics of membrane proteins "at work" in the future.

[1] H.N Chapman, P. Fromme, A. Barty, T.A. White, R.A. Kirian, A. Aquila, M.S. Hunter, J. Schulz, D.P. DePonte, U. Weierstall, R.B. Doak, F.R.N.C. Maia, A.V. Martin, I. Schlichting, L. Lomb, N. Coppola, R.L. Shoeman, S.W. Epp, R. Hartmann, D. Rolles, A. Rudenko, L. Foucar, N. Kimmel, G. Weidenspointner, P. Holl, M. Liang, M. Barthelmess, C. Caleman, S. Boutet, M.J. Bogan, J. Krzywinski, C. Bostedt, S. Bajt, L. Gumprecht, B. Rudek, B. Erk, C. Schmidt, A. Hömke, C. Reich, D. Pietschner, L. Strüder, G. Hauser, H. Gorke, J. Ullrich, S. Herrmann, G. Schaller, F. Schopper, H. Soltau, K.-U. Kühnel, M. Messerschmidt, J.D. Bozek, S.P. Hau-Riege, M. Frank, C.Y. Hampton, R.G. Sierra, D. Starodub, G.J. Williams, J. Hajdu, N. Timneanu, M.M. Seibert, J. Andreasson, A. Rocker, O. Jönsson, M. Svenda, S. Stern, K. Nass, R. Andritschke, C.-D. Schröter, F. Krasniqi, M. Bott, K.E. Schmidt, X. Wang, I. Grotjohann, J.M. Holton, T.R.M. Barends, R. Neutze, S. Marchesini, R. Fromme, S. Schorb, D. Rupp, M. Adolph, T. Gorkhover, I. Andersson, H. Hirsemann, G. Potdevin, H. Graafsma, B. Nilsson, and J.C.H. Spence, "Femtosecond x-ray protein nanocrystallography," Nature, 470, 73–77.

Experiments were carried out at the Linac Coherent Light Source and the Advanced Light Source, operated by Stanford University and the University of California (respectively) on behalf of the U.S. Department of Energy (DOE), Office of Basic Energy Sciences. We acknowledge support from DOE through the PULSE Institute at the SLAC National Accelerator Laboratory and by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, the National Institute of Health (award 1R01GM095583-01), the National Science Foundation (awards 0417142 and 1021557), the Helmholtz Association, the Max Planck Society for funding the development and operation of the CAMP instrument, P.F. was partially supported by the Center for Bio-Inspired Solar Fuel Production, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001016.

WK6

Making Robotic Protein Crystal Harvesting Work: Improvements in Cryo-protection and Controlled Hyper-quenching

Bernhard Rupp[1] and Marc C. Deller[2]

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The beta-test unit of the Square One Systems Design Universal Micromanipulation Robot (UMR) capable of semi-autonomous, protein crystal harvesting was installed a year ago at the high throughput protein crystallography facility of the Joint Center for Structural Genomics (JCSG). During extensive demonstrations and user evaluations, the viability of the concept of robotic harvesting of single crystals has been validated. Beyond the initial conversion of manual harvesting procedures into robotic processes, a number of unique developments and generally applicable technologies have evolved. Tape cutting and resealing has been simplified and improved, and an automated cryo-protection procedure has been developed that combines low-viscosity oil cryo-protection with hyper-quenching directly into the shipping cassettes. At present, the focus is on the development of novel procedures for reliable, consistent, and generally applicable cryo-procedures in order to enable a better understanding of the underlying science and to reduce rate of expensive late-stage failures during cryo-protection and hyper-quenching. Further developments are under way to integrate automated diffraction screening of harvested crystals to permit systematic optimization of cryo-protection and cryo-cooling procedures. The ultimate goal of this robotic harvesting project is a fully autonomous system where real-time crystal localization can directly interface with UMR controls and feedback. The crystal harvesting system offers several advantages over typical manual manipulations, especially for smaller crystals and though remote operation at lower temperatures, in controlled or inert atmosphere, or in high-level biohazard environments. We envision the UMR as a versatile and open toolbox for novel techniques providing new scientific opportunities in emerging crystallization technologies. .

Inertial development of the UMR was sponsored by NIH STTR Phase II Grant No. 2 R42 GM073278-02A1.

WK6

Towards Automated Protein Crystal Detection and Centering by Nonlinear Optical Imaging

Garth J. Simpson

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Reliable, high-contrast protein crystal detection remains a major bottleneck in high-throughput approaches for crystallization screening and in automated crystal diffraction at synchrotron sources. SONICC (second order nonlinear optical imaging of chiral crystals) and TPE-UVF (two-photon excited UV fluorescence) are proposed as new contrast mechanisms for protein crystal detection. SONICC is based on second harmonic generation (SHG), or the frequency doubling of light, which is symmetry forbidden in disordered systems but allowed in the large majority of protein crystals. TPE-UVF provides contrast based on an independent mechanism similar to conventional UV fluorescence imaging, but with much lower diffuse background and no substantial loss of image quality in highly scattering media. The fundamental principles of these complementary techniques will be discussed. Applications of SONICC and TPE-UVF for high-throughput protein crystal screening in 96-well plates will be critically assessed. In addition, an overview will be given of progress toward development of automated instrumentation for routine crystal positioning at a synchrotron source by combined SONICC and TPE-UVF.

CNM Workshop 7
NanoBio Interfaces: From Materials Design to Complex Systems

Location: *Bldg. 401, Room A5000*

Organizer: Elena Rozhkova and Chris Fry (Center for Nanoscale Materials)

Nature possesses the ability to design highly functioning, regenerative materials that cover every imaginable process and physical characteristic desired in modern materials. Energy production and storage, mechanics, and catalysis are but a few of these processes that nature handles well. It is therefore no surprise that attempts abound to utilize nature, either directly or through 'inspiration', for developing new and useful materials. One example to be presented in this workshop is electronic materials derived from and inspired by light-harvesting proteins. Biological self-assembly is a phenomenon often exploited in order to incorporate high levels of organization leading to higher functionality. In order to generate more efficient, robust, and novel functionality, biological systems are often interfaced with nanomaterials (e.g., metallic or metal-oxide nanoparticles). The nanomaterials can serve as a switch, whether driven by light, magnetism, or charge separation, to drive the functionality of the material. Furthermore, coupling nanomaterials to biomolecules has led to biosensing applications that have dramatically enhanced the sensitivity of early stage disease detection. Here, the nanomaterial possesses the sensing role and the biomolecule is used specifically for detection/targeted binding. This workshop will help identify many overlapping themes at the NanoBio interface that continue to produce a wide spectrum of materials attributing their functional inspiration from nature.

8:45 – 9:00	Welcome and Introductory Remarks
9:00 – 9:40	Ana Moore (Arizona State University) *The Photoanode of Photoelectrochemical Cells for the Splitting of Water and Production of Fuel*
9:40 – 10:00	Shankar Balasubramanian (Center for Nanoscale Materials) *Bacteriorhodopsin-modified* TiO_2 *Photocatalyst for Solar Hydrogen Generation*
10:00 – 10:30	Break
10:30 – 11:10	J.D. Tovar (Johns Hopkins University) *Supramolecular Bioelectronic Nanostructures Derived from the Self-assembly of Pi-conjugated Peptides*
11:10 – 11:50	Matthew Tirrell (University of Chicago/Argonne National Laboratory) *Multivalent Ionic Interactions in Multicomponent Polyelectrolyte Mixtures: From New Physics to New Materials*
11:50 – 1:30	Lunch
1:30 – 2:10	Milana Vasude (Wright Patterson Airforce Base) *Peptides Interfaces for Assembly of Materials*
2:10 – 2:50	Jared Lewis (University of Chicago) *Artificial Metalloenzymes for Adaptive Transition Metal Catalysis*
2:50 – 3:20	Break

3:20 – 4:00	Caroline Ajo-Franklin (Lawrence Berkeley Labs – Molecular Foundry) *Engineering Nanoscale Biological-to-Electrical Adapters for Electronic Communication Betweeen Living and Non-living Systems*
4:00 – 4:40	Milan Mrksich (Northwestern University) *Controlling Cell Function with Nanopatterned Substrates*
4:40 – 4:50	Closing Remarks

WK7

The Photoanode of Photoelectrochemical Cells for the Splitting of Water and Production of Fuel

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The design of bio-inspired schemes that couple solar energy conversion to the oxidation of water and the subsequent use of the reducing equivalents to synthesize energy-rich compounds such as hydrogen or fuels based on reduced carbon is the main objective of our present research [1, 2]. In order to establish the design principles for a tandem, two-junction (or threshold) photochemical cell, we are assembling Grätzel-type photoelectrodes that model aspects of photosystems I and II (PSI and PSII) of plants. The photoanode model of PSII contains a mimic of the donor side (water oxidizing side) of PSII reaction centers. In PSII, tyrosine Z (TyrZ) mediates charge transport between the photo-oxidized primary donor (P680$^{\bullet+}$) and the oxygen-evolving complex (OEC). The oxidation of TyrZ by P680$^{\bullet+}$ likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190). This coupling of proton and redox chemistry is thought to poise the TyrZ oxidation potential between those of P680$^{\bullet+}$ and the OEC. We have prepared several bioinspired systems (BiP-PF$_{10}$) consisting of a high oxidation potential porphyrin (PF$_{10}^{\bullet+}$/PF$_{10.}$ 1.59 V vs. NHE, a model of P680) that is covalently attached to different benzimidazole-phenol pairs (BiP) that mimic the TyrZHis190 pair in PSII. Electrochemical studies show that the phenoxyl radical/phenol couple of the model system is chemically reversible with a midpoint potential of 1.24 V vs. NHE and is therefore thermodynamically capable of water oxidation in conjunction with the appropriate catalyst. When BiP-PF$_{10}$ constructs are attached to metal oxide nanoparticles and excited with visible light, they undergo photoinduced electron transfer. In some of the constructs electrons are injected into the semiconducting oxide and the corresponding holes are localized in the phenol. EPR provides a clear spectroscopic picture of these processes [3]. Transient absorption studies of triads containing electron acceptors such as tetracyano porphyrins to replace the semiconductor are being used to characterize the kinetic parameters of the multistep electron transfer process.

[1] M. Hambourger, G.F. Moore, D.M. Kramer, D. Gust, A.L. Moore and T.A. Moore, *Chemical Society Reviews,* **38,** (2009) 25–35.

[2] D. Gust, T.A. Moore and A.L. Moore, *Acc. Chem. Res.,* **42,** (2009) 1890–1898.

[3] G.F. Moore, M. Hambourger, M. Gervaldo, O. G. Poluektov, T. Rajh, D. Gust, T.A. Moore and A.L. Moore, *J. Am. Chem. Soc.,* **130,** (2008) 10466–10467.

WK7

Bacteriorhodopsin-modified TiO_2 Photocatalyst for Solar Hydrogen Generation

Shankar Balasubramanian, Tijana Rajh, and Elena A. Rozhkova

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Photocatalysis remains one of the efficient ways to capture solar energy on a large scale. Here, I discuss on the application of light harvesting proton pumps such as bacteriorhodopsin for solar hydrogen generation. Bacteriorhodopsin (bR) molecules are visible light-driven proton pumps found in halobacteria. bR molecules are naturally evolved to be stable under demanding conditions such as high salinity (3-M NaCl), temperature over 80 °C (in water) and 140 °C in dry condition as well in wide pH range (5–11) without losing photochemical activity. In Nature, bR molecules capture visible light (560 nm) and pump protons across the cell membrane driving the ATP synthesis. Such wild-type bR protein molecules were self-assembled on to Pt/TiO_2 photocatalyst for H_2 generation activity under green light illumination and an efficiency of the hybrid system was characterized by gas chromatography. H_2 generation was detected both in the presence of electron donor triethanolamine (TEOA) under green light illumination and when no electron donors were added (under white light illumination). Several factors such as the nature of the electron donor molecules and the stability were studied. Photoelectrochemical measurements under green light illumination show a four-times increased current density in the presence of bR on TiO_2 electrodes. Such enhancement in current density points to a favorable band alignment of molecular orbitals of bR with TiO_2 band edge. In addition, transient absorption studies indicate a possible charge transfer between bR protein molecules and TiO_2 nanoparticle thus extending the visible light activity of the photocatalyst. Hence, a bio-nanocomposite containing a visible light harvesting protein (bR) and a semiconductor photocatalyst is very promising for solar hydrogen generation. Such a system might overcome the limited stability of other photocatalytic systems based on hydrogenases and chlorophyll-based photosystem for H_2 generation.

WK7

Supramolecular Bioelectronic Nanostructures Derived from the Self-assembly of Pi-conjugated Peptides

Brian D. Wall[1], Stephen R. Diegelmann[1, 3], Allix M. Sanders[1], and J.D. Tovar[1, 2, 3]

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Peptide-based nanomaterials have attracted increasing attention in both biomedical and energy sciences. Supramolecular interactions can be engineered within peptide frameworks to encourage the self-association of molecular components into discrete nanostructures, and peptide residues can be chosen to control solubility or biological interaction. The design of electronically relevant biomaterials capable of energy migration and interaction with the biotic interface would be the first step towards the transduction of artificial and natural energy currencies for harvesting or transport. This talk will describe our efforts to synthesize and understand pi-conjugated self-assembling peptides that form one-dimensional electronically delocalized materials under completely aqueous conditions. Prospects for tissue engineering applications will be addressed.

1 S.R. Diegelmann, J.M. Gorham and J.D. Tovar, "One-dimensional optoelectronic nanostructures derived from the aqueous self-assembly of π-conjugated oligopeptides," in the Journal of the American Chemical Society, 2008 (130) 13840-13841.

2 G.S. Vadehra, B.D. Wall, S.R. Diegelmann and J.D. Tovar, "On-resin dimerization incorporates a diverse array of pi-conjugated functionality within aqueous self-assembling peptide backbones," in Chemical Communications, 2010 (46) 3947-3949.

3 B.D. Wall, S.R. Diegelmann, S. Zhang, T.J. Dawidczyk, W.L. Wilson, H.E. Katz, H.-Q. Mao and J.D. Tovar, "Aligned macroscopic domains of optoelectronic nanostructures prepared via the shear flow assembly of peptide hydrogels," cover article in Advanced Materials, 2011 (23) 5009-5014.

4 S.R. Diegelmann, N. Hartman, N. Markovic and J.D. Tovar, "Synthesis and alignment of discrete polydiacetylene-peptide nanostructures," in the Journal of the American Chemical Society, 2012 (134) 2028-2031.

WK7

Multivalent Ionic Interactions in Multicomponent Polyelectrolyte Mixtures: From New Physics to New Materials

Matthew Tirrell
Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637

Highly charged polymer chains in monovalent salt media exhibit a fairly simple range of behaviors, swelling in low salt, shrinking in high salt, based on the screening of repulsive electrostatic interactions among the segments. In the presence of other multivalent constituents, attractive forces arise. These attractions produce strong collapse of polyelectrolyte chains, adhesion between polyelectrolyte bearing surfaces, precipitation, and in the case of mixtures of oppositely charged polyelectrolytes, formation of fluid complex coacervate phases. We have measured the attractive forces between layers of polyelectrolyte brushes immersed in multivalent ionic media as a function of ionic strength. We have characterized coacervate formation in mixtures of model polyelectrolytes. We demonstrate how coacervate formation can be used to create new self-assembled materials, such as physically crosslinked hydrogels.

WK7

Peptides Interfaces for Assembly of Materials

Rajesh R. Naik
Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433

Biological systems exemplify the utilization of highly specific recognition processes with a diverse set of building blocks for the synthesis and assembly of precisely defined materials. Peptides, an example of building blocks, are appealing for synthesis and as templates, across multiple length scales, for creating hierarchically assembled materials and structures. Our research activities are aimed at the fundamental understanding of how biomolecules interact with abiotic surfaces, and how they can be used in the creation of functional materials. In this talk, I will describe some our recent work on understanding peptide interactions with materials using both experimental and modeling tools with "model materials" and highlight some unexpected properties that arise due to the biotic-abiotic interactions.

WK7

Artificial Metalloenzymes for Adaptive Transition Metal Catalysis

Jared Lewis
Department of Chemistry, University of Chicago, Chicago, IL 60637

Controlling the selectivity of chemical reactions and conducting these reactions in biological systems, where they could have a transformative impact, stand as key challenges in synthetic chemistry. Artificial metalloenzymes (ArMs) could achieve these goals by combining the reactivity of synthetic metal catalysts and the adaptability and efficiency of enzymes. New approaches for the development of ArMs generated from protein or enzyme scaffolds and metal catalysts bearing reactive anchoring groups will be discussed. The impact of scaffold control on reaction selectivity, approaches to evolve this selectivity, and potential tandem reaction sequences using ArMs and other engineered enzymes will be described.

WK7

Engineering Nanoscale Biological-to-Electrical Adapters for Electronic Communication Betweeen Living and Non-living Systems

Caroline M. Ajo-Franklin

The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The field of synthetic biology aims to design biological systems to perform tasks to better understand analogous natural systems and for a wide range of applications. My laboratory is particularly interested in manipulating processes at the interface between living cells and inorganic materials. In my talk, I will discuss our efforts to engineer bi-directional electronic communication between living cells and non-living systems. We have recently demonstrated that by transplanting synthetic genes into the model organism *Escherichia coli* we can confer upon these cells the ability to reduce metal ions, solid metal oxides, and electrodes. This work provides the first example of a predetermined, molecularly defined route for biological-to-electronic adapter between living cells to non-living materials. Ultimately we seek to exert such control over electron transfer between living cells and inorganic materials that we can develop new technologies based on programmable, self-replicating cellular electronics.

WK7

Controlling Cell Function with Nanopatterned Substrates

Milan Mrksich

Howard Hughes Medical Institute, Northwestern University, Evanston, IL 60208

This presentation will describe the use of patterned substrates to control cell shape with examples that illustrate the ways in which cell shape can regulate cell function. Most cells are adherent and must attach to and spread on a surface in order to survive, proliferate and function. In tissue, this surface is the extracellular matrix, an insoluble scaffold formed by the assembly of several large proteins—including fibronectin, the laminins and collagens and others—but in the laboratory, the surface is prepared by adsorbing protein to glass slides. To pattern cells, gold-coated slides are patterned with microcontact printing to create geometric features that promote cell attachment and that are surrounded by inert regions. Cells attach to these substrates and spread to adopt the shape defined by the underlying pattern and remain stable in culture for several days. Examples will be described that used a series of shapes to reveal the relationship between the shape of the cell and the structure of its cytoskeleton. These geometric cues were used to control cell polarity and the tension, or contractility, present in the cytoskeleton. These rules were further used to control the shapes of mesenchymal stem cells and in turn to control the differentiation of these cells into specialized cell types. For example, stem cells that were patterned into a 'star' shape preferentially differentiated into bone cells whereas those that were patterned into a 'flower' shape preferred a fat cell fate. These influences of shape on differentiation depend on the mechanical properties of the cytoskeleton. These examples, and others, reveal that shape is an important cue that informs cell function and that can be combined with the more common soluble cues to direct and study cell function.

EMC Workshop 8

In situ and Environmental Science: How Can Electron Microscopy and Spectroscopy Help?

Location: *Bldg. 402, Room E1100*

Organizers: Charudatta Phatak (MSD, Argonne National Laboratory)
and Drew Latta (BIO, Argonne National Laboratory)

Among the many scientific challenges in the research of complex systems is the direct observation and visualization of fundamental processes that govern the behavior of these systems at near atomic to micro length scales. This workshop will focus on *in situ* science, enabled by the use of advanced techniques in electron microscopy and spectroscopy. This session will include areas such as (but not limited to) transformations; processes and interfacial dynamics under various environments; and *in situ* analysis of materials at extremes, including deformation, temperature, and irradiation.

8:45 – 9:00	Introductuctory Remarks
9:00 – 9:30	Mitra Taheri (Drexel University) *Application of* In Situ *TEM Methods to “Real” Devices and Structures: Challenges and Opportunities*
9:30 – 10:00	Gregory Vetterick (Drexel University) In-situ *Observations of Fundamental Radiation Tolerance Mechanisms in Nanocrystalline Iron*
10:00 – 10:30	Carlos Alvarez (Northwestern University) *Study of the Evolution of Nanoparticle Crystallization in Glass Ceramics*
10:30 – 10:50	Coffee Break
10:50 – 11:30	Peter Crozier (Arizona State University) In Situ *and* Operando *Transmission Electron Microscopy of Catalysts*
11:30 – 12:00	Jungwon Park (University of California, Berkeley) In-situ *Study of Colloidal Nanoparticles in Atomic Resolution by Using Graphene Liquid Cells*
12:00 – 1:30	Lunch
1:30 – 2:00	Joseph Conny (NIST) *Determining the Chemical Structure of Individual Atmospheric Particles with Scanning Electron Microanalysis*
2:00 – 2:30	E. O’Loughlin (Argonne National Laboratory) *Microbial Transformations of Fe(III) Oxides: Characterization and Reactivity of Biogenic Fe(III) Minerals*
2:30 – 3:00	Drew Latta (BIO, Argonne National Laboratory) *Observation of Metal Reducing Bacteria on Iron Oxide Thin-films Using* **In-situ** *Environmental SEM*
3:00 – 3:20	Coffee Break

3:20 – 3:50	Haiping Li (U.S. Food and Drug Administration) *Pathogen Internalization and Fresh Produce Safety*
3:50 – 4:20	Philipp Heck (Field Museum of Natural History) *Laboratory Analysis of Extraterrestrial Dust*
4:20 – 4:40	EMC User's Meeting & Conclusion

WK8

Application of *In Situ* TEM Methods to "Real" Devices and Structures: Challenges and Opportunities

Mitra L. Taheri

Drexel University, Department of Materials Science & Engineering, Philadelphia, PA 19104

In situ TEM techniques have improved considerably in recent years with respect to their ability to understand materials behavior with high temporal and spatial resolution. While significant advances have been made in elucidating atomic-scale mechanisms that control properties of materials for a wide range of applications, geometric compromises made to accommodate *in situ* TEM experiments could play a detrimental role in the ability to apply data to "real-life" structures or devices. This talk examines the interplay between the need to mimic a true application and the need to access microstructural features at the nanoscale. Case studies of high electron mobility transistors, ferroelectric memory devices, and alloys for energy applications will be reviewed. Finally, opportunities to combine recent *in situ* TEM stages and various forms aberration correction will be discussed as a path forward.

WK8

In-situ Observations of Fundamental Radiation Tolerance Mechanisms in Nanocrystalline Iron

G. Vetterick[1], C. Barr[1], J.K. Baldwin[2], K. Hattar[3], M. Kirk[4], A. Misra[2], R. Unocic[5], and M.L. Taheri[1]

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[4] IVEM-Tandem Facility, Argonne National Laboratory, Argonne, IL 60439
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Radiation damage phenomena in metallic alloys are driven by the formation and subsequent diffusion of individual point defects and defect clusters (e.g., dislocation loops). Traditionally, studies of point defect kinetics are performed in low dislocation density, large-grained pure iron. As a result, there is limited knowledge of the effect of individual microstructural features such as line dislocations, voids, and grain boundaries on radiation damage. Models in nanocrystalline iron with high volume fractions of interfaces have shown a strong influence of grain size on primary damage production, including reduced interstitial survival and clustering and excess vacancy production. However, the use of molecular dynamic simulations limits the solution to primary defect movement after the primary cascade event, excluding the effects of diffusion. The facilities at Argonne National Laboratory permit the observation of grain boundary sink effects on point defect cluster kinetics on time scales not obtainable by models. Using the Hitachi H-9000NAR TEM in the IVEM Tandem facility, a study of the aggregation of point defect clusters as a function of grain size in nanocrystalline iron, which can be used to obtain fundamental information about the kinetics of point defects under irradiation.

WK8

Study of the Evolution of Nanoparticle Crystallization in Glass Ceramics

Carlos Alvarez[1], Yuzi Liu[2], Jacqueline Johnson[3], and Amanda Petford-Long[2]

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[3] Materials Science and Engineering Department, University of Tennessee Space Institute, Tullahoma, TN 37388

Fluorochlorozirconate (FCZ) glasses are a class of material being developed for uses in advance mammography systems [1]. The FCZ of interest have been doped with Eu (II) for use as a either scintillator or storage phosphor material in these systems. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu^{2+} present in the $BaCl_2$ nanocrystals. The nanocrystals nucleate and grow throughout the glass matrix from annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The crystals formed are known from x-ray diffraction experiments to be hexagonal and orthorhombic $BaCl_2$ depending on the annealing temperature, 265˚C and 295˚C, respectively [2]. *In-situ* and *ex-situ* transmission electron microscopy (TEM) experiments were used to study the nucleation and growth process of the nanocrystals. Through the TEM investigations of FCZ glass, previously unreported phases of crystalline BaF_2 in face-centered cubic and orthorhombic have been found. These phases have been found in multiple compositions which vary the content of Cl and F. This indicates that annealing produces both polymorphic crystals of $BaCl_2$ and BaF_2, common in glass-ceramic systems, of which vary in size from a 10 nm to 100 nm.

[1] J.a. Johnson, S. Schweizer, and A.R. Lubinsky, Journal of the American Ceramic Society **90**, 693-698 (2007).

[2] S. Schweizer, B. Henke, P.T. Miclea, B. Ahrens, and J.a. Johnson, Radiation Measurements **45**, 485-489 (2010).

WK8

In Situ and *Operando* Transmission Electron Microscopy of Catalysts

Peter A. Crozier

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Environmental transmission electron microscopy (ETEM) is an important tool for *in situ* catalyst characterization because reactive gases may have a strong influence on the structure and composition of materials. The ability to study materials at elevated temperatures under reactive gases makes it possible to investigate the atomic scale changes taking place during materials synthesis and in materials under reactor conditions. For example, by correlating catalytic reactor data with suitably designed ETEM observations, it is possible to map out structure-property relations in catalysts. In ETEM, the gas is mostly confined to the region around the TEM sample and not allowed access to the rest of the column or the electron gun. Heating can be performed up to 1000˚C or higher although the thermal conductivity and gas pressure can make precise temperature determination more challenging for some configurations. We are currently extending the capability of ETEM by developing *operando* techniques and introducing variable wavelength light illumination. *In-situ* transmission electron microscopy is a powerful tool for atomic-level investigations of gas-induced structural and compositional changes taking place in high surface area materials. However, a significant problem with this approach has been the lack of any direct measurement of gas-phase products that may be generated by the catalyst during the structural observation. This limits the ability to explore the links between catalyst structure and activity. To overcome this deficiency we are developing an *operando* TEM technique that combines the nanostructural characterization of the catalyst during the reaction with the simultaneous measurement of the catalyst performance. We employ electron energy-loss spectroscopy (EELS) of gases [1] to detect catalytic products inside the microscope while simultaneously determining the nanoscale structure of the catalyst.

One of the challenges in developing an "*operando* TEM" technique is associated with the TEM sample preparation. The amount of catalyst present in the TEM is very small (less than micrograms) and in most cases, product gases generated in the ETEM cannot be detected by EELS. A sample preparation technique was developed to get high catalytic loadings onto a TEM sample to make products detectable. CO oxidation on Ru catalyst was investigated with *operando* TEM. A 2.5 wt% Ru/SiO_2 catalyst was prepared by using incipient impregnation method, by impregnating SiO_2 with $RuCl_{3.x}H_2O$ solution. *In-situ* catalytic activity measurements were performed with EELS. Figure 1a shows the background subtracted energy-loss spectra of C p* peaks obtained while heating the Ru/SiO_2 catalyst inside the environmental cell in the presence of CO and O_2 (2:1) mixture at 1 Torr pressure. A peak started to appear at 289.7 eV at 150°C corresponding to C p* peak from CO_2. This observation confirms that the catalysis has been detected inside the TEM using EELS. As the temperature increases, the C p* peak from CO_2 also increases. Figure 1b shows the corresponding CO conversion to CO_2 on Ru/SiO_2 during catalysis at different temperatures and corresponds closely to *ex-situ* reactor data. Catalytic conversions of about 1% can be detected with this EELS approach. A detailed discussion on the challenges associated with developing *operando* TEM will be presented.

Motivated by a desire to improve solar energy conversions, we are also incorporating a variable wavelength high-brightness light source into our FEI Tecnai F20 ETEM. Current photocatalysts have very low efficiencies or stabilities and it is critical to investigate the surface and bulk phase transformations that take place in the presence of reactive gases during photon irradiation. In our design, we employ an Energetiq laser driven light source and couple light into the reaction cell of the microscope using a quartz fiber. The fiber is kept some distance from the TEM sample holder so that heating in reactive gas environments can be performed without damage to the fiber. We investigate the phase changes taking place on the surface of the catalyst as a function of wavelength, photon intensity, temperature, and gas.

[1] Peter A. Crozier and Santhosh Chenna, Ultramicroscopy, 111 177-185, (2011).

[2] The support from the National Science Foundation (NSF-CBET-0553445), US Department of Energy (DE-SC0004954) and the use of TEMs at the John M. Cowley Center for High Resolution Microscopy at Arizona State University are gratefully acknowledged.

WK8

In-situ Study of Colloidal Nanoparticles in Atomic Resolution by Using Graphene Liquid Cells

Jungwon Park

Paul A. Alivisatos Research Group, University of California, Berkeley, CA 94720

Colloidal nanocrystals are synthesized in wide range and appreciated in many applications including energy harvesting systems. Although this is mainly attributed to the facile control of their physical properties by tuning size and shape, our understanding of nanoparticle formation and its dynamics is rather empirical. Experimental study of dynamics in nanoparticle colloids is still waiting since we lack the ability to study dynamics in small-size regime: nanoscale. The recent development of micro-fabricated liquid TEM cells by our group has enabled the study of colloidal nanocrystal growth and two-dimensional superlattice formation from colloidal nanocrystals solution in real time.

Here, a recent breakthrough in *in-situ* mechanistic study of colloidal nanparticles will be introduced: the introduction of graphene sandwich liquid cells allows for atomic-scale resolution of particles in solution. Since graphene sandwich liquid cell is a double layer of inert carbon sheets encapsulating a liquid sample between them, it improves spatial resolution and contrast nanocrystals in liquid medium significantly without giving chemical and physical effect on nanoparticle motion. We introduce real-time atomic-resolution movies of nanopaticle growth in liquid. These *in-situ* movies elucidate the growth mechanism of colloidal nanoparticles at an unprecedented level from any other currently available analysis.

WK8

Determining the Chemical Structure of Individual Atmospheric Particles with Scanning Electron Microanalysis

Joseph M. Conny

Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Scanning electron microscopy (SEM) along with transmission electron microscopy are essential techniques for assessing the diversity of atmospheric aerosols and for understanding particle transformation processes in the atmosphere. Electron microscopy is also important in climate change studies because the extent that particle optical properties affect Earth's radiative balance depends largely on a particle's internal chemical structure as well as its overall size and shape. Analytical methods associated with electron microscopy such as elemental mapping with energy-dispersive x-ray spectroscopy (EDX) are problematic, however, because ambient particles typically have complex shapes and surface features that lead to analytical artifacts. This talk will present SEM work at NIST toward accurately determining the identity and spatial arrangement of chemical phases in heterogeneous atmospheric particles. In addition to conventional EDX analysis to acquire two-dimensional high-resolution maps of elemental phases, research will be presented on the analysis of the internal structure of particles using focused ion beam (FIB) tomography with SEM. In FIB tomography, individual particles are sequentially sliced, imaged, and mapped. The outcome is the three-dimensional representation of elemental phases in an individual particle for a more accurate understanding of how the particle's internal structure might affect its single-scattering albedo and, therefore, Earth's radiative balance.

WK8

Microbial Transformations of Fe(III) Oxides: Characterization and Reactivity of Biogenic Fe(II) Minerals

Ed O'Loughlin

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The reduction of Fe(III) oxides by Fe(III)-reducing microorganisms may result in the production of a suite of Fe(II)-bearing secondary mineralization products (Fe(II)SMPs), including magnetite, siderite, vivianite, green rusts, and ferrous hydroxy carbonate. Fe(II)SMPs provide a reservoir of reducing capacity in many suboxic and anoxic environments that may contribute to the reduction of contaminants such as U(VI). However, there can be substantial differences in the ability of different Fe(II)SMPs to reduce soluble U(VI) to insoluble U(IV). Thus, to understand the potential for the reduction of U(VI) by Fe(II)SMPs in subsurface environments we need to identify the key microbial and geochemical parameters that control the types of Fe(II)SMPs that form. To this end, we examined the Fe(II)SMPs formed from the bioreduction of a series of natural and synthetic Fe(III) oxides (including akaganeite, feroxyhyte, ferric green rust, ferrihydrite, goethite, hematite, lepidocrocite, and maghemite) by *Shewanella putrefaciens* CN32, a dissimilatory Fe(III)-reducing bacterium. Our results showed that the types of Fe(II)SMPs that formed were dependent on both the mineralogy of the parent Fe(III) oxide as well as the solution composition. For example, the presence of sufficient concentrations of phosphate resulted in the formation of micron-sized green rust or vivianite instead of nanoparticulate magnetite. We examined the uptake and reduction of U^{VI} in the presence of biogenic green rust (BioGR), magnetite (BioMAG), and siderite (BioSID). Uptake of U(VI) by BioGR and BioMAG was accompanied by formation of nanoparticulate uraninite. U(VI) interaction with BioSID resulted in partial U(VI)/U(IV) substitution for Fe(II) in the surface layer of the siderite particles and adsorption of U(IV). These results clearly demonstrate significant differences in reactivity among biogenic Fe(II)SMPs with respect to U(VI) uptake and reduction.

WK8

Observation of Metal Reducing Bacteria on Iron Oxide Thin-films Using *In-situ* Environmental SEM

Drew E. Latta[1], Deirdre Sholto-Douglas[1], Edward J. O'Loughlin[1], Bhoopesh Mishra[2], Maxim I. Boyanov[1], Barry Lai[3], and Kenneth M. Kemner[1]

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The biogeochemical cycling of iron is linked to the cycling of many elements including carbon, nutrients such as nitrogen and phosphorus, and heavy metal contaminants such as uranium. The iron cycle is largely mediated by diverse groups of dissimilatory metal reducing microorganisms that couple oxidation of organic carbon sources to reduction of ferric (Fe^{III}) iron to ferrous (Fe^{II}) iron. Here we are studying coupled micro-scale biogeochemical processes that influence the immobilization of uranium by Fe oxides and metal reducing organisms. Our focus is on determining the role of micro-environments on the speciation and distribution of uranium on and near cells respiring on Fe^{III}-oxide films. Previously, we have used hard x-ray spectro-microscopy to localize and determine the valence state of uranium on cell surfaces under hydrated conditions. In concert with this approach, we are using *in-situ* environmental scanning electron microscopy (ESEM) to image the morphology of Fe oxide films and bacteria in their live, hydrated state. Using ESEM at high water vapor pressure (~6 torr) avoids the harsh treatments (chemical fixation, dehydration, and gold-coating) typically used in SEM studies of bacteria. Using this approach avoids changes in bacteria and Fe-oxide morphology observed when films are chemically fixed and dehydrated. Results from x-ray microscopy and ESEM experiments will be presented.

WK8

Pathogen Internalization and Fresh Produce Safety

Haiping Li

Division of Food Processing Science and Technology, Center for Food Safety and Applied Nutrition,
U.S. Food and Drug Administration, College Park, MD 20740

Foodborne pathogen outbreaks associated with human consumption of leafy greens have increased greatly in recent years. One of the major research efforts in our institute (FDA/CFSAN/Chicago Moffett Campus) is to identify the risk factors in pre-harvest/post-harvest practices that cause pathogen contamination in the final products and to understand the molecular mechanisms of how bacteria survive from processing stresses, thus to develop the intervention and preventive measures. Pathogen internalization in produce tissue or sprout seeds imposes great risk since the standard industry washing process cannot access and inactivate the pathogen. This presentation will introduce the application of imaging study in pathogen internalization in lettuce/spinach tissue and the implications in improving industry practices to produce safe food.

WK8

Laboratory Analysis of Extraterrestrial Dust

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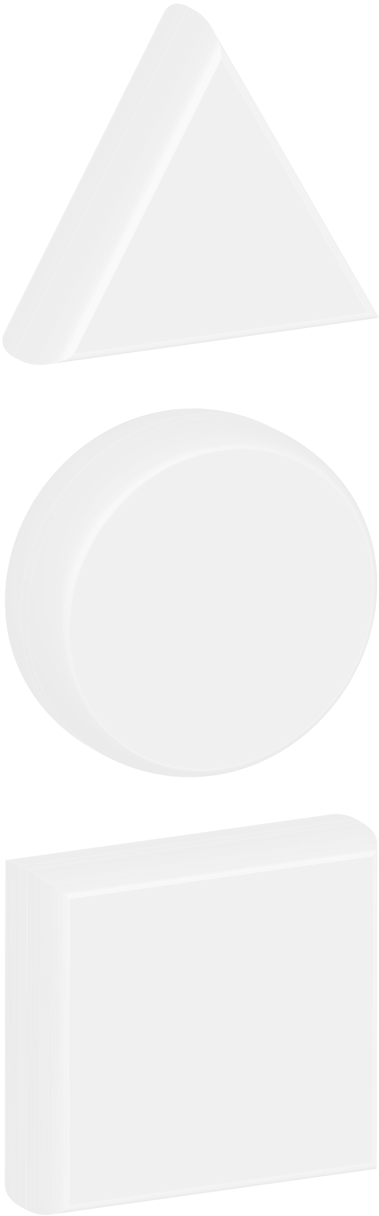
[2] Chicago Center for Cosmochemistry, The University of Chicago, Chicago, IL 60637

About 40,000 tons of extraterrestrial dust reaches Earth annually. The bulk of it enters Earth's atmosphere directly as interplanetary dust particles and micrometeorites. A smaller fraction of the dust gets to Earth embedded in primitive meteorites, which are about 4.6 billion years old. Cosmic dust is also returned to Earth by spacecrafts and stratospheric aircrafts. Because of the primitive nature of cosmic dust grains, they contain a wealth of information about environmental conditions at the time of their formation in the early solar system. Cosmic dust is also found in marine sediments and can be used to study collisional events in the solar system. A small fraction of cosmic dust grains survived processing in their parent bodies for 4.6 billion years and are the oldest solid samples of material available for laboratory study. They preserve information about their circumstellar origins in the outflows of evolved, now extinct stars. Thus, learning more about these conditions is a strong motivation for studying cosmic dust, which helps to better understand our cosmic origins. Physicochemical methods are used to extract cosmic dust grains from the meteorites. Scanning electron microscopes, electron microprobes, and ion microprobes are used to find, image, and characterize the elemental and isotopic compositions of extraterrestrial dust samples. Special applications and other techniques such as atom probe tomography often require sample preparation with focused ion beam microscopes. In my talk, I will present examples of cosmic dust studies that I perform in collaboration with Argonne National Laboratory.



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Advanced Photon Source

Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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Electron Microscopy Center

The electron microscopy was accomplished at the Electron Microscopy Center for Materials Research at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

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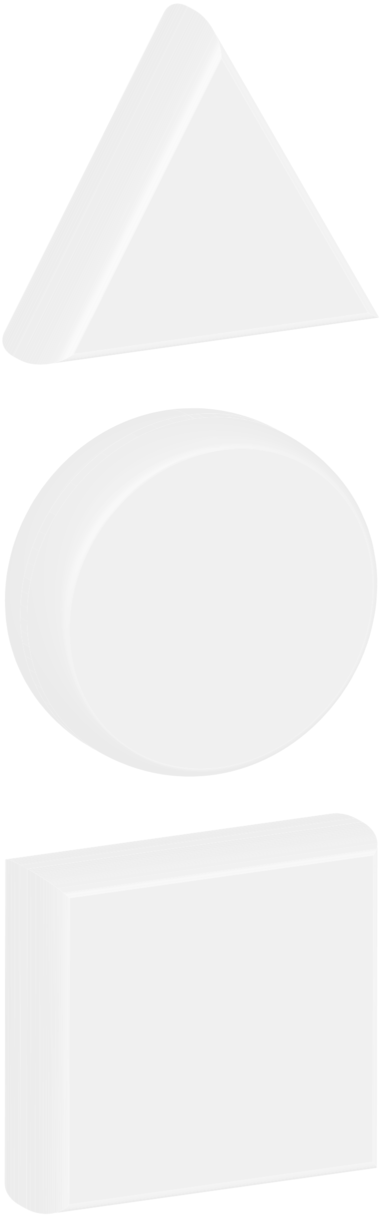

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POSTER
ABSTRACTS

BIOLOGY

A-00

Finding and Keeping Small Crystals in the Beam

Michael Becker[1], Craig Ogata[1], Stephen Corcoran[1], Derek W. Yoder[1], Sergey Stepanov[1], Mark Hilgart[1], Oleg Makarov[1], Ruslan Sanishvili[1], Shenglan Xu[1], Dale Ferguson[1], Nagarajan Venugopalan[1], Christopher Dettmar[2], Scott Toth[2], Jeremy Madden[2], David J. Kissick[2], Garth J. Simpson[2], Janet L. Smith[3], and Robert F. Fischetti[1]

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Working with crystals of only a few microns on a side—including those that seem "invisible" due to being grown *in meso*—provides challenges to synchrotron beamlines. It is essential to provide hardware that moves and maintains crystals with high precision. In carefully controlled experiments relevant to high throughput, we observe time-dependent shifts of samples after initial mounting by a cryo-cooled automounter, where the sample may shift laterally by ~15 microns with a time constant of ~2–4 minutes. Because time is usually spent centering a crystal at low resolution initially, this shift often goes unnoticed by users. We attribute this shift to thermal expansion of components of the sample support system, including the mounting pin and base, due to the temperature difference between liquid nitrogen and a cryostream held at 100 K. Time-dependent shifts for a variety pins and bases, as well as temperature measurements of the goniometer, have been conducted; an analysis of contributing factors to the thermal shift will be presented. Another important factor for working with small crystals includes providing tools for locating crystals that are mounted on the goniometer. Towards this aim, x-ray diffraction rastering has proven extremely valuable for working with small crystals. However, this method exposes samples to x-ray damage and may take many minutes per raster scan. To minimize x-ray dose on samples and to increase speed for high throughput, we present alternative methods for locating crystals, including x-ray fluorescence raster, and recent efforts at installation of a SONICC system (Second Order Non-linear Imaging of Chiral Crystals) at GM/CA CAT for sample visualization.

A-01

Amyloid Aggregation and Inhibition Explored by SAXS

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Amyloidogenic proteins are associated with the occurrence and progression of a variety of neurodegenerative diseases. Amyloid proteins self-assemble to form fibrillar structures and can further aggregate to form larger structures such as plaques or Lewy bodies. Insulin, a 51-residue polypeptide hormone used in the treatment of diabetes, is also known to form fibrils *in vitro*. Insulin has been investigated as a model protein to explore amyloid aggregation and fibril formation in the presence of metacresol and rifampicin, compounds which stabilize insulin conformations and are thought to inhibit protein aggregation and fibrillation. Metacresol is also formulated in commercial forms of injectable insulin. The aggregation of insulin was tracked by rheology and by small-angle x-ray scattering (SAXS) during a programmed heating protocol.

SAXS shows us an initial dimer conformation for insulin protein at room temperature in pH 2 solution, while larger fibrils are observed after heating. As the protein is heated through 75°C, aggregation is tracked in the low q region by the use of Guinier analysis. Time-resolved SAXS experiments show inhibited aggregation of the protein in the presence of the additives. These results are compared with kinetic results obtained by rheology tracking the aggregation of the protein during heating by associated complex viscosity.

A-02

BioSAXS-1000: A New Tool for Gaining Structural Insight When Crystallographic Methods Are Not Enough

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X-ray crystallography is a fundamental technique for obtaining atomic resolution structural information about macromolecules. However, the requirement for diffraction quality crystals often limits its efficacy for studying protein complexes or systems with inherent structural disorder. In cases where crystallographic methods fall short, small-angle x-ray scattering (SAXS) provides a complementary tool for extracting structural information from biological systems. In particular, SAXS proves ideal for studying partially disordered macromolecules, for monitoring structural changes in response to environmental perturbations, and for monitoring conformational changes due to ligand binding. It also provides a useful tool for probing molecular interactions, such as those associated with crystallization. Here we introduce the first commercial system specifically designed for high-throughput solution scattering experiments with macromolecules, the BioSAXS-10001. Comprised of specially designed focusing optics and a Kratky block, the BioSAXS-1000 system eliminates smearing issues common to traditional Kratky cameras. The system includes a high sensitivity pixel array detector and intuitive data collection software that includes full automation of the Kratky alignment hardware. Together, the many features of the BioSAXS-1000 system allow for synchrotron-quality SAXS data from a home laboratory source in as little as 15 to 30 minutes for most protein samples.

A-03

Brain Imaging with X-ray Fluorescence: Analysis of Biologically Relevant (Fe, Cu, Zn) and Toxic (Mn, Pb) Metal Ions

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Consuming 40% of body oxygen, the brain is known for its high metabolic activity. Metalloproteins play an important role in various brain processes and, thus, the availability of essential transition metal ions is important for normal brain function. Knowledge on the transport into and distribution within the brain of Mn, Cu, Fe and Zn is limited. X-ray fluorescent imaging is an excellent technique for visualization of metal distributions in brain tissues down to single cell resolution. Intracellular cryogenic- x-ray absorption near-edge structure can provide information on the oxidation state of metal ions and on their coordination environment. To connect this information with the biological function of particular metal ions, x-ray fluorescence (XRF) images can be co-localized with particular proteins or various biological markers visualized by immunohistochemistry. Transgenic animals can be used to selectively knockout the protein in question to visualize its effect on the metal ion transport and binding in the brain.

Results for rodent (mice and rat) brains will be presented.

The results for Cu highlight its highly inhomogeneous distribution with accumulations along the ventricle walls. These accumulations were found to occur inside astrocytes confirming earlier proposals assigning astrocytes a role as Cu-storage/buffering cells in the brain. The Cu-buffering protein was found to be metallothionein I,II (MT I,II). Attempts to deplete the Cu accumulations in the astrocytes by Cu-starvation or MT(I,II) knock out were unsuccessful indicating the presence of a strong compensatory mechanisms.

The distribution of the neurotoxic (in conditions of elevated exposure) Mn ion in the rodent model of Manganism was also highly specific. Mn accumulated in the gabaergic (Globus Pallidus) and dopaminergic neurons (Substantia

Nigra compacta) resulting in the dysfunction of these groups of neurons with emergence of well known neurological symptoms. It remains unknown why these particular neurons accumulate higher levels of Mn. The intracellular target of Mn toxicity is likely mitochondria.

Detection of the neurotoxic Mn and Pb in brain with XRF is challenging due to their (about 10 times) lower concentrations compared to the essential Cu, Fe and Zn ions. Using the highest possible flux of the ID beamline and relatively long dwell times, we managed to map the Pb distribution in a Pb treated mice model of Alzheimer's disease. Biological observations have previously demonstrated an earlier onset of plaque formations in mice exposed to Pb. XRF demonstrated Pb accumulations in plaques.

The last two examples demonstrate potential connections between environmental exposure to elevated Mn and Pb and the onset of neurodegenerative diseases. To gain more insights, further technical developments and larger imaging capacity at APS are needed.

A-04

Manganese Accumulation in the Substantia Nigra Compacta and Hippocampus of the Rodent Brain

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Manganese (Mn) is an essential element necessary in small amounts for proper brain function. However, excessive Mn exposure results in manganese-induced Parkinsonism, a condition resembling Parkinson's disease (PD). Welders and smelters are susceptible to this condition through occupational exposure, as well as those suffering from chronic liver failure. Furthermore, epidemiological studies suggest that an increased environmental exposure to Mn could contribute to an increased incidence of PD. Mn enters the brain by three pathways: through the capillary endothelial cells of the blood-brain barrier (BBB), by the epithelial cells of the blood-cerebrospinal fluid barrier, or via the olfactory nerve from the nasal cavity directly to brain. However, knowledge regarding the structures responsible for Mn transport into the brain remains incomplete. As Mn is tightly regulated at the BBB, it is hypothesized that Mn utilizes channels primarily reserved for other biologically relevant transition metals such as calcium, iron, copper, and zinc.

X-ray fluorescence imaging (XRF) imaging was performed on coronal brain sections (10–30mm) of Mn-treated rodents and age-matched controls. This study found the highest Mn content in dopaminergic neurons of the substantia nigra compacta (SNc) and gabaergic neurons in the globus pallidus and thalamus. While Mn accumulation in GP is well established, this is the first direct visualization of Mn distribution in the SNc. Mn accumulation in the SNc visualized by XRF provides a potential rapport between Mn exposure and PD. As further support, tyrosine hydroxylase staining for dopaminergic cells is substantially decreased in Mn treated samples, indicating possible cell death in the SNc. We also identified increased Mn within the hippocampal substructures of the dentate gyrus and CA3 of Ammon's horn. A strong Zn/Mn correlation was observed across the hippocampal structures suggesting a possible utilization of zinc transport/storage mechanisms. Negative, moderate correlations of Fe/Mn and Cu/Mn were also observed as compared to control, potentially explained by the competition for and saturation of Fe- and Cu-related transport mechanisms.

A-05

Assessing the Role of Copper in Neurogenic Activity in the Subventricular Zone: Combined Neurogenesis Assessment and XRF Imaging

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Neurogenesis in developed brains is a well established yet incompletely understood phenomenon. Elucidation of the mechanisms underlying neuronal proliferation would yield pharmaceuticals to actively combat the effects of blunt-force brain trauma and prevent neurodegenerative diseases such as Alzheimer's and Parkinson's disease [1]. Using x-ray fluorescence (XRF) mapping, our group has recently found dense copper accumulations (on the order of 100 mM) along the ventricle wall in rodent brains. Micro-cryo-XANES with subcellular resolution ($0.3 \times 0.3\ \mu m^2$ at beamline 2-ID-D) revealed a major source of this copper to be copper metallothionein (I,II) (CuMT(I,II)), a protein associated with combating oxidative stress, protection against heavy metal toxicity, and aiding neuronal repair [2, 3]. XRF techniques, which directly provide spatial metal concentrations, have been combined with established immunohistochemical techniques to assess the role that CuMT(I,II) plays in neurogenesis. The effects of copper content in the subventricular zone were examined by employing MT(I,II) knockout mice and mice fed a copper starvation diet.

XRF mapping of MT(I,II) knockout mice reveals MT(I,II) to be a major source of copper accumulations along the ventricle wall with accumulation and overall density greatly diminishing in the absence of MT(I,II), though concentrations remain elevated compared to other subventricular structures. Furthermore, immunohistochemical staining for MT(I,II) shows that MT(I,II) proteins reside in astrocytes, cells known to act as progenitor cells in the subventricular zone while colocalization of copper by autofluorescence and astrocytes by immunostaining (GFAP), demonstrates that the copper accumulations are hosted in astrocytes. Mice fed a copper deficient diet, interestingly, show increased copper concentrations along the ventricle wall and decreased copper sums in the cortex (XRF imaging performed at BioCAT, $5 \times 5\ \mu m^2$ resolution). Despite the increased astrocyte copper concentration, cell proliferation neither increases nor decreases as determined by quantification of Ki67 immunostaining. The inability to deplete copper in the subventricular zone by both starvation and MT(I,II) knockout mice demonstrates that robust compensatory mechanisms ensure sufficient copper availability in astrocytes. These mechanisms likely simultaneously provide a means for neurogenesis, explaining why changes in the number of actively dividing cells have not been observed and further suggesting a fundamental relationship between copper accumulations and neurogenesis in the subventricular zone.

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CHEMISTRY

A-06

Simultaneous Diffuse Reflection Infrared Spectroscopy and Pair Distribution Function Measurements at 11-ID-B

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Complex problems in real-world materials often cannot be fully understood using an individual structural probe. *In situ* pair distribution function and Fourier transform infrared spectroscopy are complimentary tools for probing the structure and surface chemistry respectively. Both techniques were implemented simultaneously at 11-ID-B to elucidate the changes in material structure and the surface functional group. A more complete understanding of a material system is achievable through the combination of these two methods.

A-07

Probing Material Reactivity Using X-ray Pair Distribution Function Methods

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Understanding how advanced functional materials react and transform, at an atomic scale, is a characterization challenge with many diverse phenomena possible; components with varying particle size, morphology, and microstructure can evolve from multi-atom clusters to multi-million atom crystals. The pair distribution function (PDF) method shows great promise for providing quantitative insight such reactions. Recent advances in experimental methods, have improved the efficiency of x-ray PDF measurements, to allow time-resolved experiments with sufficient resolution to study reactions in solid materials. The PDF analysis probes the complete reaction from clusters to bulk, amorphous or crystalline, liquid or solid. This is in contrast to Bragg crystallographic analysis, which is "blind" to the clusters which nucleate before growing into long-range ordered materials. The structural insights from the PDF data are obtained in parallel with phase concentration to allow different components to be distinguished and a robust quantitative analysis.

A-08

Effect of Chemical Treatment on the Structure of Graphene

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Since the discovery of graphene in 2004 by its 2010 Nobel Award winning pioneers Russian-born scientists Andre Geim and Konstantin Novoselov, it has been an exploding topic in the scientific field due to its unique structure and properties. Graphene is a single layer of carbon atoms bonded densely in a honeycomb crystal lattice, attributing to its immense strength and flexibility. Thus, graphene has been considered for its potential mechanistic applications. Graphene is also being considered as a more powerful replacement for silicon, as electrons act as mass-less particles and travel near the speed of light in graphene. Combined with its flexibility, graphene is promising in both biotechnology and revolutionizing commercial technology. Although graphene's wide range of applications are in the process of being explored, there are still many unanswered quandaries regarding graphene. This experiment utilized x-ray diffraction at beamline 13-BM-D to understand how the grapheme crystal structure changes when subjected to different chemical treatments.

A-09

Pressure-induced Spin-state Switching in a Molecular Framework Material

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The targeted development of functional molecular frameworks is not only a synthetic challenge, but requires parallel characterization of their often complex structure-property relationships. Among strategic efforts to introduce specific function, the incorporation of spin crossover switching centers allows for the development of new advanced functional materials for molecular-scale electronic switching and sensing devices. Here, we present pressure-dependent *in situ* structural studies of the spin crossover phenomenon in a molecular framework material, including complementary powder diffraction (1-BM) and pair distribution function (11-ID-B) measurements at the Advanced Photon Source.

A-10

Structure and Electronic Configurations of the Intermediates of Water Oxidation in Ru-Single Site Catalysts

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Photosynthetic water oxidation is a fundamental chemical reaction that is critical to sustaining the biosphere. Mimicking this reaction in a manmade device will allow for sunlight-to-energy conversion with water providing electrons and protons for production of chemical fuels. About 30 years ago, Meyer and coworkers reported first ruthenium-based catalyst for water oxidation, known as the "blue dimer" [1], which may be considered as an artificial analog of the oxygen-evolving complex (OEC) in Photosystem II (PS II) [2]. Single-site catalysts are attractive model compounds for both experimental and theoretical studies of mechanism of water oxidation.

Electron paramagnetic resonance (EPR), Raman, and x-ray absorption spectroscopy characterization of the electronic structure and molecular geometry of catalytic intermediates in single-site water-oxidizing complex $[\mathrm{Ru^{II}(L)(4\text{-}pic)_2(OH_2)}]^{2+}$ (1) (L = 4-t-butyl-2,6-di(1',8'-naphthyrid-2'-yl)pyridine, pic = 4-picoline) are reported. Chemical oxidation of starting catalyst resulted in new EPR signals tentatively assigned to Ru(III)-HO and Ru(III)-OOH complexes (obtained with 2–4 equivalents of oxidant) and to Ru(III)-OOH and Ru(V)=O complexes (obtained with excess of oxidant). Parallel Ru K-edge x-ray absorption near-edge structure measurements are in agreement with interpretation of EPR data and show shift of Ru K-edge to higher energy for samples prepared with excess oxidant. Extended x-ray absorption fine structure and resonance Raman indicated changes in the ligand environment for samples enriched with Ru(III)-OOH intermediate. Formation of metal bound peroxides as a result of O-O coupling has been implicated in the mechanism of catalytic water oxidation by Photosystem II OEC and in Ru-based catalysts [2–3]. We believe that the intermediates described here are direct products of O-O bond formation step in the studied catalyst.

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A-11

SONICC and TPE-UVF Analysis of APIs and Common Excipients

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Second harmonic generation (SHG) occurs through the interaction of photons with chiral, noncentrosymmetric crystals, resulting in frequency-doubled light. Second-order nonlinear imaging of chiral crystals (SONICC) was recently applied towards the analysis of the crystallinity of active pharmaceutical ingredients (APIs), having shown to be successful for the sensitive detection of protein crystals. The advantages offered by this technique allow for the analysis of samples within turbid matrices, with a detection limit that is significantly lower than powder diffraction. Since the majority of active pharmaceutical ingredients are aromatic, the coupling of SONICC with two-photon excited UV fluorescence allows for the discrimination of APIs among SHG-generating excipients.

CONDENSED MATTER PHYSICS

A-12

Nanosecond Structural Response of Ferroelectric/Dielectric Superlattices to Applied Electric Fields

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The remnant polarization of ferroelectric/dielectric superlattices can spontaneously form an array of striped nanodomains. Domain walls within these stripes separate regions in which the direction of the polarization differs by 180°, either along or opposite the direction of the surface normal. The structure and dynamics of the domains depend on a detailed interaction of ferroelectric polarization, crystallographic structure, and mechanical and electronic boundary conditions. Theoretical calculations have provided a range of intriguing predictions of nanodomains under external electric fields. With time-resolved x-ray microdiffraction, we show that the dynamics of the transition from the striped domain state to a homogeneous polarization state under applied electric fields at a nanosecond timescale. Experiments were carried at station 7-ID-B of the Advanced Photon Source.

Under applied electric fields, the remnant polarization in $PbTiO_3/SrTiO_3$ superlattices of two different layer sequences transitioned from the striped-domain state into a monodomain state. The transition was accompanied by the disappearance of the domain satellite x-ray reflections arising from the domains. The rate of the striped-to-monodomain transition depends on the magnitude of the electric field, and can be as fast as a few nanoseconds. During the transition process, regions of superlattice that have been switched show lattice expansion as a consequence of the piezoelectricity. The piezoelectric response of the remaining regions of the stripe domains, however, is effectively suppressed during the transition due to mechanical clamping. We therefore propose that the transition of striped domains into a homogeneous polarization state occurs heterogeneously across the extent of our system.

A-13

Ultrafast Strain Modulation in Multiferroic Heterostructures

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Complex oxide heterostructures display a wide spectrum of emergent properties that can be activated by epitaxial control of lattice structure. The key ingredient is how strain couples to crystal structure in ways quite distinct from routes available through allowed bulk chemistries, which allows one to move to new regions of phase space. By coupling to optical excitation, we have found that ultrafast photoelastic response of complex oxide heterostructures offers a new route to dynamically modulate the structure in unexpected ways. Here we present the case of tracking ultrafast x-ray diffraction of strained $BiFeO_3$ following optical excitation. The lattice undergoes an ultrafast out of plane lattice expansion, which is potentially due to change in the depolarizing field due to screening with excited carriers. The most interesting feature though is that since the lattice is constrained by epitaxy in two of the three directions, the system can only respond by changing the unit cell volume with an out of plane expansion. This leads to a peculiar threshold behavior where there is a drop in the scattering factor that is likely due to a structural transition to lower symmetry. Such a transition is seen under large compressive strain, but in this case we are far from the phase boundary. We propose the key factor is the change in unit cell volume, which drives an isosymmetric phase transition from a rhombohedral to a tetragonal phase. This highlights a new path to manipulate phases in complex oxide heterostructures with optical stimulation.

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A-14

Generation of Acoustic Pulses from a Photo-Acoustic Transducer Measured by Time-resolved X-ray Diffraction

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The phonon Bragg switch is a potentially efficient and inexpensive method of generating picosecond x-rays from third-generation hard x-ray synchrotron sources [1]. This method uses a high-wavevector coherent phonon to modulate the intensity of a hard x-ray beam on a picosecond timescale, making it possible to significantly enhance the time-resolution of third generation sources. In this work, we aim to generate an acoustic phonon Bragg switch of hard x-ray radiation by directly printing a high-wavevector metallic grating onto a crystalline substrate. This method has recently been used to generate an acoustic phonon switch of ultraviolet radiation [2] as well as a generating high-wavevector coherent optical phonons in bismuth films [3].

As the first step of building and characterizing the acoustic phonon hard x-ray switch, we have investigated the generation of acoustic pulses from thin gold films on crystalline substrates using picosecond time-resolved x-ray diffraction. We utilize ultrafast x-ray pulses from laser-driven hard x-ray source to investigate the coherent strain generated by sub-picosecond optical excitation of a 100-nm thick gold film deposited on a (111) germanium substrate. The resulting optical pump/x-ray probe spectra reveal that the spatiotemporal structure of the acoustic pulse is bipolar with acoustic wave-vectors up to inverse of the film thickness [4]. Future experiments at the APS will investigate the realization of the acoustic phonon Bragg switch for time-resolved x-ray studies.

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A-15

A Novel Approach for X-ray Scattering Experiments in Magnetic Fields Utilizing Trapped Flux in Type-II Superconductors

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We introduce a novel instrument to x-ray scattering studies in applied magnetic fields by exploiting vortices in superconductors. This approach opens an unrestricted optical access to the sample and allows magnetic fields to be applied precisely along the x-ray momentum transfer, facilitating polarization-sensitive experiments that have been impractical or impossible to perform to date. This method is based on trapping magnetic flux in a small disk-shaped superconductor (known as a trapped flux/field magnet, TFM). The TFMs remain stable and provide practically uniform magnetic fields for days after magnetizing using an external magnet. A sample (typically a single-crystal) is mounted on a cold finger such that its distance from the TFM can be varied in order to change magnetic field at the sample position. The dual-stage TFM instrument and its use in a resonant diffraction study of incommensurate ordered states in an axial meta-magnet, $TbNi_2Ge_2$, are described.

A-16

Phonon Spectrum of Chromium at High Pressure

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Chromium is a transition metal with many fascinating properties. It exhibits antiferromagnetic ordering with an incommensurate spin-density-wave (SDW) state when the temperature is lower than 311K. Chromium undergoes a quantum phase transition above a critical pressure of about 9.7 GPa. We present high-energy-resolution (1.5 meV) inelastic x-ray scattering studies of the phonon spectrum in chromium above and below the critical pressure. A high-purity chromium single crystal at room temperature was pressurized using a diamond anvil cell. The phonon dispersions of both longitudinal and transverse modes along the [100] direction were measured, with emphasis on wavevectors close to the SDW wave vector. The pressures used in the experiment were 1.29 GPa, 8.15 GPa, and 10.6 GPa. We compare our data with density functional calculations made using Quantum Espresso.

A-17

Unconventional Exchange Coupling Mechanism in Manganite-Cuprate-Manganite Trilayers

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Interfaces between correlated transition metal oxides offer opportunities for both fundamental physics and technology [1, 2]. Particularly, it has been found that a ferromagnetic exchange field can be induced in the cuprate layer at cuprate-manganite interfaces, which underlies several intriguing phenomena, such as an induced net Cu moment [3] and the inverse superconducting spin switch effect [4–5]. Here we report that the interface-induced exchange-field may also give rise to an unconventional magnetic coupling mechanism.

We have performed x-ray resonant magnetic scattering (XRMS) and x-ray magnetic circular dichroism (XMCD) experiments at Cu and Mn L2,3 edges to examine epitaxial trilayers with nominal structures of 8-nm $La_{0.7}Ca_{0.3}MnO_3$/ (2–6)-nm $PrBa_2Cu_3O_7$/ 50-nm $La_{0.7}Ca_{0.3}MnO_3$ (LCMO/PBCO/LCMO), where LCMO is a half-metallic ferromagnet and PBCO is an insulating antiferromagnet. The samples are fabricated with the high-pressure pure oxygen sputtering technique. SQUID magnetometry and polarized neutron reflectometry studies indicate that the two LCMO layers have different magnetic anisotropies and Curie temperatures. XRMS experiments show that there are induced net Cu moments at both cuprate-manganite interfaces. The Cu total electron yield (TEY) signal is predominately from the cuprate near the top interface, as indicated by the similar temperature dependences of the XMCD signals of Cu and Mn. We have further measured the XMCD spectra when the two LCMO layers are in parallel and anti-parallel magnetization configurations, respectively. We find that, in samples with 6-nm PBCO, both the Mn and Cu XMCD signals decrease when switching from the parallel state to the antiparallel state, but the relative change of the Cu XMCD signal is much larger. This implies that there is appreciably overlap between the induced exchange-fields corresponding to different interfaces. Therefore, for sufficiently thin PBCO barriers the interface-induced exchange-field may magnetically couple the LCMO layers, mediated by the spin-polarized Cu electrons in the CuO_2 planes. This unconventional exchange coupling mechanism may provide a key concept to design the novel functionalities for oxide-based spintronics.

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A-18

The Structure of Liquid Water

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The importance of water is self-evident, yet the structure beyond the H_2O molecule has long been a matter of debate that continues to the present day. Some of the earliest temperature-dependent structural models of liquid water by Bernal and Fowler [1] proposed in 1933 were based largely on x-ray diffraction data. These pioneers suggested a continuous transition between two different intermolecular arrangements below 200°C; tetrahedral ice-like (tridymite) like up to 4°C, tetrahedral quartz-like between 4°C and 200°C.

More recently the validity of tetrahedral structural models for liquid water has been questioned [2]. This has led to two currently debated perspectives on the structure of water. The first, by Soper [3] argues that the preferred structural model of water is tetrahedral (rather than chain-like) and that water is essentially homogeneous on a nanometer scale. In contrast, the second by Nilsson and Petterson [4] interpret structural data in terms of a model comprising of a fluctuating heterogeneous low-density and high-density mixture. Both authors agree, however, that it would be useful to measure obtain a more accurate O-O radial distribution function, which essentially describes the distribution of molecule centers.

Towards achieving this, our experimental team has recently made very careful high-energy x-ray (115 keV) structure factor measurements at the advanced photon source. This data, which was taken over the temperature range 4–70°C significantly improves on existing literature data, particularly at high-Q. One interesting result form this was the non-linear behavior of the main peak position around 2.80Å in the x-ray distribution function.

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A-19

How Fast Does A Body Expand, If Heated Instantaneously?

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Intuitively, it is understood that in the absence of mass transfer phenomena mechanical disturbances caused by the induced thermal stress will propagate with the speed of sound. However, it is unclear whether sound propagation is the only mechanism that affects the inherent dynamics of thermal expansion and if it is, how long does the sound have to travel until a change in the dimensions of the body is observed? In most experimental situations it takes time for the heat to be transferred to a studied expanding volume. Only a few studies make clear distinction between these two different phenomena with distinct time scales (e.g., [1–3]), yet the fundamental questions outlined above have been unaddressed so far.

We report time evolution of thermal expansion in the crystal lattice of diamond on the time scale from 100 ps to 18 ms upon nearly instantaneous (≈10 ps) heating of the crystal through the entire thickness. We found that an onset of a change in the lattice parameter corresponding to the initial averaged level of thermal expansion is solely due to the induced thermal stress, which generates strain propagating at the speed of sound for longitudinal waves from the crystal surfaces into the bulk. Within a single pass of the strain wave across the crystal thickness (a few nanoseconds) the crystal adopts a new expanded state. This enlargement in the lattice parameter equilibrates on the microsecond time scale as a result of heat dissipation.

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A-20

Influence of Symmetry on the Octahedral Rotations of Epitaxial $RNiO_3$ Thin Films

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Understanding the structural and electronic behavior of ABO_3 thin films subjected to confinement, lattice misfit and broken symmetry at the interface in the ultra-thin limit is fundamentally important for the rational design of new materials [1]. However, the epitaxial strain will not only result in a change the in-plane lattice constants but also the octahedral rotations connected to bond angles and crystallographic symmetry. Here we present a study of the effect of the bulk lattice symmetry on octahedral rotations under epitaxial strain in thin films of $RNiO_3$ (R = La, Pr, Nd) grown on various substrates by pulsed laser deposition with *in situ* monitoring by reflection high energy electron diffraction. A combination of high-resolution x-ray diffraction, polarization-dependent soft x-ray absorption spectroscopy, and first-principles density functional calculations has been applied to elucidate structural and electronic properties of the samples.

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A-21

Optical Control of Structural Evolution of Ultrathin VO_2 Film Following a Photoinduced Metal-insulator Phase Transition

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Optical control of phase transitions offers new routes to harness strongly correlated electron systems. We have demonstrated the crystallographic symmetry change of ultrathin (13 nm) VO_2 film across photoinduced metal-insulator transition can be controlled by optical pump fluence in time domain, using synchrotron-based ultrafast x-ray diffraction technique. By adjusting the fluence of the pump pulse, the structural state of VO_2 film 100 ps after excitation can be prepared to a selected structural state and transits through the known structural phases. At high pump fluence, a new transient structural state was found to be non-thermally induced 100 ps after excitation. It recovers to the tetragonal phase within one nanosecond, and further to the monoclinic phase in tens of nanoseconds. This study elucidates the time scale of the structural recovery of thin VO_2 film from photoexcited tetragonal metallic phase to monoclinic insulating phase, providing crucial time-domain information for the future design of optoelectrical devices based on metal-insulator phase transition.

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A-22

Structural Phase Transition of $BiFeO_3$ Thin Films in the Ultrathin Regime

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Bismuth ferrite ($BiFeO_3$: BFO) is one of very few materials exhibiting multiferroic properties at room temperature, being both ferroelectric (T_C ~1103 K) and G-type antiferromagnetic (T_N ~ 643K) [1]. In its bulk form, it possesses a rhombohedrally distorted quasi-cubic perovskite structure with ferrodistortive displacements along the (111) direction, giving rise to a spontaneous polarization in the same direction.

The structure of epitaxial thin films, however, depends critically on the amount of substrate-induced strain. BFO thin films grown on $SrTiO_3$ (STO) substrates (-1.4% compressive strain) have been shown to exhibit an R-like monoclinic structure (M_A) for films thicker than 26 nm [2].

Although it has been reported that the BFO thin film structure depends strongly on film thickness [3], there are no structural investigations on ultrathin films of less than 26-nm thickness. We report results from three ultrathin BFO thin films (10, 20, and 50 unit cells thick, respectively) on STO substrates using surface x-ray diffraction (SXRD). Reciprocal space images during CTR scans, which are obtained from a PILATUS 100K area detector, allowed us to reconstruct three-dimensional reciprocal space maps (RSMs) around integer order film Bragg peaks and half-integer order film superstructure peaks.

For the 50 unit cells film, the film Bragg peak splitting corresponds exactly to the reported pattern for M_A structure [2]. Interestingly, as the film thickness decreases to 20 unit cells, a reduction in the peak splitting is clearly observed, while no splitting at all exists on the 10 unit cells film. To confirm the symmetry, all peaks at four-fold symmetrically equivalent positions were measured, and the same peak positions and splitting patterns were reproduced. This clearly indicates a transition from monoclinic to tetragonal symmetry for thinner films.

Moreover, the octahedral tilt pattern derived from the half-order diffraction peaks also supports this transition. For the 50-unit cell film, all half-integer order peaks except (h=k=l) were observed. This is compatible with an $a^-b^-c^0$ octahedral tilt pattern [4], which corresponds to a monoclinic structure. However, for the thinner film, a clear broadening of half-integer order peaks is observed only for h=k peaks. This indicates that the tilt pattern becomes $a^0b^0c^-$, which corresponds to a tetragonal symmetry.

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ENVIRONMENTAL & GEOLOGY

A-23

Tin Isotope Fractionation Studied Using Nuclear Resonant Inelastic X-ray Scattering

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NRIXS provides a new experimental method to determine the equilibrium stable isotope fractionation factors, which has been an extensive and important field of study in geo- and cosmo-chemistry. Over 60 years ago, Bigeleisen and Goeppert-Mayer proposed a theory relating isotope fractionation factor to its kinetic energy. One of the atomic dynamics quantities can be derived from NRIXS spectrum is isotope specific kinetic energy, thus it provides a direct and straightforward application of Bigeleisen and Goeppert-Mayer formalism. We summarize some of the tin NRIXS studies have been done so far and derive the tin isotope fractionation factors for the materials under study.

A-24

Evaluating the Effectiveness of Home Eater Filters Using Synchrotron X-ray Fluorescence

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Water filters are commonly used in the home to filter the impurities present in municipal water supplies. In some cases, water may contain metals and metalloids that are potentially harmful if ingested in significant quantities. In this experiment, our group analyzed commercially available household water filters to evaluate their effectiveness in filtering cadmium, arsenic, and lead. We are primarily interested in analyzing both the contaminants left over in the water after it has been processed in the filter and evaluate the distribution of the metals in the filter itself. For the experiment distilled water was spiked with known quantities of each of these elements. These contaminated water solutions were then pumped through a set of commercially available graphite filters at a fixed flow rate. Following this process each filter was dissected and samples were prepared representing the filter material at the center of the filter, filter material at the outer surface of the filter and the outer paper membrane. Samples were also prepared from blanks filters. These samples along with the water that had been filtered were then analyzed at beamline 13-BM-D via x-ray fluorescence to determine where the metals were sequestered in the filter media and the filter's effectiveness in extracting each metal from the contaminated water.

HIGH PRESSURE

A-25

High-pressure X-ray Diffraction Study for Piezoelectric Materials

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The structural stability of two piezoelectric materials under high pressure has been investigated through *in situ* high-pressure angle-dispersive x-ray diffraction experiments at room temperature. For the $Pb(Yb_{1/2}, Nb_{1/2})O_3–PbTiO_3$ (PYNT) case, the crystal structure evolution up to 50.1 GPa was measured, which revealed a ferroelectric–paraelectric phase transition at about 8.0 GPa. The bulk moduli of ferroelectric and paraelectric phases were estimated as $B0$ = 99(3) and 204(4) GPa, respectively. The structural stability of another piezoelectric material, $BaTiO_3$, was studied as well. These experimental results will give us insight into the origins of piezoelectric properties, and provide input for the better design of this kind of materials with optimized structure-property relationship.

A-26

The Study of Structural Stability for Transition Metallic Silicides under High Pressure

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Over the past decades, metallic silicides have attracted considerable interest because of their special properties for engineering applications in hostile environment of extreme temperature and pressure [1].

In-situ angle-dispersive synchrotron x-ray diffraction experiments were conducted on metallic silicides $TiSi_2$ and $TaSi_2$ up to around 50 GPa. The lattice parameters were refined using Rietveld method. The evolution of the unit cell volume of them with pressure was fitted by a second-order Brich-Murnaghan equation of state [2], giving the bulk modulii of 230(6) GPa and 243(7) GPa, respectively. No change in the diffraction patterns has been observed in the investigated pressure range, suggesting that the C54-type $TiSi_2$ and C40-type $TaSi_2$ are stable up to around 50 GPa.

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A-27

16-ID-D: High-pressure Spectroscopy Beamline at HPCAT

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As part of a third-generation synchrotron radiation beamline dedicated to high-pressure research, 16-IDD of HPCAT at the Advanced Photon Source engages in x-ray spectroscopy research of samples under high pressures, typically in diamond anvil cells (DAC) [1].

The spectroscopy line consists of IDA with a newly installed liquid nitrogen cooled Si (1 1 1) double crystal monochromator with ~1eV energy resolution, transport lines; IDC with an interchangeable high-resolution monochromator at ~2meV energy resolution and two 1-meter K-B mirrors; and IDD, the experiment station, with a 2.7 meter 0-90 degree horizontal spectrometer and a dedicated XES setup. Typical beam size at sample position is ~25(V) x 50 (H) μm^2 at FWHM when using meter-long KB mirrors, smaller beam size (4x5 μm^2) can be achieved by using a pair of 200-mm KB mirrors.

Current techniques include x-ray emission spectroscopy (also resonant x-ray emission spectroscopy), inelastic x-ray scattering (also x-ray Raman scattering), and nuclear resonant scattering (nuclear resonant inelastic x-ray scattering and nuclear forward scattering). Examples of high-pressure studies using these techniques and recent developments (including a short working XES spectrometer for DAC application and using polycapillary optics for x-ray Raman scattering and x-ray emission spectroscopy) will be discussed in details in the meeting.

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A-28

High-pressure X-ray Diffraction Study for 122-type Compounds

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The recent discovery of superconductivity in iron-based superconductors brings new excitement to the field of superconductivity. Pressure is 'clean' way to tune the structural and physical properties without changing the chemistry. We report the high-pressure and low-temperature synchrotron x-ray diffraction studies on powder $EuFe_2As_2$ using a membrane diamond anvil cell technique up to 31.5 GPa and down to 12 K. The temperature-pressure phase diagram of crystal structures of tetragonal (T, *I*4/*mmm*), orthorhombic (O, *Fmmm*) and collapsed tetragonal (CT, *I*4/*mmm*) phases of $EuFe_2As_2$ is presented. The geometry configuration variation of Fe_2As_2 layers for $EuFe_2As_2$ with various pressure at 12 K was studied. And as 122–type ($EuFe_2As_2$) superconductor, moderate distortion of $FeAs_4$ polyhedron is favorable.

A-81

Aseismic Deformation of Serpentinite undergoing Dehydration

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Serpentinite is one of the main constituents of the subducting slabs. Its dehydration, associated with the deformation processes that take place in the subduction zones, has long been thought to be responsible for triggering earthquakes at intermediate depths (i.e., 60–300 km) [1]. However, the origin of the so-called intermediate seismicity remains unclear and the role of serpentinite dehydration is still highly debated. In fact, a recent experimental study showed that the dehydration of serpentinite could lead to ductile rather than brittle deformation [2].

In order to address this issue, we have carried deformation experiments on natural serpentinite rock samples using the deformation-DIA (D-DIA) device (cubic multi-anvil press) available at sector 13 of the APS. A monochromatic incident beam was used with both a 2D MAR-CCD detector and a CCD camera to collect respectively full diffraction rings and radiographies of the sample. The data allow us to retrieve the stress and the strain of the sample [3]. In addition, the acoustic signal (i.e., the microseismicity) from the sample was monitored by the use of piezo-ceramic transducers glued on the basal truncation of the anvils.

The samples were deformed at strain rates of 10^{-5}–10^{-4} s^{-1} under confining pressures of ~4 GPa. The dehydration was triggered during the deformation by heating the samples at rates ranging from 5 to 60 K/min. Before the onset of the dehydration, the x-ray diffraction data show that the serpentinite sustains high levels of stress, which drop when dehydration occurs due to the soft character of the dehydration products. This stress drop was never accompanied by acoustic emissions, which suggests ductile deformation. Hence, unlike many previous studies, we document here an aseismic interplay between deformation and dehydration of serpentinite. The newly developed acoustic emissions setup now available at 13-BM-D has proven to be a very valuable addition to the classic D-DIA experimental setup and will be used further to assess the relations between mineral reactions, deformation and seismicity.

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INSTRUMENTATION

A-29

The X-ray Streak Camera at the APS

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Many processes in chemistry and solid-state physics occur on time scales faster than the 50 to 150 ps bunch duration of the APS. To obtain a time resolution of a few ps, one has to use a source with faster intrinsic time scale (XFEL, laser-plasma source), or, at the APS, use a fast detector. Sector 7 of the APS currently operates an x-ray streak camera with a time resolution of 2 ps, and upgrades are underway to reach 1 ps. Experiments are typically done in the pump-probe mode where the pulsed laser of sector 7 triggers a chemical or physical process in the sample, and x-rays transmitted or scattered by the sample provide information on subsequent processes in it. The streak-camera program also helps establish a viable picosecond-x-ray-science community at the APS, and thus contributes to the development of the future picosecond source.

A beamline infrastructure has been built around the streak camera including a set of pre-adjusted interchangeable experimental setups, an x-ray chopper to match the x-ray repetition rate to that of the laser, and a set of x-ray lenses with very long, continuously adjustable focal lengths to focus the x-rays simultaneously into the sample and onto the entrance slit in the streak camera. Recent upgrades include the use of microwave power technology instead of a photoconductive switch to generate the deflection voltage. The entire signal chain from a photodiode picking up a trigger pulse from the laser to the RF power drivers is fully linear (as opposed to the use of avalanche transistors, or a photoconductive switch), ensuring minimal jitter. Another upgrade is the use of a liquid-nitrogen-cooled CCD camera for readout from the phosphor screen, which permitted the removal of the amplifying micro-channel plates. This eliminated a major source of image noise, and enabled the detection of 0.1-percent transmission changes in x-ray spectroscopy.

The streak camera has been used for studies of solution-phase chemical reaction dynamics [1], phasetransition kinetics, and photoexcited charge-carrier dynamics in GaAs.

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A-30

The Hydra Trigger Module: An FPGA-based Solution for Multiple Detector/Device Triggering

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Structured around an Altera Cyclone II FPGA, the Hydra trigger electronics are a flexible, digital solution for triggering multiple detectors. The architecture developed will trigger up to four detectors, and has additional digital IO lines for external triggering or coordination with additional beamlines devices or electronics such a stepper motors or a shutter. The FPGA offers the possibility to develop custom triggering modes, and a on-board micro-controller further enhances flexibility as some triggering parameters may be controlled through an IOC interface. Accepting input from the accelerator timing signal, the module is an ideal platform for coordinated triggering with x-ray pulses for fast applications. This poster will focus on the architecture and capabilities of the electronics, and detail an initial implementation at 1-ID.

A-31

2D/3D Elemental Mapping of Frozen-hydrated Cells Using the Bionanoprobe

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X-ray fluorescence (XRF) microscopy is one of the most sensitive imaging techniques to study trace elemental distributions in biological specimens. By using spatially coherent, highly brilliant x-rays as the excitation source and advanced x-ray optics, current synchrotron-based XRF microprobes at the Advanced Photon Source (APS) at Argonne National Laboratory reproducibly achieve a 150-nm spatial resolution on biomaterials. Conventional sample preparation approaches for XRF imaging usually require dehydration, which may limit the ability to preserve "natural" element distribution at sub-100-nm spatial resolution. Additionally, even dried samples could accumulate radiation damage during repeated imaging and ultimately cause resolution degradation. As a comparison, imaging samples in their frozen-hydrated states not only allows the natural structure to be well preserved but also significantly increases the radiation tolerance of hydrated samples.

With the aim of studying frozen-hydrated biomaterials at sub-100 nm resolution, we have developed a Bionanoprobe (BNP). It is a sample scanning hard x-ray nanoprobe with cryogenic and robotic sample changing capabilities, and is the *first* microscope of its kind. The BNP has recently been assembled at Xradia Inc. and is currently under commissioning at an undulator beamline at Life Science Collaborative Access Team (LS-CAT) at the APS. Utilizing multiple zone plates, the BNP can be operated in an energy range from 5–20 keV, with a spatial resolution down to 30 nm for fluorescence mapping and 50 nm for spectroscopy. The cryo sample handling module and sample changing robot enable bio-samples to be well preserved around 100 K while being examined in the BNP. In addition to two-dimensional scans, the BNP also enables semi-automated tomographic data collection. In this presentation, we will show first results from this new instrument and highlight applications in the area of life sciences.

This research was supported by ARRA: NIH/NCRR High End Instrumentation (HEI) grant (1S10RR029272-01), and by Argonne LDRDs 2010-183-R1 9088 AND 2010-193-R1 9113. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

A-32

Integrated Platform for Combined XRD and SONICC/TPE-UVF Measurements for Identification and Centering of Protein Crystals

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An instrument is under development for integrating second-order nonlinear imaging of chiral crystals (SONICC) and two-photon excited ultraviolet fluorescence imaging (TPE-UVF) with a synchrotron x-ray diffraction beamline, targeting rapid screening for identification and centering of protein crystals. In SONICC, two photons of infrared light combine to form one photon of visible light at twice the frequency. The symmetry requirements of this process make it sensitive to non-centrosymmetric crystalline order, including the large majority of protein crystals and excluding most common salts, cryo-protectants, solvents, and aggregated protein. In TPE-UVF, the simultaneous absorption of two photons of visible light, the energy equivalent of one photon of UV light, results in emission of a photon in the near UV to blue range. The wavelengths used are sensitive to aromatic amino acid residues, particularly tryptophan, making ~80% of proteins detectable through a mechanism unique and complementary to SONICC. These imaging methods are sensitive to micron-sized crystals, including those grown in the lipidic mesophase that are otherwise difficult to visualize. Positioning by nonlinear optical imaging may reduce or eliminate the need for large area x-ray raster scanning thereby reducing x-ray induced radiation damage and increasing throughput of synchrotron x-ray diffraction. Integration with the synchrotron beamline allows a sample to be mounted on the goniometer, imaged, crystal centered, and ready for diffraction in just a few minutes.

A-33

The APS-U Short-pulse X-ray Instruments

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The Short-pulse X-ray (SPX) facility will extend time-resolved x-ray scattering and spectroscopy to the picosecond timescale while retaining the powerful characteristics of synchrotron radiation, i.e., user-controlled continuous tunability of energy, polarization and bandwidth combined with exquisite x-ray energy and pulse length stability over a wide energy range. Experiments at the SPX facility will produce two-picosecond stroboscopic snapshots of molecular rotations, molecular excited-state transient structures, stress/strain wave propagation, magnetic domain wall dynamics, phase transitions, and the coupling between electronic, vibrational, and magnetic degrees of freedom in condensed matter systems. Time-resolved studies of transient dynamics will be possible with simultaneous picosecond time resolution and picometer structural precision for a variety of atomic, molecular, supramolecular, nanoscale and bulk material systems. Transformational developments are now taking place in high-average-power pulsed laser technology, with substantially increased repetition rates that promise to make highly efficient use of the MHz x-ray repetition rates of the SPX. We propose to develop, in the context of the APS-U through regular and contingent scope, five endstations with scattering, diffraction, spectroscopy, imaging and microscopy capabilities.

A-34

Combining Altera FPGAs with Arcturus µC5282 Microcontrollers for Beamline Instrumentation at the APS

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At the Advanced Photon Source (APS), we continue to combine the power and flexibility of Altera Field Programmable Gate Arrays (FPGA) with Arcturus µC5282 embedded microcontrollers to provide low cost EPICS controlled solutions for beamline instrumentation.

In this paper, we discuss an application which couples an Altera Cyclone-II FPGA with an embedded Arcturus μC5282 microcontroller to implement an instrument for a time-resolved, pump-probe timing experiment.

A-35

50-MHz Voltage-to-frequency Converter for Beamline Applications

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The Voltage-to-Frequency Converter (V2F) is an instrument commonly used in synchrotron beamline experiments for converting a slowly varying voltage signal representing x-ray flux to a high-frequency pulse train, with each pulse representing a packet of x-ray energy. The pulses are then integrated with a digital counter to calculate total x-ray energy incident on a sample during an exposure. As x-ray experiment data is taken faster and faster and exposure times shrink, V2F frequencies must necessarily increase to preserve precision in measuring total x-ray energy. Because commercial V2F equipment is limited to 2 MHz, we have designed and built two custom 50-MHz V2F instruments for APS beamline experiments. The two instruments are designed to be used in a NIM crate and respectively reside at APS sector 12-BM, and in the APS Detector Pool.

A-36

Scanning High-resolution CCD Detector for Powder Diffraction

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We have designed and built a custom high-resolution CCD detector, called the "MiniX," for synchrotron powder diffraction experiments. The detector is mounted on a moving diffractometer arm with line-by-line image readout synchronized with arm movement, thereby creating a "film strip" of the powder diffraction pattern. The detector utilizes a commercial Kodak KAF-16801 high-sensitivity CCD with 4K × 4K 9-micron pixels that is thermo-electrically cooled, a 1:1 fiber-optic faceplate, and a Scint-X high-resolution structured phosphor. As the diffractometer arm is moved, pulses generated by the diffractometer motor system are used to trigger individual CCD line readout, thereby synchronizing the CCD to the motor system. The detector, made of plastic parts, is small and light enough to mount on the arm without disturbing existing experiments and is easily multiplexed. Because the CCD is an area detector rather than point detector like the current sector 11-BM-B PMT-based crystal analyzer instrument, data collection can be made orders of magnitude faster. Preliminary data collected at 11-BM-B suggest that the MiniX detector gives <2× the diffraction peak widths compared to what the current detector system at 11-BM gives, but collects data in one-tenth the time. This compares well with large area detectors (200-micron pixels) where the peak widths are >5× that of the 11-BM-B crystal analyzer system.

A-37

EPICS support for Ethernet Version of Turbo PMAC2 Motion Controllers

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Motion controllers are critical tools used in experiments carried out at synchrotron radiation beamlines. For nearly a decade, the GM/CA facility for macromolecular crystallography at the Advanced Photon Source has successfully used the VME-based Delta Tau Turbo PMAC2- UltraLite motion controllers as a sole source for all motion controls tasks. Given the proven efficiency, speed, and robustness in 24/7 users operations this system has been adopted by other beamlines (LS- and IMCA-CATs at the APS, at the Diamond Light Source and at the Australian Synchrotron). A powerful EPICS [1] client infrastructure was built on top of this motion controls layer, including various automations with fast on-the-fly scans and the highly praised JBluIce software for automated data collection in macromolecular crystallography. Given these prerequisites, it is crucially important to keep the compatibility with already developed infrastructure when upgrading a beamline to more modern motion controllers.

At GM/CA we are developing a new microfocus experimental station and have chosen Delta Tau's next generation motion controller solution. This compact, standalone controller uses an Ethernet port for communications; and therefore, does not requiring a VME host. This UMAC Turbo CPU Communications Board [2] is a member of the Turbo PMAC2 family of boards. In spite of its compactness, the new board does not sacrifice the advantages of the VME version such as the capability of controlling up to 32 axes, availability of various accessories for reading encoders, end-of-travel and home sensors, etc. Different kinds of axes interface boards also can be selected to control analog ±10V amplifiers, stepper drivers and direct digital PWM amplifiers.

We have developed a new EPICS driver for this motion controller. It runs within a soft IOC on a LINUX computer and uses a dedicated Ethernet connection with the motion controller. The new driver is completely compatible with the EPICS databases that were developed for the previous TPMAC2 driver [3] for VME-based EPICS IOC, and thus all client controls such as fast scans and JBluIce are seamlessly preserved with the new controller.

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[1] http://www.aps.anl.gov/epics/

[2] http://www.deltatau.com/

[3] http://www.gmca.aps.anl.gov/makarov/TPMAC2/

A-38

Status of Microwave Kinetic Inductance Detectors at APS

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We present the current status of microwave kinetic inductance detector (MKID) development at APS. We will compare MKIDs to other energy-dispersive detectors as well as with wavelength-dispersive systems for a variety of x-ray spectroscopic applications. We will present an overview of the instrumentation for testing MKID devices including cryostat, microwave electronics, and data analysis. We will present our in-house fabrication efforts and present results on a new material for MKIDs, tungsten silicide. Finally, we will present our short- and long-term plans.

A-39

EPICS at Home

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We demonstrate the use of EPICS (Experimental Physics and Industrial Control System) to control a custom-built Langmuir trough used for research on soft matter interfaces. This gives us great flexibility for customized control and easy integration into the APS beamlines software control environment. We will show how we implemented EPICS with Soft IOC (Software Input Output Controller) together with the PyEpics (Epics Channel Access for Python) for the data acquisition and archiving into MySQL database.

We facilitated the data visualization and processing entirely with web-based user interactive tools i.e. time-series javascript visualization library dygraphs making server-side ajax calls to the MySQL database stored procedures. Various javascript tools are used for the data annotation and browsing attempting to provide lab logbook capabilities.

A-40

X-ray Excited Luminescence Microscopy

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We have developed an imaging technique based on x-ray excited luminescence microscopy (XELM), that will enable elemental and magnetic specific imaging of a wide range of materials such as those used in solar cells, magnetic materials, spintronic devices, ferroelectrics, and solid-state lighting. This new scientific tool utilizes the benefits of pulsed, polarized, tunable synchrotron radiation excitation with microscopic detection of the resulting optical emission. A unique offshoot of the microscope is the ability to perform element specific magnetic microscopy of micron-sized features or domains in magnetic fields. X-rays transmitted through thin films are attenuated and the resultant absorption spectrum can be determined by changes in the substrate luminescence. Since many substrates, such as $SrTiO_3$ and GaAs, used in thin film growth have intense optical emission, this tool should impact many materials where photoelectron emission microscopy (PEEM) cannot be performed since it is not useable on insulating materials or if magnetic or electric fields are required. This approach will be especially useful at low temperatures where luminescence yields are highest, and PEEM has difficulties. In this presentation we will present some initial results from the microscope on some prototype solar cell materials and lithographically patterned Permalloy/GaAs and trilayer Cobalt/Cu/Permalloy/GaAs samples. The results demonstrate the potential of XELM for elemental and magnetic specific imaging.

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A-41

Progress in X-ray Detector Instrumentation at the APS

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We continue to develop x-ray detection systems for timing and hard x-ray imaging applications. We discuss plans and results from our work with single-photon-counting time-resolved detectors such as avalanche and picosecond range photo diodes. We also discuss our continued developments of pixel array detectors with emphasis on our clean room fabrication of the thick high-resistivity silicon x-ray sensors and the readout application specific integrated circuitry.

A-42

Using MEMS Devices to Control Synchrotron X-ray Pulses

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We demonstrate the use of electrostatically driven micro-electromechanical systems (MEMS) devices to control and deliver synchrotron x-ray pulses at high repetition rates. Torsional MEMS micromirrors, rotating at duty cycles from 2 kHz to 75 kHz, were used to modulate grazing-incidence x rays, producing x-ray bunches as short at 1 μs. We find that dynamic deformation is a limiting factor in the duration of the x-ray pulses produced and describe adaptations to the micromirror design that minimize that deformation. Finally, we discuss prospects for reaching higher operating frequencies and eventually isolating individual x-ray pulses or spatially separating nearby x-ray pulses.

A-43

Optomechanical Design of Ultrahigh-resolution Monochromator and Analyzer for Inelastic X-ray Scattering Spectrometer at the Advanced Photon Source

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A prototype of a novel ultrahigh-resolution inelastic x-ray scattering spectrometer has been designed and tested at undulator-based beamline 30-ID, at the Advanced Photon Source (APS), Argonne National Laboratory. This state-of-the-art instrument is designed to meet challenging mechanical and optical specifications for producing ultrahigh-resolution inelastic x-ray scattering spectroscopy data for various scientific applications [1]. The optomechanical design of the ultrahigh-resolution monochromator and analyzer for inelastic x-ray scattering spectrometer as well as the preliminary test results of its precision positioning performance are presented in this poster [2].

This work is supported by the U.S. Department of Energy, Office of Science under Contract No. DE-AC02-06CH11357.

[1] Yu. Shvyd'ko, S. Stoupin, D. Shu, and R. Khachatryan, Phys. Rev. A 84, 053823 (2011).
[2] D. Shu, S. Stoupin, R. Khachatryan, K. Goetze, T. Roberts, and Yu. Shvyd'ko, Proceedings of SPIE Vol. 8125-6, San Diego, CA, Aug. 2011.

A-44

Near 100% Bragg Reflectivity of X-rays

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Ultra-high reflectance mirrors are essential for the most sophisticated optical instruments devised over entire frequency spectrum. In the x-ray regime, super-polished mirrors with close to 100% reflectivity are routinely used at grazing angles of incidence. However, at large angles of incidence and especially at normal incidence, such high reflectivity has not been previously achieved.

We demonstrate by direct measurements that synthetic, nearly defect-free diamond crystals reflect more than 99% of hard x-ray photons backwards in Bragg diffraction, with a remarkably small variation in magnitude across the sample [1]. This is a quantum leap to the largest reflectivity measured, which is at the limit of what is theoretically possible. It is attained under most challenging conditions of normal incidence and with extremely hard x-ray photons.

[1] Yu. V. Shvyd'ko, S. Stoupin, V. Blank, and S. Terentyev, "Near 100% Bragg reflectivity of x-rays," Nature Photonics, 5, 539542, 2011.

A-45

Using Angular Dispersion and Anomalous Transmission to Shape Ultra-monochromatic X-rays

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Optical spectrometers, instruments that work with highly monochromatic light, are commonly rated by the spectral bandwidth, which defines the ability to resolve closely spaced spectral components. Another equally important feature is the spectral contrast, the ability to detect faint objects among these components. Here we demonstrate that a combined effect of angular dispersion (AD) and anomalous transmission (AT) of x rays in Bragg reflection from asymmetrically cut crystals can shape spectral distributions of x-rays to profiles with high contrast and small bandwidths.

The AD&AT x-ray optics is implemented as a five-reflection, three-crystal arrangement featuring a combination of the above mentioned attributes so desirable for -ray monochromators and analyzers: a spectral contrast of ≈ 500, a bandwidth of ≈ 0.46 meV, and a remarkably large angular acceptance of ≈ 107 mrad with 9.1 keV x-rays [1]. The new optics can become a foundation for the next-generation inelastic x-ray scattering spectrometers for studies of atomic dynamics.

[1] Yu. Shvyd'ko, S. Stoupin, D. Shu, R. Khachatryan, "Using angular dispersion and anomalous transmission to shape ultramonochromatic x rays," Phys. Rev. A, 84, 053823 (2011).

A-46

Diamond Crystal Optics for Self-seeded Hard X-ray Free-Electron Lasers

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We present design, fabrication and results of x-ray characterization of thin synthetic type IIa diamond plates developed for the Hard X-ray Self-seeding Project (HXRSS) at the LCLS. The goal of the project was to achieve generation of fully coherent x-rays by the x-ray free-electron laser using the self-seeding concept and the single-crystal diamond wake monochromator [1, 2]. High crystal quality and a small thickness of ≈ 0.1 mm were the main required parameters for the diamond crystals. Nearly defect-free diamond plates of (001) orientation, $4\times4\times0.1$ mm^3 in size, and of a trapezoidal shape were fabricated and preliminarily evaluated at the Technological Institute for Superhard and Novel Carbon Materials (Russia). The plates were further characterized using x-ray topography at the Advanced Photon Source (Argonne National Laboratory). These tests helped to minimize strain in the crystals induced by the crystal holder and to determine defect-free crystal regions. Self-seeding experiments were conducted at the LCLS in January 2012 using the diamond plates selected by our studies. Fully coherent 8.33 keV x-rays with 5×10^{-5} relative bandwidth were produced [3].

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A-47

Fast CCD X-ray Detector Collaborations between ANL and LBNL

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This poster presents an update on the Fast CCD detector collaborations between the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL).

The detector collaboration now consists of two different x-ray detectors. The initial collaboration developed and built a number of 480 Fast CCD detectors [1], with a nearly column parallel readout. Over the past few years, the 480 FCCD detectors have been used at APS, ALS, and at LCLS. The collaboration is now focused on completing an ARRA project, which is to build a number of 1K Frame-Store CCD (1kFSCCD) x-ray detectors which can be operated as a 1920 x 960 CCD detector or a 960 x 960 frame store CCD detector [2]. Also introduced is a possible future phase of this collaboration, which is to develop a CCD detector with a fully column parallel readout.

Work supported by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

[1] D. Doering, Y.-D. Chuang, N. Andresen, K. Chow, D. Contarato, C. Cummings, E. Domning, J. Joseph, J.S. Pepper, B. Smith, G. Zizka, C. Ford, W.S. Lee, M. Weaver, L. Patthey, J. Weizeorick, Z. Hussain, and P. Denes. "Development of a compact fast CCD camera and resonant softx-ray scattering endstation for time-resolved pump-probe experiments," Rev. Sci. Instrum. 82, 073303 (2011).

[2] Dionisio Doering, Nord Andresen, Devis Contarato, Peter Denes, John M. Joseph, Patrick McVittie, Jean-Pierre Walder, John Weizeorick, Bob Zheng "High Speed, Direct Detection 1k Frame-Store CCD Sensor for Synchrotron Radiation" (NSS/MIC), 2011 IEEE, Digital Object Identifier: 10.1109/NSSMIC.2011.6154370.

A-48

A Compact Visual Beam Imaging System on the GM/CA-CAT BM Beamline

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A typical problem encountered on a beamline with a sagittal focusing monochromator is difficulty optimizing the crystal alignment because the full width of the monochromatic, unfocused beam cannot be visualized. This problem is particularly acute on beamlines with a fixed experimental setup and constrained apertures that only allow the focused beam to pass through to the focal position. To address this problem, an imaging system has been designed and implemented on the GM/CA-CAT bending magnet beamline at the Advanced Photon Source at Argonne National Laboratory. This imaging system consists of a 30 mm x 50 mm flat YAG crystal, right-angle prism/mirror and video camera located downstream of the vertical collimating mirror, sagittally focusing monochromator and vertical focusing mirror. The YAG crystal was installed in a six-way vacuum cross in the beam path, and was mounted on a linear translation feed through allowing remote insertion and removal of the crystal form the beam path. The video camera was mounted outside the vacuum chamber and views the x-ray induced scintillation form the YAG crystal through a window. This visualizer allows one to optimize the twist, yaw and roll of the monochromator second crystal, facilitates proper sagittal focusing and serves as a remote controlled diagnostic tool. An overview of the design and the performance of the imaging system will be presented.

A-49

The Microfocus Beamline at GM/CA-CAT

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For many years it was thought that micron-sized crystals of proteins and other macromolecules were too small to yield useful structural information. Given the success of the pioneering work at the ESRF's ID-13, other beamlines sought to provide micro-crystallography capabilities. At the General Medicine and Cancer Institutes' Collaborative Access Team (GM/CA-CAT), we developed the mini-beam quad collimator to allow users to rapidly (a few seconds) select a 5-, 10-, or 20-μm diameter beam or a scatter guard (which permits the full focused beam to be slit down to ~30 μm). To fully exploit the capabilities of the mini-beams, we developed software tools such as "raster" and "vector collect" and incorporated them in our JBluIce-EPICS control software. Access to such tools has significantly altered how biologists approach structure determination, resulting in the solution of the several important structures and increasing the demand for high-intensity microcrystallography capabilities.

To meet this demand, GM/CA is upgrading one of its insertion device beamlines (23-ID-D) to provide a high-intensity beam whose size can be varied from 1 to 20 μm. New on-axis visualization will provide high-resolution images of micron-sized crystals. An air-bearing-based goniometer is being developed with a target peak-to-peak sphere-of-confusion of ~100 nm for reliable centering and rotation of micron-sized crystals in the focus beam. The goals for the new microfocus optics include two overlapping modes of operation that allow the beam size to be varied rapidly (a few seconds) within a mode and quickly (a few minutes) between modes. The micro-beam (1–5 μm), and mini-beam (3–20 μm) modes will increase the intensity 100-fold and 10-fold, respectively, over that currently available on our beamlines. The details of these plans will be presented.

MATERIALS SCIENCE

A-50

Spatio-temporally Separating Electron and Phonon Thermal Transport in Nanostructured Magnetic Thin Films Using Picosecond Time-resolved Laser Pump/X-ray Probe Diffraction

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Lattice dynamics and the associated nanoscale thermal transport under laser heating have attracted much attention in both areas of fundamental science and applications. Here, we report an *in-situ* study of nanoscale thermal transport in FePt/Ag/MgO media films through lattice dynamics using picosecond time-resolved laser pump/X-ray probe measurements. It shows that the Ag heat sink layer gave a fast cooling and a nearly instant decrease of lattice expansion and temperature of FePt magnetic layer. Furthermore, we demonstrate a method to fit the decay of thermally induced lattice expansion using the exponential decay function derived from the thermal diffusion equation with the convolution of x-ray beam temporal profile. In particular, the electron and phonon contributions to thermal conductance are separated in the hybrid nanostructured interfaces, opening up new possibilities for probing the dynamic thermal processes in complex nanostructures.

A-51

EXAFS from Technetium Alloys

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Technetium metallurgy represents a largely unexplored topic owing to the natural scarcity of technetium and the inherent difficulties of working with this radioactive element. There are few practical applications for technetium, the most notable being the short-lived Tc^{99m}, which is widely used for medical imaging, although not in its metallic state. In the environment of nuclear fuel, however, technetium is not soluble in the UO_2 matrix, and exolves, along with other 4d metal fission products into a separate, metallic phase, known as an epsilon particle. The complex chemistry of technetium also lends itself to relative stability in certain metallic alloys. A suitably durable alloy would be desirable for a technetium waste form to be made from nuclear fuel reprocessing by-products. For these reasons we have examined the chemical and structural behavior of technetium using EXAFS in a variety of metallic alloys and intermetallic compounds, including spent fuel-derived epsilon particles. These results are presented along with other data to develop an understanding of technetium behavior in metals.

A-52

In situ High-energy X-ray Diffraction Study of Phase-stress Partition and Mechanical Damping in NbTi/NiTi Nanocomposite

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The phase-stress partition and mechanical damping in a NbTi/NiTi nanocomposite were investigated by employing *in situ* high-energy x-ray diffraction during tensile cycling. The phase-stress partition behavior in the nanocomposite is significantly different from that previously reported in the metal-matrix composites. Beyond the initial elastic deformation, the stress carried by the NbTi nanowires increased significantly with increasing macroscopic strain, while the stress taken by the NiTi matrix decreased gradually. It is revealed that the stress-induced martensitic transformation of NiTi matrix still proceeded even though the matrix carried decreasing stress rather than constant or increasing stress well known in binary NiTi alloys. The mechanical damping of the nanocomposite measured under an applied 8% strain is up to 54 MJ/m^3, which is over three times higher than that (16 MJ/m^3) found in the well-known Ni-Ti alloys. It is revealed that a redistribution of stress between the nanowires and matrix was evidenced from an abrupt change in residual lattice strains. The ultrahigh mechanical-damping property originated from a combination of the strong interaction of nanowires and matrices and the plastic deformation occurring in NbTi nanowires during deformation causing large energy dissipation.

A-53

Time-resolved SAXS Measurements of UV-induced Restructuring in Photogelling Nanoparticle Dispersions

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Responsive systems exhibiting a phase change have become the subject of increasing amounts of research in the recent years. These range from shape memory alloys to stimuli-responsive polymers and composites. The current work focuses on a nanocomposite system consisting of a dispersion containing Laponite nanoparticles (3 wt. %), a triblock copolymer (Pluronic F127, 3.6 wt %) and a photo acid generator (PAG, <20 mM). While Laponite dispersions are known to form a physical gel based on electrostatic inter-particle interactions, the present formulation only undergoes a liquid to gel transition only upon ultraviolet (UV) illumination. We attribute this to the synergistic interactions between the nanoparticles and block copolymer result in a screening effect preventing inter-particle interactions. Exposure to UV light results in a chemical reaction that results in a deshielding process enabling the electrostatic interactions between particles and resulting in the formation of a gel. We have probed the liquid to gel transition kinetics using *in-situ* photorheology; however, the structural changes that occur are not well understood.

Here, we use simultaneous *in-situ* UV small-angle x-ray scattering (SAXS) as a method of tracking structural changes induced as a function of UV exposure at room temperature. Our data shows that this system exhibits a shows a peak in a Kratky plot (I(q).q2 vs. q) which can be correlated to the inter-particle spacing within the probed volume. The changes in this peak position and shape over time can then be related to the physical structure within the sample and the time scale taken for the system to undergo reach a stable state. Our results shows that this time scale differs from those measured via *in-situ* photorheology and we attribute these changes to the different volumes being probed. Initial work also shows that the system chemistry, such as the type of PAG used, has a significant effect on the structural evolution.

A-54

In-situ Structural Characterization of Layered $NaLiMnNiO_2$ Cathode in Operating Na-ion Battery Using XAS

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There is a growing demand of large-scale energy storage systems for stationary applications. Due to relatively more abundance and lower cost of Na than Li, research on rechargeable Na-ion batteries has received renewed interest in recent years. An understanding of the local structural changes of the cathode during electrochemical Na^+ extraction/insertion would expectedly help designing newer electrode materials, which will increase overall energy density. Owing to the success of Li-ion batteries based on layered $LiMO_2$ (M=first low transition metals) cathodes, various layered Na analogues are being studied as cathodes in rechargeable Na-ion batteries. We have performed *in-situ* x-ray absorption spectroscopy (XAS) experiments on layered $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ cathode in a working Na-ion cell in order to understand the charge compensation mechanism and local structural changes during Na-ion battery operation, which showed that Ni centers were primarily responsible for the observed electrochemical activity. The details of the observed local structural evolution around Ni and Mn in layered $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ cathode during electrochemical Na extraction/insertion will be presented.

A-55

Development of Oxide Molecular-beam Epitaxy for *In-situ* Synchrotron X-ray Study

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The layered complex oxide materials offer a broad range of functionalities including magnetic, ferroelectric, and dielectric properties. Unfortunately, the growth of such oxide materials remains a major challenge due to the lack of quantitative feedback during synthesis. For the systematic exploration of oxide synthesis, we have developed world's first oxide molecular-beam epitaxy system with *in-situ* synchrotron x-ray scattering capability. The molecular-beam epitaxy is equipped with a x-ray diffractometer, a highly concentrated ozone supply, and differentially-pumped effusion cells. During synthesis, x-ray crystal truncation rods and reflection high electron energy diffraction can provide information for surface reconstruction, interface structure, film relaxation, and more. Our x-ray studies have been focused on the growth of SrO and TiO_2 layers and the Ruddlesden–Popper homologous series of $Sr_{n+1}Ti_nO_{3n+1}$ by using oxide molecular-beam epitaxy. Layering of each oxide (SrO and TiO_2) at growth temperature has been investigated to improve the film structure and stoichiometry of Ruddlesden-Popper series. We anticipate that the combination of oxide molecular-beam epitaxy and *in-situ* x-ray will contribute substantially to the advancement of complex oxide science.

A-56

Electrostatics-driven Assembly of Uni-lamellar Catanionic Facetted Vesicles

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Nature utilizes shape to generate function. Organelle and halophilic bacteria wall envelopes, for example, adopt various polyhedral shapes to compartmentalize matter. The origin of these shapes is unknown. A large variety of shell geometries, either fully faceted polyhedra or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shells, can be generated by coassembling water-insoluble anionic (–1) amphiphiles with high valence cationic (+3) amphiphiles. Electron microscopy, x-ray scattering, theory, and simulations demonstrate that the resulting faceted ionic shells are crystalline, and stable at high salt concentrations. The crystallization of the co-assembled single tail amphiphiles is induced by ionic correlations, and modified by the solution pH. This work promotes the design of faceted shapes for various applications and improves our understanding of the origin of polyhedral shells in nature.

A-57

Wide-angle X-ray Scattering Characterization of Paracrystalline and Amorphous Thin Films

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In light of advances in detector technology, we revisit wide-angle x-ray scattering techniques including anomalous x-ray scattering and their application to paracrystalline and amorphous thin films that are of technological importance. For thin film materials, the asymmetrical reflection geometry is employed to avoid the substrate signals. Incident x-ray angles are typically set close to the critical angles. There are various complications related to this geometry and raw scattering patterns are distorted. In addition, because these materials are typically weak scatterers due to disorder, increased data collection efficiency is always desired. In this presentation, we report our activities at the DND-CAT 5-BM-D beamline using a four-element vortex Si-drift detector for anomalous wide-angle x-ray scattering experiments and describe some preliminary results on transparent conducting oxide thin films.

A-58

Synthesis and Characterization of High-Capacity Cathode Materials for Lithium Ion Cells

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Lithium-ion batteries (LIBs) power most portable consumer electronic devices due to their high energy density, good efficiency, ability to recharge, and reasonable cost. New worldwide efforts are focused on expanding the applications of LIBs to transportation and storage of renewable energies; however, the high cost and poor durability of state-of-the-art LIBs are main obstacles for such applications. Commercial LIBs have durability problems; their performance decays with charge/discharge cycles (voltage decay) due to degradation of the cathode. One of the most important challenges in the improvement of Li-ion technology is the development of more efficient, durable, and low-cost cathode materials.

We have synthesized a series of 'layered-layered' (xLi_2MnO_3•(1-x) $LiMO_2$), 'layered-spinel' and 'layered-rocksalt' composite electrode structures with improved electrochemical properties. To obtain a deeper understanding of the significant voltage decay exhibited by 'layered-layered' lithium-metal-oxide cathode materials, high-resolution x-ray diffraction (HRXRD) and pair-distribution function measurements (PDF) have been initiated at the Advanced Photon Source. As an example, xLi_2MnO_3•(1-x)$LiCoO_2$ samples with x=0.1, 0.3, 0.7, and 0.9 were prepared and annealed at 850°C. These preliminary data suggest the formation of a complex structure, exhibiting solid-solution behavior within a composite "Li_2MnO_3" and "$LiCoO_2$" matrix. Structural refinement and fitting are being conducted that will provide additional insights into the framework connectivity before and after cycling.

This work was supported by the Office of Vehicle Technologies, Office of Energy Efficiency and Renewable Energy of the U.S. Department of Energy. MB and Sector 20 facilities at the Advanced Photon Source of Argonne National Laboratory, and research at these facilities, are supported by the U.S. DOE, Basic Energy Sciences, and National Sciences and Engineering Research Council of Canada and its founding institutions.

A-59

The Role of Thermo-mechanical Loads on Depth-resolved Strain in EB-PVD Thermal Barrier Coatings—*In-Situ* Synchrotron Studies

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The durability of thermal barrier coatings (TBC) applied on turbine blades are greatly influenced by the cyclic thermal and mechanical loads experienced in gas turbines. Although the TGO increases thermal efficiency, it experiences critical stresses due to the thermal expansion mismatches within the TBC system leading to failure. To measure the in-cycle strain behavior responsible for failure, EB-PVD TBC samples were examined under *in-situ* thermal-mechanical operating conditions using x-ray diffraction from the high-energy synchrotron at the Advanced Photon Source. Measurements were obtained throughout the duration of the thermal-mechanical cycle for the various layers of the TBC system. Strain relief from the mechanical loading at high temperature (1121°C) was determined from our measurements to be approximately 3.2 MPa per unit applied axial stress. At an applied stress of 64 MPa, the TGO experiences tensile strains at the initial high operating temperature point. This is a critical point within the cycle for possible initiation and propagation of through-thickness cracks. These in-cycle measurements give new insight to the strain evolution throughout the thermal-mechanical cycle. The determined strain measurements can accurately validate models providing a realistic representation of the life expectancy and failure mechanisms seen in TBCs.

A-60

Structural and Mechanistic Revelations on an Iron Conversion Reaction from Pair Distribution Function Analysis

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Nanoscale electrodes (1–100 nm) are expected to play a significant role in the next-generation of high-performance batteries [1, 2]. However, due to the nano-size of both starting materials and products during operation, characterizing their structure and behavior presents a challenge that is yet to be fully addressed. High-energy x-ray pair distribution function (PDF) methods are capable of providing direct, atomic-level structural insights into nanomaterials, greatly enabling the understanding of their complex phase-behavior [3–5]. As such, the technique is well suited to investigate conversion electrode materials and the multiple phases that form and coexist during battery operation. Here, we present an *ex situ* PDF study on the complete electrochemical lithiation of α-Fe_2O_3, revealing new details regarding the local structure of the intermediate phases and the formation of iron nanoparticles during discharge. An emphasis will be laid on the merits of using PDF analysis to characterize and study nanoscale electrode materials for energy storage applications.

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A-61

Time-resolved, *In-situ* SAXS/WAXS Analysis of Pt Nanoparticle Synthesis at the Atomic Cluster to Nanocrystal Transition

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We have recently discovered a previously unknown Pt structure that exhibits substantially enhanced electrocatalytic oxygen reduction reactivity (ORR) relative to state-of-the-art commercial systems [1]. This new Pt structure exists as a tightly packed but non-crystallographic assembly of atoms that bridges the transition from atomic clusters to single-crystal nanoparticles. Such a novel arrangement of Pt atoms presents an opportunity for new research across a range of fields including magnetics [2], electrocatalysis [1, 3, 4], optics [5, 6], and selectivity in gas-phase synthesis [7]. We hypothesize that the enhanced catalytic activity of this transitional structure occurs due to the cooperative interplay of closely arrayed surface active sites. The synthesis technique we have developed to produce this transitional structure has been shown to yield fine discrimination of particle sizes with small standard deviations and permits systematic, well controlled alteration of bulk atomic structure (as observed using HAADF-STEM). Our vision for this research is to use these well-defined nanoparticles to understand the fundamental basis of size-dependent ORR activity; to use this information for the rational design of highly active electrocatalysts; and to apply this understanding to other heterogeneous catalyst systems. Control over nanoparticle size and structure requires knowledge of growth mechanisms. The need for his information is common to all nanoparticle synthesis methods but has only recently begun to be addressed through experiment using time-resolved, *in-situ* x-ray scattering data [8–11].

Despite significant progress understanding the impact of synthesis parameters on the resulting size and shape of Pt nanoparticles [12–16], experimental data concerning fundamental growth processes is difficult to gather [17] due to the need for rapid, in-situ measurements. Instead, laborious trial-and-error experiments have previously been used to determine optimum synthesis conditions for a given nanoparticle shape, size, and distribution. Time-resolved examination of evolving particle size, shape, and distribution for greater mechanistic insight can be facilitated by synthesis methods with more gradual but distinct particle nucleation and growth steps. In this study, we present a detailed analysis of x-ray scattering data obtained during the autocatalytic reduction of a Pt-Sn complex in aqueous solution to form stable, monodisperse nanoparticle suspensions without the use of organic surfactant. A diffusion-limited, primary-particle coalescence mechanism is revealed from fitted data made possible by this sufficiently wellresolved synthesis scheme and extended q-range observations from combined small-angle and wide-angle x-ray detectors. We also show the generation of critical nuclei as hypothesized by LaMer [18] from scattering data on a length scale approaching 2 Å. Our results suggest that particle size control is achieved through non-specific $SnCl_2$ ligand binding. This work provides fundamental correlations between synthesis conditions, growth mechanisms, particle size, number density, and polydispersity that may be extended to other catalytic materials of interest. The work also demonstrates a need to extend the observed scattering angle using combined small-angle and wide-angle detectors as a means to achieve a complete understanding of nanoparticle growth characteristics at sub-nm lengths scales.

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A-62

From Kidney Stones to Gold: Lessons from Biology to Build Better Nanomaterials

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Almost every living organism, from the smallest bacteria to giant whales and elephants, can manufacture highly ordered, organized, and multi-functional hybrid materials, i.e. biominerals. They can control the size, shape, morphology, and orientation of inorganic crystals and deposit them together with organic materials in a multi-level organization from atomic to macroscopic length scales. Moreover this precise assembly of molecules happens in ambient conditions and relatively dirty environments compared to our ultra-high-vacuum techniques and high-temperature treatments for material synthesis. The molecular interactions between the organic and inorganic components of biominerals during nucleation and growth are the underlying basis of this process. However, probing the molecular interactions between the organic matrix and inorganic crystals *in vivo* as real biomineralization occurs is not possible for most biological systems. Therefore it is necessary to develop some *in vitro* models that mimic biomineralization, where *in situ* experiments are doable. We use Langmuir monolayers, floating monolayers of amphiphilic molecules on aqueous subphases, which make it possible to use synchrotron x-ray scattering techniques to study the organic-inorganic interface *in situ* at the molecular level during biomimetic crystallization.

We have studied a wide range of materials to see the effects of organic template in the crystallographic orientation of inorganic crystals. We show that the same organic template can act very differently while growing calcium oxalate monohydrate (kidney stone) or calcium phosphate (bone) minerals. In contrast to assumptions generally made in biomineralization research, our results show directly that both organic monolayer and mineral structures can change during biomineralization and epitaxial interactions are mainly responsible from this change. We also demonstrate how we can utilize what we learn from calcification in biological systems to grow oriented gold nanoparticles in a biomimetic way.

A-63

Probing Structures of Electrolytes at Graphene Surface: Coupling X-ray Interface Scattering with Molecular Modeling

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The interactions of electrolyte fluids with carbon-based electrodes control many complex interfacial processes encountered in electrochemical energy storage systems. However, our knowledge of the atomic/nanoscale reactivity at interfaces of electrolytes with electrodes remain scares due to the incomplete understanding of interfacial structures and processes in-situ and real-time encountered in real operation conditions. In this talk, we will present our efforts to obtain a molecular-scale perspective of the interactions of electrolytes with carbon surfaces near "real world" conditions. Structures of various electrolytes including aqueous and ionic liquids on atomically flat graphene (epitaxially grown on a SiC substrate), an ideal model fluid-solid interface system, were investigated by coupling high-resolution interface x-ray scattering techniques with molecular modeling-simulation approaches. These results provide a baseline for understanding relevant electrolyte/carbon interactions and will lead to fundamentally new insights and provide unique tests of atomistic fluid-solid interface models for energy storage systems.

NANOSCIENCE & NANOTECHNOLOGY

A-64

Closed-loop SEM Dimensional Feedback of FIB Milling Process on a FIB-SEM

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A dedicated software and hardware-based lithography platform is used on a common FIBSEM tool to provide non-destructive, closed-loop, SEM-based metrology corrections during the FIB milling process. Dual-use FIB-SEM tools are increasingly used for more demanding patterning tasks that rely on precise pattern placement and/or dimension control. Easily verifying (and subsequently correcting for) pattern accuracy during the milling process in an automated or otherwise dynamic way has previously not been possible. This has now been achieved by controlling both the ion optics and electron optics via a common interface. The lithography-based pattern generator and software suite provides for independent alignments for each column, beam drift and stage offset corrections, dimensional metrology and feedback algorithms, etc. In an automated fashion, we have used SEM-based metrology results as feedback to the FIB milling process to achieve final size accuracy of better than 0.2%.

A-65

A Novel Synthesis and Characterization of Copper Chloride Nanocrystals in a Sodium Chloride Matrix

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Copper chloride nanocrystals of various sizes are grown using simple materials, methods and standard lab heat sources, without the need for sophisticated crystal growth apparatus or control of atmosphere. The size and volume distribution of the nanocrystals is studied with small-angle x-ray scattering and confirmed, along with morphology, using transmission electron microscopy. The composition of the nanocrystals is investigated using optical fluorescence emission and verified using energy dispersive spectroscopy.

A-66

Withdrawn

OTHER

A-67

Time-resolved Mn KβX-ray Emission Spectroscopy Analysis of the Photosystem II Protein Complex

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Large-scale implementation of man-made systems based on artificial photosynthesis to harvest solar energy could lead to an abundant chemical storage of solar power in the form of hydrogen. The process of splitting water ($2H_2O\ O_2+4e^-\ +4H^+$) in Photosystem II, the trans-membrane metalloprotein complex responsible for splitting water in the photosynthetic process, requires a catalyst, the oxygen- evolving complex (OEC) Mn_4Ca cluster. Characterization of sub-millisecond reactive intermediates in this system is central to understanding the catalysis involved in water splitting. X-ray emission spectroscopy (XES) is an informative technique for the analysis of the oxidation and spin states of the Mn center, as well as its ligand environment [1].

The challenge is to build an XES spectrometer that can be efficiently utilized in time-resolved experiments and provide sufficient sensitivity for the analysis of dilute samples such as Photosystem I. (0.5-mM Mn concentration). Two new dispersive short working distance miniXES instruments provided the instantaneous Mn Kβ spectrum collection necessary for rapidly damaging samples with sufficiently low background [2]. Two different geometries were tested Johansson (Ge 440 crystals with ~1.7-eV energy resolution and a range of detected emission energies, 6450–6530eV, sufficient for the analysis of K. lines as well as the Kβ cross-over region) and von Hamos (GaP 440 crystals with ~0.3-eV energ. resolution and a range of detected emission energies, 6446–6506 eV).

Following the progression of x-ray induced damage by Mn Kβ x-ray emission spectroscopy, we demonstrate the feasibility of collecting room temperature (RT) data on the electronic structure of the dark stable S_1 state of Photosystem II. Two different beam structures were tested during these measurements: continuous monochromatic beam (at 20-ID), and pulsed pink beam (22-μs pulse width at 14-ID). The dosage/damage relation for continuous beam measurements matches preliminary RT models well [3]; the XES spectral shape obtained at RT and low T are similar indicating that no significant charge redistribution is happening within the OEC upon freezing PS II [4]. The determined damage threshold (~100 ms for continuous monochromatic beam; ~100 μs in pulsed pink beam mode) is sufficient for the analysis of electron dynamics and the catalytic mechanism. The reported timeframes are expected to be representative of other metalloproteins. In addition, preliminary time-resolved Kβ emission laser pump (to advance the catalytic cycle to the subsequent S_2 state), x-ray probe experiments conducted in pulsed pink beam mode show promise when compared to previously published cryogenic data [5]. The short working distance dispersive spectrometer instrumentation and experimental methodology is broadly applicable to time-resolved x-ray emission analysis at synchrotron and x-ray free-electron laser light sources.

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A-68

The APS Detector Pool

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The APS Detector Pool provides users with access to many different types of x-ray detectors and related equipment. The most popular devices include: area detectors (Pilatus 100K, Mar 165 CCD), microscopy Cameras (CoolSNAP, Prosilica, Scint-X), spectroscopic Detectors (Vortex SDD, Germanium), point detectors (Oxford Cyberstar, Mythen silicon strip, Diodes), and temperature control stages (Linkam). It also coordinates equipment loans between beamlines, assists with hardware troubleshooting and repairs, and provides EPICS support for data acquisition.

The Detector Pool is undertaking a quantitative characterization and calibration program. In the first phase, area detectors will be corrected for flat-field distortions using an x-ray tube located at Sector 6-BM. Within the next two years, testing will shift to a dedicated beamline allowing for a multitude of additional calibrations including energy response and timing performance. The goal of this program is to provide scientists with a better understanding of the detectors available, and a first level of correction for data analysis.

POLYMERS

A-69

Withdrawn

A-70

Phase Separation in Dilute Solutions of Poly(N-isopropylacrylamide)

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The appearance of larger particles with narrow distribution resulting from the phase separation in dilute solutions of poly(N-isopropylacrylamide) has been observed by static, (polarized and depolarized) dynamic light scattering and small-angle x-ray scattering. The effects of polymer molecular weight, polymer end group charge, polymer concentration, heating history on the particles' properties were investigated. Hysteresis effect was also observed. The formation and stabilization mechanism of these particles has been discussed based on the experimental results.

TECHNIQUE

A-71

X-ray Analyzers for Polarization Measurements in Resonant Inelastic X-ray Scattering

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Resonant inelastic x-ray scattering (RIXS) is a powerful x-ray scattering technique for the study of complex electronic excitations in correlated electron systems. In current RIXS instruments, during the scattering process, changes of energy and momentum of the scattered photons are measured to characterize the nature of the excitations. However, the polarization of the scattered photons is not currently measured due to significant technical challenges. A powerful extension of the RIXS technique is the measurement of the polarization state of the scattered photons, which contains information about the symmetry of the excitations.

We present a design of an outgoing polarization analysis system using a polarization analyzer with a double-concave surface fabricated using highly oriented pyrolytic graphite for the measurements at Cu *K*-edge. The efficiency and overall resolution of the polarization analyzer are presented. Measured data showing the instrumental resolution function and the inelastic spectra of $CuGeO_3$ are also presented. To improve the reflectivity and energy resolution, a new type of Si polarization analyzer is being developed using a biaxial bending technique for the measurements at Cu *K*-edge and Ir *L*-edge. This bent Si analyzer is expected to have 10–20 times higher efficiency than the graphite analyzer at the Cu *K*-edge.

A-72

The Structural Biology Center User Program: A Beamline for Cutting Edge Structural Biology Research

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The Structural Biology Center (SBC) at Argonne National Laboratory operates a national user facility for macromolecular crystallography at Sector 19 of the Advanced Photon Source. The fully tunable beamlines are optimized for cutting edge research at atomic resolution, and for large and complex molecular systems. The beamlines deliver x-ray mini-beams with very low angular divergence. On 19-ID the micrometer-size crystals are placed in x-ray beams using ACTOR crystal mounting robotic system. Diffraction data is recorded on large, fast, and efficient CCD area detectors with sophisticated control and data analysis software. Beamlines can be operated on site or remotely.

The presentation will highlight new and upgraded advances to the SBC beamlines including: 19-BM upgrade, remote data collection, crystal mounting using either Rigaku or Uni-Puck/ALS sample pucks, on-axis crystal viewing, beam visualization, point-and-click sample alignment, auto-loop alignment, adjustable mini-beam with apertures to 7 microns, auto energy changes, fluorescence scanning, high-energy 30-KeV and 10K data collection options, the HKL3000 program suite for data collection, processing, structure solution and model building in near real time, and rapid access beamtime scheduling. Research highlights from the Sector 19's PDB deposits will be presented. Information on the user program and the Sector 19 beamlines will be provided and can also be obtained from the SBC web site (http://www.sbc.aps.gov).

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A-73

Transmission X-ray Microscopy in 3D and 4D for Materials and Life Science Applications

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Transmission x-ray microscopy (TXM) is a versatile technique for high-resolution (down to 30 nm) imaging and 3D tomography with a wide range of applications. Examples in materials science include quantification of particle size, porosity, or oxidation state in battery electrode materials, *in-situ* monitoring of chemical reactions or nanoparticle assembly, or studies of the nanostructure of catalysts. In the life and environmental sciences, examples include studies of bone nanostructure, heavy metal uptake in plants, or imaging of cell and tissue ultrastructure in the natural, hydrated state. Further applications can be found in geosciences or electronics.

In this poster, we present recent instrumentation and methods developments, as well as application examples, in TXM with both hard and soft x-rays. A lot of recent focus has been on the addition of further dimensions to the dataset beyond 2D and 3D imaging, such as time evolution, spectroscopy/chemical state, or temperature. We present techniques such as marker-less automated tomography to sub-50 nm resolution, the combination of tomography and near-edge spectroscopy (XANES) for chemical state mapping in 3D, cryogenic sample handling for life science specimens, *in-situ* imaging using furnaces or chemical reactors, and *in-operando* imaging of battery cells.

A-74

A New Kind of X-ray Grating: Multilayer on a Staircase Substrate

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Traditional hard x-ray transmission gratings are fabricated using lithography processes. They are constrained by the maximal attainable aspect ratio of the vertical walls, which limits the smallest attainable grating periods. Advanced x-ray phase contrast imaging techniques require large-area, high-density transmission gratings with smaller periods and higher aspect ratio to cover larger energy range for thicker samples. A new type of grating using multilayers grown on staircase substrates may meet this requirement. A thin Si substrate can be anisotropically etched to a staircase. With each stair surface supporting a multilayer as a micro grating and an x-ray beam shining through the layers at an oblique angle to the substrate and parallel to the layer surfaces, one has a large-area transmission grating with small grating periods. This method represents a new way to make gratings for hard x-rays. A [93-nm W/93-nm Si] 81 multilayer was grown on a 20 mm x 20 mm, 26º-blaze-angle Si staircase substrate using dc magnetron sputtering deposition. The multilayer thickness matches the stair height. A nitride layer was coated before multilayer deposition so that the Si substrate can be etched away to reduce x-ray absorption. Efforts have been made to grow the multilayer so that a major portion of layers is parallel to the stair surface with minimal amount on the sidewall. The sample was tilted during multilayer deposition to face the target. Deposition collimators were used to direct the coating flux. Uniform coatings were achieved using the profile-coating technique with specific masks made for each sputter gun. SEM images of sample cross sections and preliminary results of x-ray diffraction and contact radiography at 25 keV are presented.

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A-75

Development of Grating-based X-ray Talbot Interferometry at the Advanced Photon Source

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Grating-based Talbot interferometry at x-ray wavelengths is a relatively new and promising method for phase sensitive x-ray radiography on centimeter-sized samples [1, 2]. Unlike other methods, this method can generate absorption contrast, differential phase contrast, and the object scattering map simultaneously [3]. Recently, it has also been shown that quantitative phase tomography [4] and time–resolved three-dimensional x-ray phase images of a living worm [5] can be realized. Here we report on the ongoing effort to develop this technique at the Advanced Photon Source at the Argonne National Laboratory. We will describe the design of the interferometer and present preliminary results obtained using a feather at 25 keV. We will also discuss the progress we made in developing this technique as a metrology tool for optics and beam wave-front characterization.

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A-76

Recent Developments For High-resolution Tomographic Microscopy at 2-BM-B

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Recent developments for high-resolution tomographic microscopy at 2-BM-B will be reported in this presentation. These developments include 1) automatic detection of rotational centers for microscopy and nano CT, 2) 3D image inpainting methods for ring artifact removal, and 3) the integration of absorption-based CT and phase-constrast CT.

An accurate and efficient rotational center detection method has been proposed for microscopy. It is based on GPU-accelerated calculation of the normalized cross correlation coefficients between the projections of 0 degree and 180 degree. This method will be combined with reconstruction-based method, where image entropy is used for performance evaluation. This method is further extended to the automatic alignment of nano-CT projection data, where the rotational center of each projection is required to be detected. A 2D-3D registration method will be applied for this problem.

We have demonstrated that image inpainting method on sinograms is an effective method for ring artifact removal. This 2D method will be extended to 3D and applied to the full projection dataset during reconstruction. A propagation-based phase contrast method will also be combined with the absorption-based method for accurate CT reconstructions.

A-77

Phase-sensitive Full-field Hard X-ray Microtomography Using the 2-BM APS Imaging Station

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Inline x-ray phase contrast is an attractive contrast mode for x-ray imaging techniques due to its increased sensitivity: by leaving a drift space between the sample and the imaging detector (frequently termed propagation distance), interfaces within the probed specimen can be visualized. A single-distance phase retrieval approach by D. Paganin et al. (*J. Microsc*. 206 [1], 33, 2002) has recently successfully been used at 2-BM: if the transmission radiographs are sent through a phase-retrieval process, the tomograms will exhibit 'area contrast' rather than edge-enhancing contrast in standard inline phase contrast mode. Advantages of this method are that it can be applied to any inline phase contrast tomographic data set; it allows phase-sensitive imaging without modification of existing experimental installations; it is extremely robust and user friendly; it can handle data from arbitrarily absorbing (multi-constituent) samples as well as tolerates polychromatic illumination. The presentation will introduce results obtained recently at 2-BM as well as outline how to overcome further limitations of the single-distance phase retrieval process such as blurring.

A-78

Watching Iridium Cluster Formation by Combining Pair Distribution Function (PDF) and DRIFTS Methods

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Ultra-small metal clusters ($<$ 1 nm), a special category of industrial catalysts, exhibit extraordinary performance, different from even nanoparticle phase [1–2]. Ir metal clusters are highly active for hydrocarbon hydrogenation reactions [2–3]. Clusters ($n < 6$) can be synthesized through removing ligands from organometallic precursors such as $[Ir(CO)_2(acac)]$ (acac, acetylacetonate) thermally or using reductive gas [1, 4–5]. Understanding the mechanism of metal clusters formation will help optimize the synthesis. Here we show that *in-situ* PDF methods combined with DRIFTS can provide unique insight into the kinetics, mechanism, and energetics for supported cluster formation from $Ir(1,5\text{-}COD)Cl_2/\gamma\text{-}Al_2O_3$. Importantly, these insights can be derived directly from gas-solid phase reactions relevant to the industrial processes, rather than being inferred from liquid-mediated reporter reactions. The PDF method can provide structural insight on a range of length scales (from Å to several nm) with sufficient time resolution to monitor cluster formation [7].

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A-79

Interatomic Coulombic Decay (ICD) in Deep Inner-shell Vacancy Cascades

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The photoionization of an inner-shell electron in a heavy atom triggers a vacancy cascade with the emission of x-ray fluorescence and Auger electrons leading to its final charge states. If the atom is part of a molecule or cluster, the decay process may involve removal of the valence electrons on the neighboring atoms thereby forming several charge centers and resulting in the Coulomb explosion of the system. This phenomenon in molecules where the valence electrons on the neighboring atoms play a significant role in the decay process is called interatomic coulombic decay (ICD) [1]. The focus of this work is to explore the ICD effect in XeF_2 [2] following K-shell ionization of the Xe atom near 34.5 keV. We compare the total charge produced following Xe Ka or Kb fluorescence decay from atomic Xe and from Xe in XeF_2 molecules. We present both experimental and calculational evidence that the fluorine atoms get involved in the decay process and the molecules start undergoing structural changes during the vacancy cascade.

Supported by U.S. Department of Energy (DOE) Office of Science, Division of Chemical, Geological and Biological Sciences.

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CHEMISTRY

C-01

Charge-Transfer Dynamics of Triphenylamino-Cyanoacrylic Acid Sensitized TiO_2 Nanocomposites: Evidence for Transient Stark Effect

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Dynamics of charge transfer processes in dye-sensitized semiconductor nanoparticles have been the focus of intense research interests in recent years because of its relevance in solar cells and photocatalysis. The research focus of our group is to use the dye-sensitized semiconductor nanoparticles for two-photon absorption applications. It has been recently suggested that the dyes on TiO_2 nanoparticles show transient stark effects, which might have significant influence on enhancing the two-photon cross-sections of the attached chromophores. However, few investigations have focused on monitoring these transient stark effects, which gave the motivation for the present investigation. Femtosecond fluorescence upconversion and transient absorption measurements were carried out on triphenylamino-cyanoacrylic acid (TPA-CA) sensitized TiO_2 nanoparticles in solution and thin films to probe the transient stark effects. The investigated dye forms good ground state complex with TiO_2 and ZnO nanoparticles. Femtosecond fluorescence upconversion measurements for TPA-CA on TiO_2 have shown ultrafast electron injection and additional slower luminescence decay, which is ascribed to charge recombination. However, the luminescence dynamics was found to be wavelength dependent, which gave a hint for the presence of transient stark effects. In addition, transient absorption measurements for TPA-CA on TiO_2 nanoparticles in solution and thin films have shown time dependent bleach maximum shifts suggesting the decay of the stark effect. The observed stark shifts were found to be different in solution and thin films. Complete results showing the evidence for transient stark effects will be presented.

C-02

Towards Photoactive Proton Shuttles for CO_2 Reduction in Organic-semiconductor Hybrids

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Charge-transfer states arise from small molecule complexation onto semiconducting surfaces. In this work we investigate the use of the charge-transfer state of 3-aminosalicylic acid on TiO_2 surface for the photoreduction of CO_2. Via surface-enhanced resonance Raman spectroscopy and electron paramagnetic resonance spectroscopies, we characterize the effect of CO_2 adsorption on the nanoparticle surface. We find that CO_2 adsorbs on an oxygen site to form a carbonate-type structure and that the amine is partially deprotonated to stabilize the CO_2. We expect that irradiation of the amine generates a drive to shuttle a proton towards the CO_2 while the electron transfers towards CO_2 in a proton-coupled electron transfer. The system is likely hindered by short-lived states but we propose a scheme whereby semiconductor and organic sensitizer could have a synergistic effect in a proton-coupled electron transfer scheme.

C-03

Ultrafast Charge-transfer Luminescence Dynamics in Catechol Derivatives Sensitized TiO_2 Nanoparticles

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Small molecules with ene-diol anchoring groups such as catechol form localized molecule-semiconductor charge-transfer complex with TiO_2 nanoparticles. We have shown in an earlier investigation that ultrafast luminescence dynamics and corresponding anisotropy can be used to probe the localized/delocalized nature of the transitions and the charge-transfer dynamics [1–3]. In this work, efforts were focused to understand the donor and acceptor strength of small molecule on the localized/delocalized nature of the charge-transfer transitions and correlate them to charge separation dynamics. The investigated molecules, include 4-nitrocatechol, 3-methoxy catechol and 3,4-dihydroxy benzoic acid, 3,4-dihydroxy benzonitrile and 3,4-dihydroxy benzaldehyde. Femtosecond fluorescence upconversion and transient absorption measurements were used to probe the charge-transfer dynamics in these catechol derivatives sensitized TiO_2 nanoparticles. Interesting charge-transfer dynamics is observed. The ultrafast luminescence dynamics and anisotropy measurements have shown that increasing the donor strength of the catechol led to relatively more delocalized charge-transfer transitions than the catechol derivatives with an acceptor. The transient absorption dynamics have shown that the charge recombination is slowed down with increasing donor strength of catechol suggesting that the hole is localized away from the surface of the nanoparticle and thus increasing the charge separation. In addition, the charge recombination dynamics for catechol/TiO_2 in solution and thin films were found to be entirely different. Though the solution phase measurements have shown ultrafast charge recombination for catechol sensitized TiO_2 nanoparticles, the thin film investigations have shown long-lived charge separation suggesting that the chromophores with catechol anchoring group can be used for solar cell and photocatalytic applications.

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C-04

Fabrication of Micron-Sized Carbon Interdigitated Array Electrodes with Photolithography

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Interdigitated array (IDA) electrodes are a tool for detecting and measuring the kinetics of reactive intermediates in electrocatalytic processes. Compared to rotating ring disk electrodes, the IDA electrode is more sensitive, can detect intermediates with shorter lifetimes and has a much higher collection efficiency (above 90%). An IDA electrode made of carbon is an attractive alternative to other electrode materials due to its wide electrochemical window, at least partly due to having little electrocatalytic activity making it useful for studying homogeneous electrocatalysts without interference form the electrode surface's catalytic activity.

We use photolithography to fabricate carbon IDA electrodes with micron size features. The carbon IDA electrodes are prepared by pyrolyzing developed photoresist patterns in a H_2/Ar atmosphere at 1000°C [1]. We fabricated carbon IDA electrodes with 50 pairs of generator and collector electrodes with widths of 2, 3, and 4 microns and gaps between them of 2, 4, 8, and 16 microns. The electrochemical response of the IDAs has been tested with simple redox systems in aqueous solution and yield collection efficiencies of over 70%. Characterization of new hydrogen producing homogeneous catalysts will also be shown.

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C-05

DFT Studies of Glycerol Decomposition on Transition Metal Catalysts

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Among the attempts to understand how to selectively de-oxygenate and dehydrogenate biomass-derived compounds for fuel productions, a reliable and efficient computational strategy was developed to make it possible to determine the entire glycerol decomposition reaction networks via dehydrogenation, C-C and C-O bond scissions on Pt-, Pd-, Rh-, Cu-, Ni-, and Pt-based alloys.

In this study, we present a bond-order-based scaling relationship developed on Pt. It is used with periodic DFT calculations to estimate the free energies of 82 glycerol intermediates, as well as the intermediates derived from methanol, ethylene glycol, erythritol, 1,2- and 1,3-propanediol dehydrogenations, with a standard error within ~0.2 eV. Coupled with the kinetics estimated from BEP relationships, it is found that both C-C and C-O bond scissions are slow in the initial decomposition stage (first 2~3 dehydrogenation steps). The C-C bond scission is more kinetically favorable, mainly via decarbonylations producing CO, as glycerol becomes more highly dehydrogenated. However, this is not the case for C-O bond scissions, allowing a higher selectivity for C-C bond scissions on Pt(111). Our analysis on Pt has been successfully transferred to a number of metal catalysts (e.g., Pd, Rh, Cu, Ni) and some Pt-based catalysts (e.g., PtCo, PtNi and PtMo). A semi-quantitative trend study helps us understand the fundamental catalytic properties exhibited by these metals in the aqueous phase reforming environment. This study also shows why some of the Pt-based catalysts possess superior performance in hydrogen productions.

C-06

Interfacial Charge Transfer Dynamics in Acetylacetonate Derivatives Functionalized TiO_2 Nanocomposites: Solution vs. Thin Film

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Chromophores with acetylacetonate (acac) as an anchoring group are considered for dye sensitization of TiO_2 nanoparticles either for solar cells or photocatalytic applications. Investigations were carried out to understand the interfacial charge transfer dynamics across molecules possessing acac as an anchoring group and TiO_2 nanoparticles in both solution phase and thin films. Femtosecond fluorescence upconversion and transient absorption measurements were carried out to probe the dynamics of charge injection and charge recombination processes. Comparative femtosecond measurements are carried out in solution phase and thin films to probe the influence of binding geometry on the overall charge transfer dynamics. Unlike the chromophores with other anchoring groups, investigated molecules with acac as an anchoring group have shown contrasting charge transfer dynamics. For the molecule/TiO_2 composites in solution phase, the transients took significant time to grow and the final transients lived long. However, for the same molecule/TiO_2 composites in thin films, the transients formed within instrument response and the transients decayed with different time constants. The differences in two phases were attributed to different binding geometries. Steady-state optical absorption and infrared measurements were able to show the evidence for different binding geometries.

C-07

Oxygen Chemisorption-induced Surface Phase Transitions on Cu(110)

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From an interplay between x-ray photoelectron spectroscopy, variable temperature scanning tunneling microscopy, and density-functional theory calculations, the structural response of the Cu(110) surface exposed to a wide range of oxygen gas pressure and temperature is determined. Under the oxygen gas varying from 1×10^{-10} Torr to 1×10^{-5} Torr, the oxidation of the Cu(110) at room temperature results in the (2×1) phase only, while raising the oxidation to 100°C leads to the coexistence of the (2×1) and c(6×2) phases at the oxygen pressure of 1×10^{-5} Torr and the oxidation at 350°C forms the c(6×2) phase only. Such a temperature dependence of the (2×1) ® c(6×2) transformation demonstrates the surface phase transition is a solid-solid transition in which the break-up of the added Cu-O-Cu rows in the (2×1) is the activated step. Comparison between the experimental observation and the theoretical surface phase diagram obtained from first-principles thermodynamics calculations reveals that the formation of both the (2×1) and c(6×2) phases takes place in a metastable equilibrium with the surrounding oxygen atmosphere, further demonstrating the existence of kinetic limitations to the surface phase transition.

Na Cai, Liang Li, and Guangwen Zhou, The Journal of Physical Chemistry B (submitted).

CNM 24626: *In-situ* UHV-STM Study of the Initial Oxidation of Cu(110) Surface.

C-08

Quantum Memories and Ultrasensitive Spin Detection Using Superconducting Circuits

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Electrons embedded in the solid-state are ideal quantum memory elements with long coherence times, and are also widely exploited in the contexts of biology and chemistry. We intend to couple a mesoscopic ensemble of electron spins to a superconducting resonator. While the individual spin coupling is small (g~50 Hz), the collective coupling to an ensemble can be large (geff~10 MHz), allowing fast interactions with superconducting qubits. We are also trying to enhance the individual spin coupling with superconducting circuits for the use in ultrasensitive measurement.

C-09

A Combined Experimental and Computational Study of Oxygen Adsorption on Cu Surfaces

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The oxidation of metals is a universal reaction caused by the simple fact that the oxide of most metals is more stable than the metal itself. While considerable progress has been made in understanding the behavior of oxygen chemisorption, the atomic details of oxygen-adsorption induced transformation of the metal crystal lattice into its oxide are not resolved. Using a combination of Density Functional Theory (DFT), kinetic Monte Carlo (KMC), and dynamic scanning tunneling microscopy imaging, we investigate the energetics of oxygen subsurface adsorption governing the onset of the bulk oxidation of Cu(100) and the surface reconstruction of chemisorbed oxygen at Cu(110).

The DFT study on Cu(100) surface reveals that the presence of boundaries formed from merged nanodomains mismatched by a half unit cell leads to preferred oxygen adsorption at the subsurface tetrahedral sites. The resulting Cu-O tetrahedrons along the domain boundary strikingly resemble that of the bulk oxide phase of Cu_2O. These results provide direct atomic-scale insight into the microscopic origin of the crystallographic orientation relationships for oriented oxide nuclei, and also demonstrate that the oxidation of an atomically flat terrace can still be a heterogeneous nucleation process controlled by defects in the oxygen-chemisorbed adlayer. A combined DFT and KMC study on the dynamic phase transitions of Cu(110) surface induced by oxygen chemisorption is also implemented. By taking the effect of dynamically formed Cu-O chains on the activation energies for surface diffusion of Cu and O atoms, we found the resulting surface structure of the KMC simulations agrees well with the STM observations of the added-row (2×1)-O. This in turn proves that the (2×1)-O surface reconstruction can be reproduced solely by the dynamic process of migration of Cu and O adatoms. As the oxygen coverage goes up, and more Cu-O chains arise, we expect this effect of Cu-O chains on the mobility of Cu and O atoms becomes increasingly significant and may ultimately accounts for the (2×1)-O to (6×2)-O surface phase transition.

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MATERIALS SCIENCE

C-10

Computational Studies of Li-ion and Li-air Battery Materials

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Lithium batteries are poised to revolutionize transportation just as they have portable electronics. Critically needed improvements in energy capacity hinges on the development of new high-capacity Li-ion electrode materials, or electrocatalysts in Li-air (Li-O_2) batteries. A fundamental understanding of these new materials and their limitations is imperative in order to overcome technology hurdles to their deployment. First principles density functional theory (DFT) calculations have been applied towards understanding silicon (Si) as a novel material for Li-ion battery anodes and manganese dioxide (MnO_2) as electrocatalysts for Li-air batteries. These materials allow up to a ten-fold increase in capacity compared to current technologies. For silicon in Li-ion batteries, we have devised a novel algorithm to simulate the insertion and removal of Li, and study the accompanying amorphization process. Using these simulations, we have achieved an understanding of the experimentally observed anisotropy in lithiation of micro- and nano-structured crystalline Si anodes. For manganese dioxide electrocatalysts, we have established the thermodynamic favorability for Li-oxygen species to be incorporated into nanoscale aMnO_2 tunnels at similar voltages as Li-O_2 reaction. We also find that the reduction of the O_2 molecule to occur readily at the entrance to the tunnels. Such understanding will ultimately allow us to devise design rules to optimize the materials.

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C-11

A New Generation of UNCD-based Drug Delivery Devices

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Proper control over drug pharmacokinetics is of paramount importance to ensure an effective pharmacological treatment while avoiding toxic side effects produced by drugs. Drug delivery systems represent an important area in medical devices due to the improvement achieved in drug transport and bio-distribution. In the last 20 years, advances in micro- and nanotechnologies have brought about new concepts in drug delivery technologies including miniaturization, integration of drug delivery devices with CMOS technology, wireless technologies for power and data transfer to implantable drug delivery devices inside the body, and new classes of biomaterials.

In this work, we present two modalities of biocompatible implantable drug delivery devices based on a novel multifunctional material called ultra nanocristalline diamond (UNCD). UNCD is a material developed and patented at Argonne National Laboratory which exhibits extraordinary mechanical, biological and electrical performance including extremely bioinertness, extremely low wear and very low coefficient of friction, capable of being integrated with CMOS and changes its electrical properties from insulator to semimetallic. All of these features makes UNCD ideally suit for using in medical implants that have to sustain the harsh environment of the human body as has been demonstrated for a retina chip, glaucoma valves, and more recently artificial heart valves. In the proposed research work two drug delivery devices are presented namely, a) a passive drug delivery device developed by creating micro-holes in an UNCD membrane created by microfabrication techniques and focus ion beam etching. The passive device operates by allowing the drug to diffuse throughout the holes, with tunable flow according to the membrane thickness and hole size and distribution. B) an active drug delivery device based on a piezoelectrically aluminum nitride film. This active device works under three different modes of operation. The first mode incorporates the piezoelectric material into a cantilever-like switch valve .The second mode works harnessing the piezoelectric vibration to break a membrane covering the drug reservoir. The third mode is based on the piezoelectric actuation which displaces the liquid containing the drug causing the breakage of the membrane by liquid pressure. Results from the design and fabrication of the device will be presented.

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C-12

Vortex Pinning Enhancement in Patterned MoGe Thin Films Coated with Magnetic Py

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Resistivity measurements on Py coated MoGe thin films containing periodic hole arrays were carried out to study the effects of magnetic material filling the hole array. Thin films of MoGe were patterned via focused-ion-beam milling to create pinning sites for the vortex lattice. A Py layer was deposited onto the hole array using magnetron sputtering. We investigate periodic hole arrays coated with magnetic material to determine the change in transport properties with varying magnetic fields. Samples with and without a Py coating were tested to determine the effect of magnetic material filling the hole array on the vortex lattice.

C-13

Conducting Oxide Nanorod Arrays and Their Optical Properties

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Transparent conducting oxides (TCOs), in general, are degenerated semiconductors with wide electronic band-gap. They have been widely used in the field of optoelectronics, photonics, and photovoltaics as they are transparent at visible spectrum while still conductive like metals. In this study, we first report the fabrications of monocrystalline TCO nanorods with controlled conductivity, length, alignment, and positioning. We then proceed to study the optical properties of TCO-nanorod arrays with designed pattern. Various unique features of these nanorod arrays were discovered in this study. In particular, we have demonstrated the tunability of collective and localized plasmonic resonances of these arrays in the infrared spectrum. These arrays can also be used in other applications, such as solar cell, biosensors, wave guides, etc.

C-14

X-ray Scattering Evidence for the Emergence of Confined Large-wavevector Phonon Modes in Silicon Nanomembranes

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A fundamental understanding of vibrational phenomena is critical to the emerging ability to control thermal and electronic properties using nanotechnology. A particularly important example is the control of these properties in silicon-based thermoelectrics and nanoelectronics. Acoustic phonons provide the dominant contribution to the thermal conductivity of Si and can also influence the mobility of electrons via scattering between valleys of the conduction band. The crucial large-wavevector phonons have eluded experimental observation in nanostructures due to the sample-size requirements of conventional bulk characterization techniques such as inelastic neutron or x-ray scattering. Optical techniques require smaller sample volumes but suffer from a fundamental mismatch between the momentum of visible photons and the wavevectors of phonons. As a result, theoretical predictions for the behavior of confined phonon modes in nanostructures have been experimentally tested only for small-wavevector modes near the center of the Brillouin zone.

Synchrotron thermal diffuse x-ray scattering (TDS) allows us to probe thermally populated phonon modes with wavevectors spanning the entire Brillouin zone. TDS measurements were performed at the nanoprobe facility at sector 26-ID-C of the APS, using suspended silicon nanomembranes fabricated in the CNM. The experiments yield information about the dispersion of acoustic phonons in silicon nanomembranes with thicknesses ranging from 315 nm to 28 nm. Previously undetected deviations from bulk-like behavior are apparent at large-wavevectors in membranes of thicknesses up to several tens of nanometers. These deviations are consistent with a modified phonon occupation resulting from the finite size effects applicable to low-energy acoustic modes in nanoscale structures.

C-15

Atomistic Simulation Studies on Oxidation of Metal Nanoparticles

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The initial stages of room-temperature oxidation of Fe and Ni metal nanoclusters in the 2–15-nm size range is investigated by molecular dynamics simulations employing dynamic charge transfer between the atoms. The simulations are used to understand the differences between oxidation behavior of finite-sized structures such as nanoclusters, thin films, and bulk materials. The simulations are also used to identify a critical size limit of the nanocluster above which oxide growth self-limits. We investigate the structural and dynamical correlation functions in the oxide film as well as the evolution of charges, self-limiting oxide thickness, atomic diffusivities, and local stresses for the different temperature and pressure conditions. We compare the oxidation kinetics on nanoscale metal clusters with typical kinetic curves observed for ultra-thin surface oxide growth on pure metal substrates. The effects of temperature and pressure on the nanoscale oxidation phenomena are clearly elucidated. Tailoring the properties of nanoscale oxide based technologies such as chemical activity, efficiency, durability, and reliability requires better understanding of the nanoscale oxide growth kinetics under various oxidation conditions, the resulting film morphology, as well as their functional properties.

C-16

Phase Transitions upon Lithiation and Pressure-induced Structural Evolution in Amorphous TiO_2

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Fast transport of ions in electrode materials is important for electrochemical performance, as fast insertion and de-insertion rates allow efficient cycling of ions in lithium ion battery anodes. Recently, efforts in this area have been devoted for the development of improved nanostructured electrodes, as they lead to reduced diffusion lengths and thus allow fast ionic transport. A fairly general understanding has been established regarding the effect of the nanoscale on the electrochemical efficiency of the electrodes. However, the atomistic details behind the enhanced performance and the effect of morphology are still not well understood, and such understanding is crucial for designing materials that allow better electrochemical performance. This work probes such atomistic details to provide insights into the design of electrode materials with fast ion transport rates. Important factors such as mechanisms and energetics together with the effects of dynamics, morphology, and concentration are discussed for Li ion diffusion in bulk anatase, amorphous, and rutile TiO_2. Additionally, such effects will be compared to those for the nanostructures. The structural transitions upon lithiation and under pressure will be discussed in detail.

The Li ion diffusion mechanism is found to depend on the morphology of the lattice. Our calculations show that diffusion of Li in anatase is 3D in nature, while that in rutile is 1D. The diffusion in rutile is found to be much faster than that in anatase and amorphous titania. Our simulations indicated that changing the Li ion concentration significantly modifies its diffusivity. However, the changes in diffusivities are found to differ from structure to structure, and are affected by the morphology of the lattice. Our results show that for both anatase and amorphous TiO_2, increasing the concentration increases diffusivities (up to 75% Li loading for anatase, and for all concentrations for amorphous), while the diffusivity decreases for rutile with increasing Li concentration. The reason for the decreasing diffusivity in the latter case is attributed to increasingly blocked diffusion sites and increasing Li-Li repulsion. The effect of concentration on the diffusivity in amorphous is different than that for the crystalline structures, as the amorphous TiO_2 undergoes structural transitions that lower the barrier for diffusion.

We have identified a structural transition for lithiated amorphous TiO_2 when it is fully loaded. The adapted phase is cubic, which leads to faster Li diffusion. We find that the configurational energy and entropy of the cubic structure is lower than that of the amorphous titania. We also examined the stability of the fully lithiated, partially lithiated and the de-lithiated cubic structures under pressure reaching to 60 GPa at 300K. Our calculations show that the delithiated structure undergoes phase transition to amorphous at 5 GPa. We find that successive increase in lithium concentration leads more stable structures. For concentrations below 75% Li we find that the phase transition to amorphous to occur with the corresponding phase transition pressure increases with increasing Li concentration. Our analysis indicate that the underlying reason for such phase transition results from the existence of large number of vacancies in the presence of low Li concentrations. More Li addition fills these vacancies and makes the structure more stable. This is further enhanced for high-pressure cases. We find the fully lithiated cubic structure to be stable for the pressure up to 60 GPa.

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NANOSCIENCE & NANOTECHNOLOGY

C-17

Nanoscale Distortions of Si Quantum Wells in Si/SiGe Quantum-electronic Heterostructures

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Devices exploiting individual quantum states of electrons promise to extend dramatically the capabilities of silicon-integrated electronics. One route to forming such devices is via coupled electrostatically defined quantum dots in which electrons are confined in a thin strained Si layer on SiGe. The unique advantage of forming such quantum dots in Si is the long quantum dephasing time afforded by the lack of a nuclear spin in ^{28}Si. It is proving challenging to build on this promise because there are significant variations in the properties of individual devices fabricated in the Si/SiGe system. The SiGe substrate in fact introduces this problem: randomness in plastic relaxation during its growth imprints a complex structural state on the silicon quantum well (QW). Structural issues are relevant because the morphology of the QW interfaces affects the subbands of the QW and single-particle states within quantum dots. We show using x-ray nanodiffraction interface structure variations within Si QWs are sufficient to alter properties of quantum information devices, and that the design of such devices must be optimized to minimize these effects. Further distortion arises from the creation of metallic gates, leading to significant rotations of the Si QW lattice planes.

C-18

Optical Characterization of CdS Window Layer for CdTe/CdS-based Solar Cell

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Cadmium sulfide thin films (CdS) have been used extensively as a window layer in CdS/CdTe solar cell devices [1, 2]. For the development and optimization of such optoelectronic devices, CdS thin films require comprehensive optical characterization. In this study, CdS thin films have been deposited on the ITO coated glass substrate using the thermal evaporation technique. The deposited films have been annealed in air ambient at 450^{o}C for a constant time of 30 minutes. The effects of annealing on the optical properties of CdS thin films have been studied. These films have been characterized by photoluminescence (PL) and Raman spectroscopy at room temperatures. It is observed that the intensity of PL, the profile of the PL spectra, and the effects of variations in photoexcitation powers depend drastically on the temperature of the post deposition annealing of the CdS thin films. Various parameters such as optical bandgap and crystal quality have also been calculated and found to vary with annealing and excitation powers.

Room-temperature PL spectra for the as-grown CdS films with the excitation wavelength of 442 nm at 1.75-μW power indicate a peak emission at about 514 nm (2.41eV). The presence of the green band with maxima at 2.41 eV is characteristic for crystalline CdS. Peak intensity of the emission spectra increased rapidly when samples were annealed at 450^{o}C for 30 min. in air ambient. Excitation power was varied from 1.75 μW to 0.275 μW for the annealed samples. The band gap varied from 2.41 eV to 2.43 eV with the decrease in photoexcitation powers. For further characterization of the n-type CdS window layer, Raman studies have been done using excitation source of 514 nm at 24-mW laser power for the as grown and annealed films. Two dominant peaks indicating the longitudinal optical (LO) phonon mode at approximately 303 cm^{-1} (1LO) and its overtone (2LO) at about 608 cm^{-1} along with multiple over tones of LO phonon modes (3LO and 4LO) for the as grown CdS films are observed. For the same samples excited at 12-mW laser power, negligible 3LO and 4LO phonon modes are visible. Quenching of the intensities of the overtones was remarkably observed as the excitation power is decreased from 24 mW to 6 mW. For the films annealed at 450°C for 30 min., sharper Raman peaks are observed as compared to as grown samples. Visibility of 3LO and 4LO peaks for the annealed samples excited at 12-mW power, which is almost negligible for the as grown samples at the same excitation power indicating an improvement in crystal quality that will be verified further by atomic force microscopy measurements.

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C-19

Photo-stimulated Luminescence Characteristics of Isolated Alumina Nanoparticles for Stress Sensing Applications

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Cr-doped α-alumina is a piezospectroscopic (PS) material that can also improve the mechanical properties of the matrix that it is added to. An applied stress results in a shift in the wavelength of distinct photo-luminescent spectral R-lines emitted by the material when excited with a laser, quantified by the PS coefficient. Nanomaterials with this capability allow for the development of a novel stress sensing method with high spatial resolution through non-invasive optical measurements. The stress sensing capability of these nanoparticles is adjustable through changes in nanoparticle size and morphology. These variables are related to the load transfer between the nanoparticle and the matrix. To achieve this adjustability, 'nanobuckets' were developed with Ebeam lithography to isolate a single alumina nanoparticle in an assumed infinite matrix for verification of stress transfer from the matrix material to the inclusion particle. Isolated particle photo-luminescence investigations were performed. The experimental findings were compared to results from theoretical formulations for particle-matrix load transfer.

C-20

Synthesis of Luminescent Graphene Oxide Nanoparticles

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Luminescent graphene oxide (GO) nanoparticles are potentially useful for studies of biological systems because they are chemically inert, cytocompatible, and ideal for coupling to biological molecules. As a probe for *in vivo* confocal microscopy applications, GO nanoparticles can preserve the optimal sensing properties while providing exquisite spatial localization. Luminescent GO quantum dots were prepared in liquid suspension by the pulsed laser synthesis technique. The GO nanoparticles were characterized using Raman spectroscopy, infrared spectroscopy, UV-visible spectroscopy, photoluminescence, transmission electron microscopy (TEM), electron diffraction, and electron energy loss spectroscopy (EELS). The Raman and EELS spectra show the features corresponding to GO. The TEM images show that the size of the GO nanoparticles ranges from 5 to 12 nm. The UV-visible and photoluminescence spectra fall in the blue-violet zone of the spectrum. These GO nanoparticles will be tested as *in vivo* bio-probes in a confocal microscope.

C-21

Rapid and Label-free Detection of Prostate Specific Antigen (PSA) with a Photoelectrochemical Lab-on-a-chip

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Current medical diagnostic efforts are based on detection of biomarkers that can serve as indicators of underlying disease. The cornerstone of these diagnostic efforts is immunodetection. This includes detecting immunological biomarkers of diseases such as cancer in blood or serum of patients and of disease causing agent such as bacteria or using immunologically derived biomolecules (antibodies) selective for them. In most cases, a promising prognosis is directly correlated with the early detection of the disease and its cause. For this reason, the demand for technologies that can rapidly and sensitively detect immunological biomarkers or disease causing agents in patient blood and serum samples is increasing exponentially. Here we report on the development of PEChem Biochip Technology that is based on the microfabricated lab-on-a-chip technology combined with photoelectrochemical properties of ligand-sensitized TiO_2 nanoparticles and demonstrate its application towards detecting Prostate Specific Antigen (PSA). TiO_2 nanoparticles sensitized with small ligands (such as dopamine, DOPAC) renders them visible light active and also acts as a linker for functionalization with antibodies for biodetection. Binding of antigens to the nanoparticles lowers the current in a concentration dependent manner that is measured on the lab-on-a-chip. We have successfully characterized the electrophoretic deposition process for forming TiO_2 nanoparticle film and found optimal photoelectric current to be produced with a 6-min. deposition at -500 mV. The technology is able to detect PSA with a limit of detection of 1fg with total assay time of less than two hours. While human prostate specific antigen, the biomarker for prostate cancer, was used as the model system in these studies, the technology is applicable for detecting a wide range of biomarkers as well as pathogens.

C-22

Measurement of Resonant Frequencies and Modes of Freestanding Nanoparticle Monolayers

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We recently showed that freestanding membranes of ligated nanoparticles can be assembled in a one-step drying-mediated process [1]. These 10-nm thin membranes can stretch over holes up to 100 microns in diameter and are supported by a substrate only along their outer edge, thereby freely suspending of the order of 100 million close-packed particles [2]. Previous work has focused on quasi-static mechanical properties [1–3]. Here we present the first investigation of the full dynamic response of freely suspended nanoparticle membranes, utilizing a high-frequency laser interferometer with picometer sensitivity at the CNM. This instrument allows us to rapidly measure the dynamical properties of freestanding nanoparticle monolayers for the first time including resonant frequencies, quality factors, and images of different modes.

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C-23

Interface-controlled High Dielectric Constant Al_2O_3/TiO_2 Nanolaminates with Low Loss and Low Leakage Current Density

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Dielectric materials exhibiting very high dielectric constant (*k*) of more than several hundreds, low leakage current and low losses, and ideally exhibiting biocompatible properties are critical for application as gate oxide for the next generation of nanoelectronics based on nanoscale CMOS devices, for supercapacitors for energy storage, for microchip embedded energy storage capacitors for biomedical implantable microchips, and for capacitors for the next generation of non-volatile memory devices. A grand challenge of such devices is that, when scaling down to sub-mm range, some high-*k* materials like (Ba, Sr)TiO_3 usually suffer from serious reduction of dielectric constant and other dielectric properties. Several reports have shown that interfaces of electrodes play an important role in the dielectric properties.

Our group recently demonstrated a novel approach to achieving dielectric thin films with extremely high dielectric constant using nanolaminates of TiO_2 and Al_2O_3 [1]. We demonstrated Al_2O_3/ TiO_2 nanolaminate films with sub-layer thickness, which exhibit dielectric constants of up to 1000 for frequencies ≤ 104 Hz. A step-like decrease in dielectric constant to ~ 50 occurred between 104–105 Hz. However, these nanolaminates exhibited relatively high leakage current and losses [1, 2]. We now have developed new Al_2O_3/ TiO_2 nanolaminates, with greatly improved dielectric properties, consisting of alternating 0.5 nm thick TiO_2 and 0.5-nm thick Al_2O_3 sublayers synthesized by atomic layer deposition. Insertion of a Al_2O_3 interfacial layer at the interface between the top Pt electrode layer and the nanolaminate structure yields Al_2O_3/TiO_2 nanolaminate with still high dielectric constant, but with orders of magnitude lower losses and leakage current density than for the prior Al_2O_3/TiO_2 nanolaminates. The unusual high dielectric constant is attributed to the Maxwell-Wagner relaxation between conducting TiO_2 and insulating Al_2O_3, while the low loss and leakage current density is attributed to effective current blocking by the interfacial Al_2O_3 layer. We also report characteristic properties of the nanolaminates as a gate-oxide and a capacitor from our test-bed devices. The results shown in this paper indicate that the substantially improved TAO nanolaminates can make a major impact in a new generation of nanoelectronic devices (nanoscale CMOS), energy storage capacitors, implantable biomedical microchips, and memory devices.

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C-24

Electroplate-and-Lift (E&L) Lithography Using Reusable, Patterned Ultrananocrystalline Diamond (UNCD) Templates for the Production of Micro- and Nanowires

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Electroplate-and-lift (E&L) lithography [1] has been developed as a fast, simple, scalable technique for the controlled, solution-based, electrochemical synthesis of patterned metallic and semiconducting nanowires. Unlike all other methods of patterning nanowires, E&L lithography allows patterned nanowires to be quickly mass-produced, without any additional vacuum or clean room processing after the initial fabrication of the template. This permits the study of nanoscale phenomena with minimal equipment and entry-level personnel, even as available at primarily undergraduate institutions.

The E&L technique employs a reusable, non-sacrificial, multi-layered, lithographically patterned ultrananocrystalline diamond (UNCD)™ template. The template is made from alternating thin layers of intrinsic UNCD, which is insulating, and nitrogen-incorporated UNCD (N-UNCD), which has semi-metallic conductivity. Intrinsic UNCD layers are used to isolate the top and bottom surfaces of the N-UNCD layer from the electrochemical bath. The diamond layers are lithographically patterned and reactive ion etched through the stack to expose only edges of the N-UNCD layer. The initial nucleation of the nanowire is thus confined to the exposed patterned edges of the 80-nm-thick N-UNCD layer. The thickness of the N-UNCD layer thus establishes the minimum achievable diameter of the electrodeposited nanowire. The maximum wire diameter can be controlled by increasing the deposition time, as presented for the model system of copper [2]. In alloy systems, such as copper-tin bronze, the composition of the deposited wires can be controlled by varying the solution composition [3]. Following electrodeposition, the nanowires may be removed by mechanically lifting them away from the template, thus regenerating the template surface for subsequent depositions. Wires of the same or a different diameter, composed of any desired electrochemically depositable material, may subsequently be plated. In preliminary experiments, the liftoff was performed manually using scotch tape or other polymers. An automated system for electroplating and removal is currently under development.

**denotes undergraduate student*

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C-25

Fabrication of High-aspect-ratio Nanopores by Interference Lithography

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Nanopore filters have a wide range of applications in many fields including medical diagnostics, drug delivery, and clean water production. Some of the key properties the nanofilters must exhibit include narrow and controlled pore size distribution, high pore density, and mechanical and chemical stability. Here we report the results on high-density high-aspect-ratio nanopores in SU-8, a biocompatible polymer with excellent chemical and mechanical properties fabricated using optical interference lithography (IL). The advantage of the IL fabrication method is the possibility of fabricating arrays of high-density periodic structures in a matter of minutes over a large substrate area and through the entire resist thickness.

The thickness of the nanofilter is limited by the maximum aspect ratio achieved; reported in literature aspect ratio is below four [1–6], which resulted in thin and hard-to-handle membranes. Our goal was to determine and to fabricate nanopores in approximately 10- µm-thick films providing structural strength without the need of a subframe. A three-beam Lloyd's mirror interferometer [7] was used to create a nanopore-array pattern with hexagonal symmetry after a single exposure. A HeCd laser (λ = 325 nm, 30 mW) was used for illumination, and the patterned area was about 4 cm^2. Nanopores of about 200 nm in diameter have been fabricated in ~10-µm-thick resist; a freestanding film with the pores of aspect ratio over 30 has been obtained.

We have demonstrated the feasibility of a high-precision method for the fabrication of high-porosity, biocompatible polymer nanofilters of high-aspect-ratios. Comparing to commercial nanopore polymer filters produced by track etching (6–25 µm in thickness), IL fabricated nanofilters have high porosity, uniform in size pores, which all oriented perpendicular to the surface. Track etch filters have random pore distribution, resulting in pore overlap and unintended larger pore sizes. To minimize pore overlap, track etch filters have low porosity. The orientations of the track-etched pores are also random.

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C-26

Comparison Between Bulk and Nanoscale Copper-Silicide

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Cu and Si are often combined in microelectronics; many studies were extensively undertaken to understand the formation and properties of copper-silicide (Cu-Si) [1–5]. However, most of these studies were conducted decades ago and on thin film structures, where the thinnest Cu film studied was approximately 100 nm [3]. As manufacturing technology improves, devices and interconnects can be fabricated on the nanometer scale. Because it is well known that the material properties of nanoscale materials differ from the bulk, those data of bulk Cu-Si structures may no longer be applicable. Therefore we investigated the formation of Cu-Si alloys at the nanoscale and to compare them with bulk properties [3, 6, 7]. Scanning electron microscopy, transmission electron microscopy, scanning transmission electron microscopy, and focused ion beam were used for the studies.

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C-27

Ultrafast Control of Absorption in Arrays of Hybrid Plasmonic MIM Nanocavities

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Plasmonics nanostructures are becoming remarkably important as tools towards manipulating photons at the nanoscale. They enable miniaturization of optical components beyond the “diffraction” limit as they convert optical radiation into highly confined electromagnetic near-fields in the vicinity of subwavelength metallic structures. These strong electromagnetic fields generated at the plasmonic “hot spots” raise exciting prospects in terms of driving nonlinear effects in an active media. A step forward in the control towards active nanoscale functionalities can potentially be accomplished in hybrid plasmonic components, which combine the use of active organics and metallic nanostructures. Such a hybrid nanostructure allows for the creation of new kinds of hybrid states, i.e. excitations due to the mixing of distinct types of materials, and not only provides tools for designing active plasmonic devices, but also paves the way to re-examine existing conventional laws governing the light-matter interactions.

We study ultrafast spectral and temporal dynamics due to electromagnetic coupling between the molecular interactions in a pi-conjugated polymer with plasmonic resonances in a periodic arrangement of hybrid MIM nanocavities. Intense, localized electric field distributions at the core of these plasmonic nanostructures alter their overall ultrafast absorption due to the induced polarizability change in the polymer. As a result, strong spectral shifts in the transient signature of these nanostructures are observed. This is accompanied by a novel phenomenon of narrowing of the transient signal at early times due to the enhanced coherence interactions. The interaction of such molecular excitations with plasmonic polarizations is investigated using ultrafast transient absorption spectroscopy, which allows for the observation in ‘real time’. The optical pump drives a nonlinear change in the polymer core whereas the probe feels the altered optical response of the system, which is the result of enhanced sensitivity of the MIM resonance to the changes in the polymer, located at the “hot spot” of these nanostructures. These results provide interesting insights into ultrafast light-matter interactions in hybrid nanomaterials.

C-28

APS, CNM, and EMC Are Making Tips Smarter

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The development of insulator-coated tips with ultra-small conducting apex is indispensible for advances in synchrotron-based scanning probe microscopy, which is an emerging technique with the potential to provide nanoscale imaging and spectroscopy with chemical, electronic, and magnetic contrast [1]. Generally, the spatial resolution in scanning tunneling microscopy (STM) depends on the sharpness of the tip. However, in synchrotron x-ray enhanced STM in addition to the tunneling current, x-ray photoabsorption can yield extra electrons that are ejected from the sample and collected at the tip. These photo-ejected electrons are generally not only detected at the apex of the tip but also at the sidewalls, which consequently will degrade the spatial resolution of any measurement. Thus, “smart” tips have to be developed and utilized that are entirely coated by an insulating film except at the very tip apex. We have utilized the unique capabilities of three user facilities at Argonne National Laboratory for the growth (CNM), nanofabrication (EMC), and nanotomography characterization (APS, CNM) in order to fabricate smart tips with an exposed length of the apex of only tens of nanometers [2]. These “smart” tips are the key enablers for the powerful new technique that combines x-rays and scanning probe microscopy.

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C-29

Orientational Interpolation of the Optical Spectra of Nonspherical Nanoparticles

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A general method called orientational interpolation (OI) is introduced to compute arbitrary-orientation and orientation averaged optical spectra of nonspherical plasmonic nanoparticles starting from a small number (4–7) of simulated spectra at fixed orientations. OI is a post-processing method independent of the choice of simulation technique. It uses scattered data approximation on the configuration manifold of the particle and exploits electrodynamic and point-group symmetries to make efficient use of simulation results. OI is shown to agree closely with the exact solution for a silver ellipsoid in the dipole limit and with the more complicated orientation dependence of a larger ellipsoid. The method is then applied successfully to describe the ensemble UV-visible spectra of colloidal silver decahedra and penta-twinned nanorods. The method provides insight into the orientation-dependent plasmon lineshapes of nonspherical nanoparticles and will be of practical use as the computational counterpart of the spectroscopy of single particles and randomly oriented ensembles.

C-30

Ultrananocrystalline Diamond Microarrays: Towards Label-free, Reliable, Multiplexed Electrochemical Sensors

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Label-free biosensors that can rapidly detect biomolecules in real time with high reliability, sensitivity, and selectivity still remain elusive. Among label-free sensors, electrical impedance spectroscopy-based biosensors are the most promising due to the simplicity of the detection technique. They have been used to detect a wide variety of antigens including bacteria, viruses, DNA, and proteins. However, their commercial development is hindered due to poor reproducibility and selectivity as a result of nonspecific binding. We overcome these issues by using a more chemically stable boron-doped ultrananocrystalline (UNCD) diamond surface to improve reproducibility and micro patterning them to improve sensitivity. This study marks the first demonstration of reliable and quantitative detection of a model bacterium, which positions this technology for rapid translation to point-of-use applications such as environmental monitoring and point-of-care diagnosis. Recent results of UNCD's novel electrochemical properties and its suitability to detect bacteria, dopamine, and other biomolecules reliably at long time periods will be presented. We also discuss an electrochemical model to better understand the impedance detection mechanism and a new scheme for detection that reduces the need for control experiments.

C-31

Fabrication of Nanoporous Ultrananocrystalline Diamond Membranes for Medical Implant Applications

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Ultrananocrystalline diamond (UNCD) exhibits excellent biological and mechanical properties, which make it an optimal implant coating material. Percutaneous implants are common medical devices in which the biomaterial crosses the skin, resulting in a permanent defect at the skin-implant interface. In many conventional percutaneous implant materials, sub-optimal skin sealing around the implant is observed and may lead to infection, resulting in loss of implant functionality or even patient mortality. von Recum and Park reported that implant materials with porous surfaces may facilitate migration of epidermal cells, enabling the development of a seal that resists movement of fluid and microorganisms [1]. Our current research efforts involve biological evaluation of diamond thin films and fabrication of precise nanoporous diamond membranes for application as percutaneous implants.

In a proof-of-concept study, we deposited ultrathin UNCD on commercially available microporous silicon nitride membranes using microwave plasma chemical vapor deposition (MPCVD). The structural, chemical, and biological properties of the UNCD-coated microporous silicon nitride membranes were examined. The results demonstrated that the UNCD films were conformal, dense, and smooth. The UNCD coating did not significantly alter the viability of the human epidermal keratinocytes, demonstrating that UNCD is an appropriate biomaterial for promoting epidermal cell migration on the surfaces of percutaneous implants [2]. In recent studies, we have altered the deposition conditions to control the surface roughness of the diamond thin films. Nanocrystalline diamond, ultrananocrystalline diamond, and chemically/mechanically polished (CMP) ultrananocrystalline diamond substrates have been fabricated. Biological evaluation is being conducted on these materials to determine the effect of surface morphology on skin cell viability, proliferation, and adhesion. In addition to these planar substrates, porous ultrathin UNCD membranes with nanoscale pores have been fabricated using microwave plasma-assisted chemical-vapor deposition, electron beam lithography, reactive ion etching, optical lithography, and wet etching. Pore sizes ranging from 50 nm to 1 um have been fabricated in arrays of varying pore density. Further optimization of the membrane fabrication process will permit synthesis of diamond membranes with accurate pore sizes and pore density, which may be tailored to achieve an optimal skin-implant interface.

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C-32

Formation of Gold Nanoparticles at the Liquid-Liquid Interface

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Gold nanoparticles are a promising tool for biotechnology and pharmaceutical applications. Much effort has been invested to develop new synthetic routes for nanoparticles tailored to specific needs. However, we still lack an understanding of the factors controlling AuNP formation that could lead to the development of a rational design strategy.

A common synthetic route is the two-phase method, in which AuNPs precipitate from reactants (i.e. gold ions and reducing agent) that are separated from one another by their location in two immiscible liquid phases. To study the processes leading to AuNP formation in the two-phase system, grazing-incidence small-angle x-ray scattering (GISAXS) provides an ideal and unique technique to *in situ* characterize the gold deposits close to the liquid-liquid interface. Our GISAXS measurements showed interesting intensity oscillations in Q_z in the range 0.02–0.08 $Å^{-1}$ upon nanoparticle formation. These oscillations became more pronounced with the progressive formation of the gold nanoparticles. As soon as a visible film of gold nanoparticles was formed, the periodicity of the oscillations increased. These observations indicate a fluctuating arrangement of the growing gold nuclei in the initial and advanced stages of gold nanoparticle formation.

C-33

Nanofabrication Methods for Diffractive X-ray Optics

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Transmission x-ray microscopy relies on the performance of diffractive x-ray optics to achieve high spatial resolution for the investigation of many different types of specimens, both organic and inorganic. Here, we present several nanofabrication methods for the preparation of high quality diffractive x-ray optics for x-ray imaging and microscopy combining several nanofabrication techniques such as electron beam lithography, gold electroplating, atomic layer deposition and electrochemical anodization of aluminum. Nanofabricated structures with high aspect ratios above 10 in the sub-100 nm range are shown.

C-34

Inducing Programmed Cancer Cell Death by Magnetomechnical Actuation of Cell Membrane

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Magnetic particles allow for non-invasive control over their spatial orientation and motion, which makes them ideally suitable for studying real-time processes in living cells. Lithographically defined ferromagnetic disks with spin-vortex ground state have the advantage of zero net magnetization in remanence. This eliminates long-range magnetic forces which otherwise lead to the interaction between particles and their agglomeration. Moreover, magnetically soft permalloy particles have high magnetization of saturation thus requiring very low external field for inducing high magnetomotive force, compared to superparamagnetic particles. Our group has previously demonstrated that micron-sized permalloy disks can be used for destruction of cancer cells (D.-H. Kim, E. A. Rozhkova, I. V. Ulasov, S. D. Bader, T. Rajh, M. S. Lesniak, V. Novosad, Nat. Mater. 9, 165-171 [2010]). Here, we report on the effects of magnetomechanical stimulation of human brain cancer cells with these particles. By utilizing fluorescent dyes that intercalate into DNA of a living cell, we demonstrate that the cells with microdisks attached to their surface develop the signs of early apoptosis following a 15 min. exposure to AC magnetic field.

C-35

Broadband Microwave Properties of Nanometer Gold Films

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Broadband high-frequency properties of metallic nanometer films are of great interest for the development of nanoelectronics, flexible electronics, and RF nanofluidics, in addition to the understanding of disordered electronic systems. In this work, we designed and fabricated a series of coplanar waveguides (CPWs) with nanometer film thickness and different characteristic impedance. Film surface roughness is reduced with wafer-bonding press. A two-port approach is followed to measure the scattering parameters (S-parameters) of the obtained CPWs. An

RLCG equivalent circuit model is used to extract the broadband microwave properties of CPWs and corresponding gold films. It is shown that the DC conductivity of sub-10 nanometer films is lower than their effective microwave conductivities; film surface morphology affects not only the magnitude, but also the frequency dependence of the microwave conductivity. The results are consistent with predictions of two-dimensional percolation theory.

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C-36

Ultrananocrystalline Diamond Nanowires: Fabrication, Structural Characterization, and Electrical Studies

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Recently, there has been great interest in making diamond nanowires (DNWs) and diamond nano-rods (DNRs), due to their extraordinary mechanical, optical and electrical properties as predicated by theory. Synthesizing or fabricating these nanostructures, however, is proving to be very challenging. To date, only a few attempts have been reported, such as etching single crystal diamond using focus ion beam (FIB) to produce diamond NRs or by coating Si nanowires with nanocrystalline diamond to produce diamond NWs. We report a top-down method based on e-beam lithography and reactive ion etching of ultrananocrystalline diamond (UNCD) to produce UNCD nanowires (UNCDNWs) with nanowire diameters as small as 30 nm. The successfully produced UNCDNWs possess well-defined feature compare to self-assembly approach, and they can be very easily released from substrate. Our UNCDNWs also maintain intrinsic diamond structure and properties without degradation after fabrication process, which has been confirmed by Raman spectroscopy (ultraviolet and visible), transmission electron microscope (TEM) and electron energy loss spectroscopy (EELS). Preliminary electrical measurement of UNCDNWs will be discussed. The ability to fabricate UNCDNWs provides an opportunity to study the fundamental mechanism of electon transport in UNCDNWs, which will enable new ideas and possibilities for the fabrication of new functional nanoelectronic devices.

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C-37

Nanotomographic Imaging of Advanced Electode Structures for Rechargeable Lithium Battery Cells

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One of the major challenges in the field of nanoscience is determining the electrochemical behavior of nanoarchitectures, particularly in the vicinity of interfaces. Understanding these properties requires the ability to observe system changes *in operando* as local structure and composition evolve because of the influence of electrochemical potentials. Equally important is the nanoscale control of the constituents in an electrochemical system, which offers the possibility of tailoring electronic, ionic, and molecular channels for novel or enhanced device functionality. Research in this area is essential for the advancement of the science underlying fuel cell and advanced battery designs and for the nation's future energy infrastructure.

Three–dimensional (3D) multifunctional battery structures show promise for improved storage capacity and scaling. We are using the unique combined x-ray nanotomography and x-ray fluorescence technologies that we have developed to study *in situ* morphological and compositional changes of 3D battery structures in order to better understand advanced battery performance.

C-38

Initial Performance of Hard X-ray Zone Plates Fabricated at Center For Nanoscale Materials by Electroplating Gold into Ultrananocrystalline Diamond Molds

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Focusing hard x-rays to less than 100-nm spot size requires advanced optics, with zone plates being the most common optic used. The main disadvantage of a zone plate is limited focusing efficiency and this problem is magnified with higher energy x-rays. Increasing the zone plate thickness can increase focusing efficiency but a fine resolution requires a small outer zone width. The combination of a large zone height and small zone width is a high aspect ratio that is difficult to achieve with current fabrication limitations. Therefore, zone plate development has concentrated improving fabrication techniques and using novel materials to fabricate high aspect ratio structures. We have fabricated zone plates at the Center for Nanoscale Materials with greater than 20 aspect ratio and sub-100-nm resolution using ultrananocrystalline diamond. This diamond was fabricated into an electroplating mold and filled with Au. Examples of zone plates fabricated include 1400-nm-thick, 60-nm-outer zone width zone plates and 2000-nm-thick, 80-nm-outer zone width zone plates. We will present the zone plates fabricated and the first results of optical characterization at the Advanced Photon Source. Future work in improving fabrication and completing characterizing will be presented as well.

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OTHER

C-39

Agglomeration Dynamics in Thermo-sensitive Polymers across the Lower Critical Solution Temperature: A Molecular Dynamics Simulation Study

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Stimuli-sensitive polymers can respond to surrounding environmental changes such as pH, temperature, light, glucose, etc. that can lead to change in their conformations. Conformational changes in these polymers can be controlled/altered by using different co-monomers, additives etc. Temperature sensitive polymers either have an upper critical or a lower critical solution temperature (UCST or LCST). Poly(N-isopropylacrylamide), a classical thermo-sensitive polymer, has an LCST at ~32°C. PNIPAM polymer chains are soluble below the LCST and insoluble above the

LCST. If the concentration of PNIPAM is >1 ppm, then polymer chains after undergoing coil-to-globule transition above the LCST, aggregates to yield a stable colloidal dispersion. However, to date the atomic scale mechanism and structure of these aggregates is not clear. Different parameters, such as minimum distance between two polymer chains, number of monomers/polymer chains needed to form such agglomerates, have not yet been studied. Dynamical properties of these agglomerates and water below and above the LCST can be studied using molecular dynamics (MD) simulations. Two PNIPAM chains, consisting of 30 monomer units each, were placed in a simulation cell at 20 Å and 40 Å distance from each other and were subsequently solvated. Simulations were carried out below and above the LCST, namely at 278 and 310 K for 20 ns. Simulated trajectories were analyzed for structural and dynamical properties of both PNIPAM and water. We observe coil-to-globule transition in PNIPAM above the LCST. We also find that the PNIPAM chains agglomerate above the LCST. Below the LCST these chains are entangled. Diffusion coefficient for water molecules was calculated, using Einstein's relation, both below and above the LCST. We observe lowering in the diffusion coefficient of water below the LCST. We also study agglomeration of five PNIPAM chains each consisting of five monomer units. There was no significant difference in polymer agglomeration behavior across the LCST for these short chain oligomers. The agglomeration behavior is thus strongly correlated to the size of the polymer chains. This study provides fundamental insights into the atomistic scale mechanism of PNIPAM agglomeration and transport properties of polymer/water across the LCST.

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C-40

Heat Transfer Nanofluids by Design: Copper-decorated Graphene Suspensions

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In an age of increasing heat fluxes and power loads in applications as diverse as medical equipment, power electronics, renewable energy, and transportation, liquid cooling systems are necessary to enhance heat dissipation, improve energy efficiency, and lengthen device lifetime. To satisfy these increasing thermal management needs, the heat transfer efficiency of conventional fluids must be improved. Nanofluids are nanotechnology-based heat transfer fluids that are engineered by stably dispersing nanometer-sized solid particles in conventional heat transfer fluids at relatively low particle volume concentrations to enhance the thermal conductivity and the heat transfer coefficient. We've applied systems engineering approach and current nanotechnology concepts to prepare nanofluids with advanced heat transfer properties. Hybrid copper-decorated graphene suspensions engage plasmonic and percolation heat transfer mechanisms and deemed to be able to dramatically boost the cooling efficiency. We report on simple, low cost, and up-scalable wet chemical synthesis method developed for hybrid nanomaterials and investigation of thermo-physical properties copper-decorated graphene dispersions.

INSTRUMENTATION

E-01

Volume Determination of Small Particles Using a Scanning Electron Microscope

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Many concentration measurements need exact knowledge of the analyzed sample volume [e.g., 1]. Such volumes are often calculated measuring an average radius using secondary electron microscope (SEM) images and assuming that the sample is spherical. We evaluated the possibility of determining volumes of particles using SEM images combined with the 3D reconstruction software package MeX from Alicona (http://www.alicona.com). To test the feasibility of the method, we used three different spheres with known dimensions and nine different minerals as test samples in the millimeter size range. All test samples where weighed on a microbalance and subsequently imaged under different tilting angles using a Zeiss EVO60 SEM at the Field Museum. The mass was used to calculate the volume using an average density. After removing the background of the images with the ImageJ photo processing software (http://rsbweb.nih.gov/ij/), the images were combined to a 3D model using MeX and the volume was determined. We compared the volumes to the ones determined by weighting the sample and the ones determined assuming them to be spheres.

The volume determination using 3D reconstruction for the spheres showed differences of 17% to 32% compared to the volumes determined by mass and by dimensions given by the manufacturer. The smooth surface of the spheres made the reconstruction of the exact form difficult due to the lack of surface detail. We furthermore analyzed nine minerals and compared the volumes from 3D reconstruction and assuming the samples to be spherical with the volume calculated using weight and density, assuming the latter to be the reference. For one mineral, the 3D reconstruction was not successful due to a lack of significant surface structure. Five mineral volumes were better determined using the 3D reconstruction than assuming spheres. The 3D reconstruction underestimates the volume by weight in six cases, whereas the spherical approach overestimates the volume in six other cases. We got the best results for minerals with a feature-rich surface as well as a sample illumination such that brightness and contrast distinguished the grain well from the substrate. The latter point demonstrates that smaller samples could be reconstructed better than larger samples—a trend that is very promising looking towards the analysis of micrometer-sized samples. In conclusion, 3D reconstruction of samples allows a simple determination of their volumes and shows advantages compared to commonly used methods.

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MATERIALS SCIENCE

E-02

Study of the Evolution of Nanoparticle Crystallization in Glass Ceramics

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Fluorochlorozirconate (FCZ) glasses are a class of material being developed for uses in advance mammography systems [1]. The FCZ of interest have been doped with Eu (II) for use as a either scintillator or storage phosphor material in these systems. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu^{2+} present in the $BaCl_2$ nanocrystals. The nanocrystals nucleate and grow through-out the glass matrix from annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The crystals formed are known from x-ray diffraction experiments to be hexagonal and orthorhombic $BaCl_2$ depending on the annealing temperature, 265°C and 295°C respectively [2]. *In-situ* and *ex-situ* transmission electron microscopy (TEM) experiments were used to study the nucleation and growth process of the nanocrystals. Through the TEM investigations of FCZ glass, previously unreported phases of crystalline BaF_2 in face-centered cubic (FCC) and orthorhombic have been found. These phases have been found in multiple compositions which vary the content of Cl and F. This indicates that annealing produces both polymorphic crystals of $BaCl_2$ and BaF_2, common in glass-ceramic systems, of which vary in size from a 10 nm to 100 nm.

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[2] S. Schweizer, B. Henke, P.T. Miclea, B. Ahrens, and J.a. Johnson, Radiation Measurements **45**, 485-489 (2010).

E-03

In-situ TEM Study on the Stoichiometry Dependence of the Evolution of Irradiated-induced Dislocation Loops in Ce$_x$La$_{1-x}$O$_2$

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In order to study the stoichiometry dependence of irradiation effects in mixed oxide (or MOX) fuel, the technique of ion implantation in La doped ceria (Ce$_x$La$_{1-x}$O$_2$) is used. Kr and Xe ions with energy 1 MeV were implanted into cerium dioxide single crystals with 0%, 5% and 25% La concentration at 800°C. *In-situ* transmission electron microscope (TEM) was used to observe the damage process and the defects created by the ion beam irradiation. A substantial difference in the evolution of dislocation loops for CeO$_2$ with different La concentration was observed at the same dose. For example, the dislocation loop growth rate in 25% La doped CeO$_2$ is about three times than that in 5% La doped CeO$_2$ during the low dose stage up to 8×10^{14} ions/cm$_2$. Dislocation loops were characterized as 1/3<111>{111} interstitial-type frank loops, which is in accordance with the Molecular Dynamic (MD) simulations.

E-04

Structural and Electrical Properties of LaNiO$_3$ Thin Films by RF Sputtering for the Growth of PLZT on Metal Foils

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Ferroelectric film-on-foil capacitors are under investigation to replace discrete passive components in the quest to develop electronic devices that exhibit superior performance and are smaller in size. We have investigated films of Pb$_{0.92}$La$_{0.08}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ (PLZT) that were deposited on LaNiO$_3$ (LNO) buffered nickel and silicon substrates. High-quality LNO thin films (100 nm thick) were first cold-deposited on silicon substrate by rf magnetron sputtering and then post-annealed in air at 500-800°C. The optimal annealing temperature at 600°C on LNO films yielded (100) preferred orientation. Scanning electron microscopic images show dense and uniform microstructure with grain size <40 nm. The room temperature resistivity is around 200 μΩ-cm, which is indicative of a good basic electrode for integrating ferroelectric capacitors. Subsequently, sol-gel-derived PLZT thin films were deposited on LNO buffered nickel substrates and characterized as a function of temperature, bias field, and frequency. The results were compared to those of the same films on silicon substrates. The comparison demonstrated that the performance characteristics of the LNO-buffered nickel substrates are similar to those of LNO-buffered silicon substrates, and suggested the integrity of the buffer layer and its compatibility with nickel substrates. The LNO films that are cold-deposited by rf sputtering can act as an effective barrier layer on nickel substrates suitable for embedded capacitor applications.

E-05

Characterization of Near-field Transducers by Analytical Transmission Electron Microscopy

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Dual-beam focused ion beam/scanning electron microscope and transmission electron microscopy were employed to study the structure of near-field transducers (NFT) for applications in heat-assisted magnetic recording (HAMR) heads. Analyses of NFTs that had been tested for their optical response showed a difference in microstructure between NFTs that had passed or failed a HAMR NFT optical test. The overall shape of the NFTs was about the same in both cases, as determined by scanning transmission electron microscopy tomography, but energy-dispersive x-ray spectroscopy analysis revealed the presence of Ta-rich regions in the alumina matrix below the failed NFT. However, the absence of a well-defined peg and the presence of a flat top on the 'FAIL' NFT disk induced poor thermal heat transfer from the NFT to the phase change medium and resulted in the optical test failure. The thermal heating around the NFT led to Ta diffusion from the adjacent tantala core and to the presence of Ta-rich particles in the alumina matrix in the plane of the NFT.

E-06

Evolution of Magnetic Domain Structure Induced by Interfacial Strain in $CoFe_2O_4$/$BaTiO_3$ Epitaxial Heterostructures

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The coupling of structural, electric, and magnetic order parameters in multiferroic materials has received significant attention due to the possibility to control one ferroic property with another order parameter. In horizontal layered heterostructures, interfacial strain induced by either a structural transition or an inverse piezoelectric effect in the ferroelectric layer can transfer to the adjacent magnetic layer, and thus via magnetostriction, the magnetic property of the heterostructures is modified. This idea has been studied in several systems by monitoring the change of magnetization as a function of temperature or electric field but the relationship between magnetic domain structure and structural transition or electrical poling have been less widely addressed.

Here we use ferrimagnetic $CoFe_2O_4$ (CFO) thin films deposited by metalorganic chemical vapour deposition on a single crystal ferroelectric $BaTiO_3$ (BTO) substrate as a model system to investigate the evolution of magnetic domain structure induced by structural phase transitions of the BTO. BTO is cubic above 398K, tetragonal above 280K, orthorhombic above 188K, rhombohedral below 188K. The ferroelectric transition temperature for BTO is 398K. We have monitored the evolution of the magnetic domain structure of the CFO from 150K to 420K using variable temperature magnetic force microscopy (MFM) including an Omicron UHV system at the CNM and an Asylum ambient system in MSD. In combination with magnetization measurements, the effects of magnetoelastic changes in the CFO films were investigated locally and macroscopically. An abrupt change of magnetization is observed at all BTO transition temperatures, and at the BTO tetragonal-cubic transition, the size of the CFO magnetic domains increases with decreased MFM contrast. Different surface unit cells can exist within the same structural phase of BTO, confirmed by peak splitting in room temperature x-ray diffraction measurements and cross-sectional TEM performed in the EMC. For example, in the tetragonal BTO phase, *a* domains (with rectangular surface unit cell) or *c* domains (with square surface unit cells) are both present. Dissimilar changes of magnetization magnitude along crystallographic equivalent [100] and [010] directions are seen as a function of temperature. This suggests an asymmetrical distribution of *a* and *c* domains in the tetragonal BTO substrate along these two directions. Strain relaxation at *a–c* ferroelectric/ferroelastic domain walls at the BTO tetragonalcubic structural transition reorients the CFO magnetization to an in-plane direction, contributing to the increase of magnetic domain size and lower overall stray field contrast.

E-07

Fabrication of Multilayer Laue Lens*: Cross-section SEM Image Processing with Marks by FIB

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MLLs can be fabricated by a variety of methods, and is an area of active research. Fabrication and beamline tests of multilayer Laue lenses (MLLs) have been reported to provide a promising path to focusing hard x-rays with high-focusing efficiency. MLLs consist of thousands of depth-graded thin layers. The thickness of each layer obeys the linear zone plate law. At APS WSi_2/Si MLLs were fabricated by magnetron sputtering. It is very challenging to accurately fabricate each layer at the designed thicknesses during deposition. Accurate measurements of the layers from several nanometers to several hundred nanometers are the key to improve the accuracy of the fabrication of the MLLs structure. Here, we report a new metrology approach for SEM image processing on the cross section MLLs images that can measure layer thickness more accurately by introducing regular marks on the cross section of thousands of layers using a focused ion beam (FIB) than the traditional method of estimating the thickness of the overlapped layers. More accurate results are obtained using the new measurement approach.

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E-08

In-situ TEM Observations of Nanocrystalline Iron Irradiation: Toward Radiation Tolerant Alloy Design

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Nanocrystalline materials contain high volume fractions of interfaces (grain boundaries) that are known to act as sinks for interstitials and vacancies created when a material is subjected to irradiation. For this reason, nanocrystalline iron provides an effective means to study the strength of the GB sink effect in iron and model the diffusion of point defects to sinks. The initial work presented here demonstrates a decrease in the size and density of point defect clusters observed in TEM for decreasing grain size. This information can be correlated to the strength of the grain boundary sinks. Such information can be used to develop radiation-resistant microstructures in materials needed for advanced reactor designs.

E-09

Effect Of Current Switching On LSM-YSZ Composite Electrode Durability

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Solid oxide cells routinely experience high operating temperatures, 800–1000°C, and moderate to high currents, 0.5–1.5 $A \cdot cm^{-2}$, over an expected lifetime of >40,000 hours. Understanding and mitigating degradation of both solid oxide fuel cells (SOFC) and electrolysis cells (SOEC) have been active topics of investigation [1–4] and are practical obstacles to commercialization of this technology. Additional engineering considerations are also necessary when considering reversible operation as both SOFC and SOEC, which has become desirable for coupling with renewable energy sources as an energy storage and generation device.

Here, a novel multi-cell experimental rig has been developed for simultaneous electrochemical testing of up to six separate symmetrical cells. The cells consist of a $(La_{0.8}Sr_{0.2})_{0.98}MnO_3/Y_{0.16}Zr_{0.84}O_2$ (LSM/YSZ) porous composite electrodes on either side of a thick, dense YSZ electrolyte. A current density of 1.5 A·cm^{-2} with polarity reversed every 30 minutes was applied for more than 1,000 hours of operation. Cells were sequentially removed from current weekly, halting microstructural evolution due to the electrical load, but left at temperature (800°C). Three of the cells were selected to be reconstructed *ex situ* to investigate the microstructural change using a 3D focused ion beam-scanning electron microscope at the EMC at Argonne National Laboratory. Accumulation of a foreign impurity phase was observed to collect in the pore phase near the electrode-electrolyte interface, and was determined by EDS analysis to be metallic silver from electrical interconnects. Similar results have been observed by Simner, *et. al.*[5] Further studies of long term operation of symmetrical cells under non-alternating loads show the silver accumulation absent from the electrode under electrolysis operation, suggesting that not only is current responsible for the mechanism, but that it is irreversible and dependent on the direction of current. Additional samples were studied at similarly reversing current densities of 1 and 0.5 A·cm^{-2}, which exhibited slower degradation.

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E-10

Multi-scale Order in Amorphous Transparent Oxide Thin Films

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The nominally "diffraction amorphous" materials represent a pervasive challenge in establishing the classical "structure-property" relationship. This stems from the inability to define structure of nominally amorphous materials and experimentally differentiate at least the short-range (within the length scale of a few Å) and medium-range (between 1 to 3 nm) order as a function of process parameters, and their subsequent influence on physical, chemical, or transport properties. Herein, we report quantitative determination of short- and medium-range order in nominally amorphous zinc and tin co-substituted indium oxide $In_{1.4}Zn_{0.3}Sn_{0.3}O_3$ (a-ZITO) thin films grown by pulsed laser deposition. These thin films are being explored as transparent conductors, which also exhibit changes in transport properties within such "diffraction amorphous" structures. The short-range order was determined by reduced density function (RDF) analysis from electron diffraction accompanied by density functional theory molecular dynamics simulation of liquid quench. Scanning transmission fluctuation electron microscopy (STFEM) indicated presence of ordered ZITO regions at the medium range. Interestingly, for a-ZITO films grown at different temperatures, the RDF analysis showed no significant change in the short range order. However, STFEM revealed notable structural (and symmetry) differences at the medium range. The existence of such multi-scale local order in amorphous ZITO thin films highlights the importance of a combined approach to unravel the interplay between structure of nominally amorphous materials and associated properties.

The ordering of medium range in amorphous materials is especially important for understanding colloidal transition mechanisms and nucleation processes among others, because for these problems it is recognized that certain phase change occurs during organization from the short range to the long range and our study has provided a potential synergistic way to solve problems of these kinds by combining the techniques mentioned above and *in-situ* TEM process.

E-11

In Situ TEM Study of Xe Implantation in Pure Mo Single Crystal

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In order to study irradiation damage and inert fission gas bubble formation and growth, *in-situ* TEM studies of Xe implantations in pure single crystal Molybdenum have been conducted. 300-keV and 400-keV Xe ion beams were used to implant Xe in pre-thinned TEM Mo single crystal specimens. The irradiations were conducted at 300°C and 600°C to ion fluences up to 2×10^{16} ions/cm^2.

Formation of dislocation loops was observed at the low dose regime of the irradiations. A rather fast kinetics was seen where surface effect was observed to be pronounced. Dislocation loops were seen to migrate to the surface and "disappear" within 2–3 seconds of their generation in the thinner region. At the temperature of 300°C, dislocation loops in both thinner and thicker specimen regions show nearly no growth in either size or number density. At higher temperature of 600°C, coarsening of dislocation loops can be clearly seen in the thicker regions indicating a higher kinetic rate of dislocation loop coalescence compared to that at 300°C. Dislocation loops observed in the low dose regime of the ion irradiations at 300°C have one dimensional migration behaviors. The migration paths for dislocation loops have been preliminarily determined as along the <111> set of directions. Nanometer-size Xe gas bubbles were observed at dose levels beyond 1×10^{16} ions/cm^2. Xe bubbles were observed to be immobile.

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E-12

Investigation of MoS$_2$ and BN Nanolubricants and Their Effect on the Tribological Behavior of Combustion Engine Parts

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Poly-alpha-olefin (PAO10) base oil formulations with BN and MoS$_2$ nanoparticles were tested on gray cast iron cylinder-liner segments reciprocating against aluminum alloy piston-skirt segments. The friction and wear test results showed that BN did not offer any improvement in friction, while the addition of MoS$_2$ nanoparticles was effective is reducing both friction and wear over the base oil. The viscosities of all formulations were similar, which allowed for direct comparison between them. Analysis of Raman spectra of the tested surfaces showed that MoS$_2$ in PAO10 formed a tribofilm of aligned MoS$_2$ sheets, which provided friction reduction and wear protection. BN nanoparticles in PAO10 did not improve the friction coefficient and were not detected on the surface of cast iron after the test.

E-13

Atomic Surface Structure of Strontium Titanate Nanocuboids

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Strontium titanate ($SrTiO_3$) nanocuboids are promising catalytic supports for the well-defined shape and small size (~20 nm). The atomic surface structure of $SrTiO_3$ nanocuboids has been solved by using aberration corrected high resolution electron microscopy for the first time in sub-Å resolution. The surface of $SrTiO_3$ nanocuboids is strontium oxide terminated with structural relaxation. The simulated image using a structure model relaxed by first principle calculation matches the experimental image very well.

E-14

Observation of Transformation of Calcium Ion to Calcium Oxide on Graphene Oxide Membrane Support by *In-situ* HRTEM

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Graphene oxide as a branch of graphene derivatives, made from graphite by chemical exfoliation, having a lot of oxygen-containing functional groups. With those functional groups carrying negative charges can be used as strong oxidizing reagents in varied applications. Here, we added calcium ions into graphene oxide solution to observe the oxidation of calcium ions by *in-situ* high-resolution transmission electron microscopy (HRTEM). The calcium ions will be attracted on graphene oxide by oxygen-containing functional groups and form into complex compound. By radiation of TEM direct electron beam, the complex compound will form into calcium oxide. Not only the reaction was observed, but also the coalescence phenomena were recorded. Electron energy-loss spectra also show the chemical composition, and the carbon peak reveals that the graphene oxide turns into graphene. In this paper, we will discuss the transformation mechanism.

E-15

AEM Studies of Localized Surface Plasmon Coupling in Ion-beam Fabricated Gold Nanostructures

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Localized surface plasmons (LSP's) are electron density oscillations, which are concentrated on the exterior of nanostructured materials (NSM). Their behavior is influenced by size, aspect ratio, and composition of the NSM and can be engineered to have tailored dielectric/optical responses at the nanometer scale. Today most engineered LSP materials have been created by lithography or controlled chemical growth/dissolution; unfortunately, these methods do not always allow precision control of complex shapes. In this work, we report on high-resolution/analytical electron microscope studies of engineered nanostructures of Gold fabricated using focused gallium and helium ion beam systems.

Fabrication of nanoscale plasmonic objects was accomplished using two focused ion beam instruments: a Zeiss 1540 Cross-Beam FIB and a Zeiss Orion Helium Ion Microscope. Patterns were cut into single and polycrystalline Gold freestanding thin films, which were nominally 100 and 50 nm thick respectively. AEM characterization was carried using FEI Tecnai F20 and FEI Titan (Cs/Cc corrected) transmission electron microscopes. The smallest structures fabricated were achieved using the He Ion instrument, where individual through thickness "holes" as small as 5 nm in diameter could be created in the Au films. Using the Ga-based system, the smallest feature that could be created was ~ 50 nm in diameter, but more importantly the Ga beams introduced stress gradients in the thin films, which severely compromised the stability and also the practical size of shapes milled in the thin film structures.

After ion beam fabrication, we carried out high-energy resolution electron spectroscopy of the localized surface plasmon resonances in single- and antenna-shaped gold structures as a function of shape and relative position. In these experiments, we were able to visualize and measure coupling of the surface plasmons modes of adjacent structures.

E-16

Hydrogen Gas Sensing with Ultrasmall Palladium-based Nanostructures

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The newly developed hydrogen sensor based on a network of ultrasmall pure palladium nanowires sputter-deposited on an aluminum oxide membrane takes advantage of single palladium nanowires in high speed and sensitivity while eliminating their nanofabrication obstacles. This new type of sensor, as those with single palladium nanowires, however, cannot distinguish hydrogen concentrations above 3%, limiting the potential applications of the sensor. Here we report hydrogen sensors based on networks of ultrasmall Pd/Cr bilayer and PdNi alloy nanowires. They are not only able to outperform their pure Pd counterparts in speed and durability but also to detect hydrogen at concentrations up to 100%. Pd/Cr nanowire networks consist of a thin layer of palladium on top of a Cr layer of 1–3 nm thick. Though the Cr layer is insensitive to hydrogen, it enables the formation of a network of continuous Pd nanowires with thickness down to 2 nm. The PdNi alloy nanowire networks were conveniently achieved by sputtering an alloy target. These improved performances of these sensors can be attributed to the increased surface area to volume ratio and the confinement-induced suppression of the phase transition from Pd/H solid solution (α-phase) to Pd hydride (β-phase) in the extremely thin Pd layer.

A-80

The Advanced Photon Source at Argonne National Laboratory

Susan Barr Strasser

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

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C-41

Center for Nanoscale Materials at Argonne National Laboratory

Kathleen Carrado Gregar

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

The Center for Nanoscale Materials (CNM) at Argonne National Laboratory is a premier user facility, providing expertise, instruments, and infrastructure for interdisciplinary nanoscience and nanotechnology research. Academic, industrial, and international researchers can access the center through its user program for both nonproprietary and proprietary research. The center's goal is to support basic research and the development of advanced instrumentation that will help generate new scientific insights, create innovative materials with unique functionality, and contribute significantly to energy-related research and development programs. High-impact staff and user science is accommodated within the primary cross-cutting theme of "Energy and Information Transduction at the Nanoscale". There are three critical pillars underpinning this theme in the areas of Materials Discovery, Manipulation, and Visualization.

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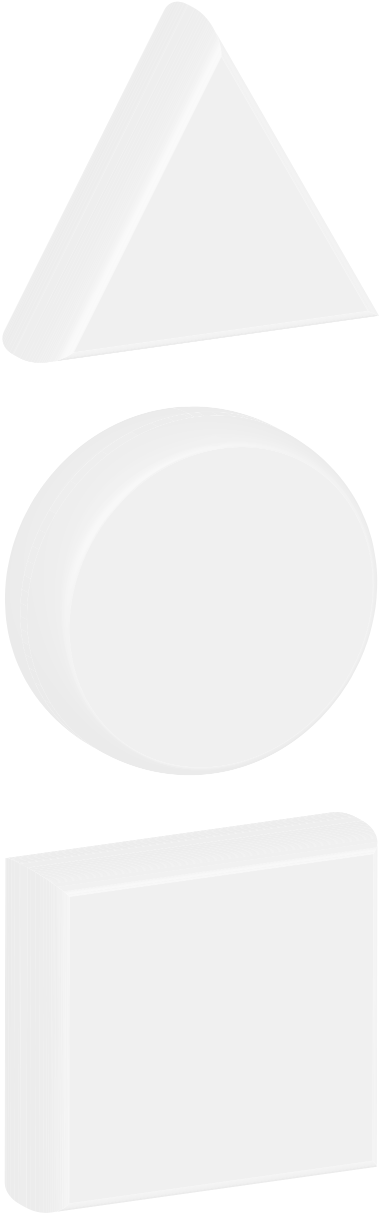

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MICOS supplies micro- and nano-positioning equipment with a focus on the research market. We offer a full range of precision positioners and control electronics as well as complete system integration services. Additionally, MICOS is known as the premier supplier for vacuum to 10-10 torr, clean room, and extreme temperature applications.

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url: www.midwestvacuum.com

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url: www.newport.com

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Middleton, WI 53562 USA
phone: 1.608.824.1770
fax: 1.608.824.1774
url: www.npoint.com

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NT-MDT
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Santa Clara, CA 95054 USA
phone: 1.408.988.8409
fax: 1.408.988.8442
url: www.ntmdt.com

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NT-MDT's has a complete line of SPM products that cover a diverse and dynamic range of imaging modes and applications including: MFM, EFM, SKM, PFM, AFAM, liquid scanning, nanolithography, nanomanipulation, nanomechanics and many more.

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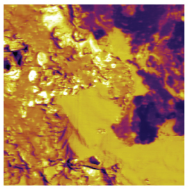

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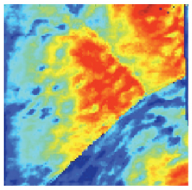

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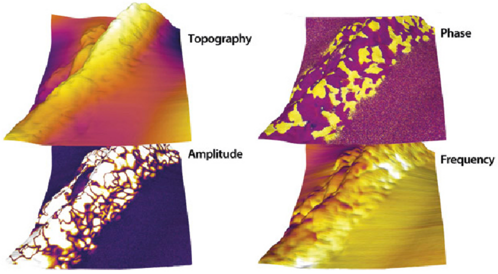

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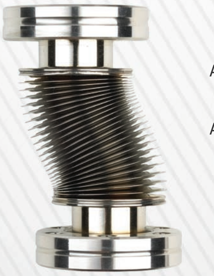

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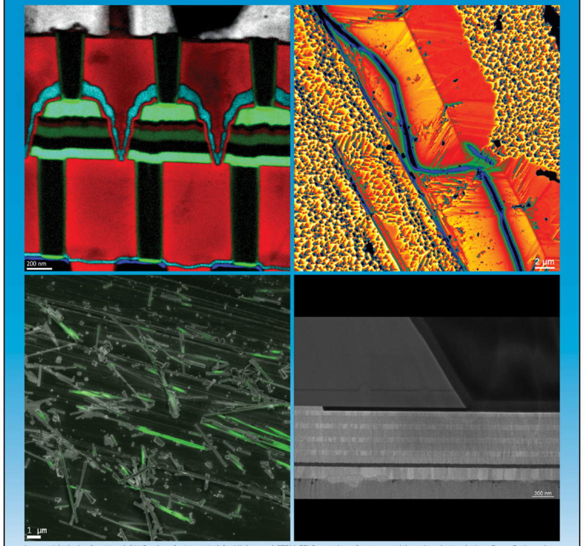
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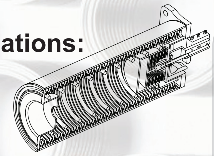


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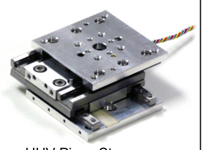

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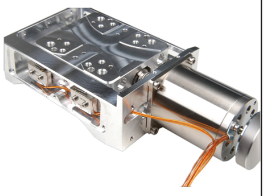

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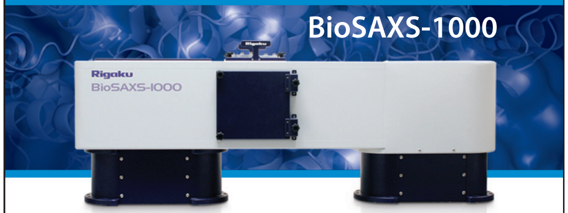

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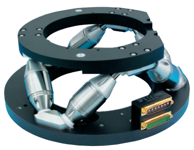

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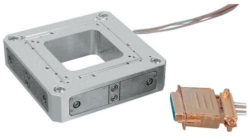

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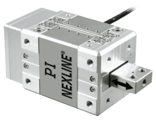

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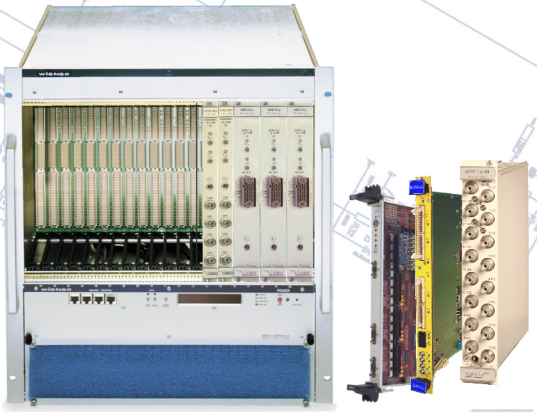

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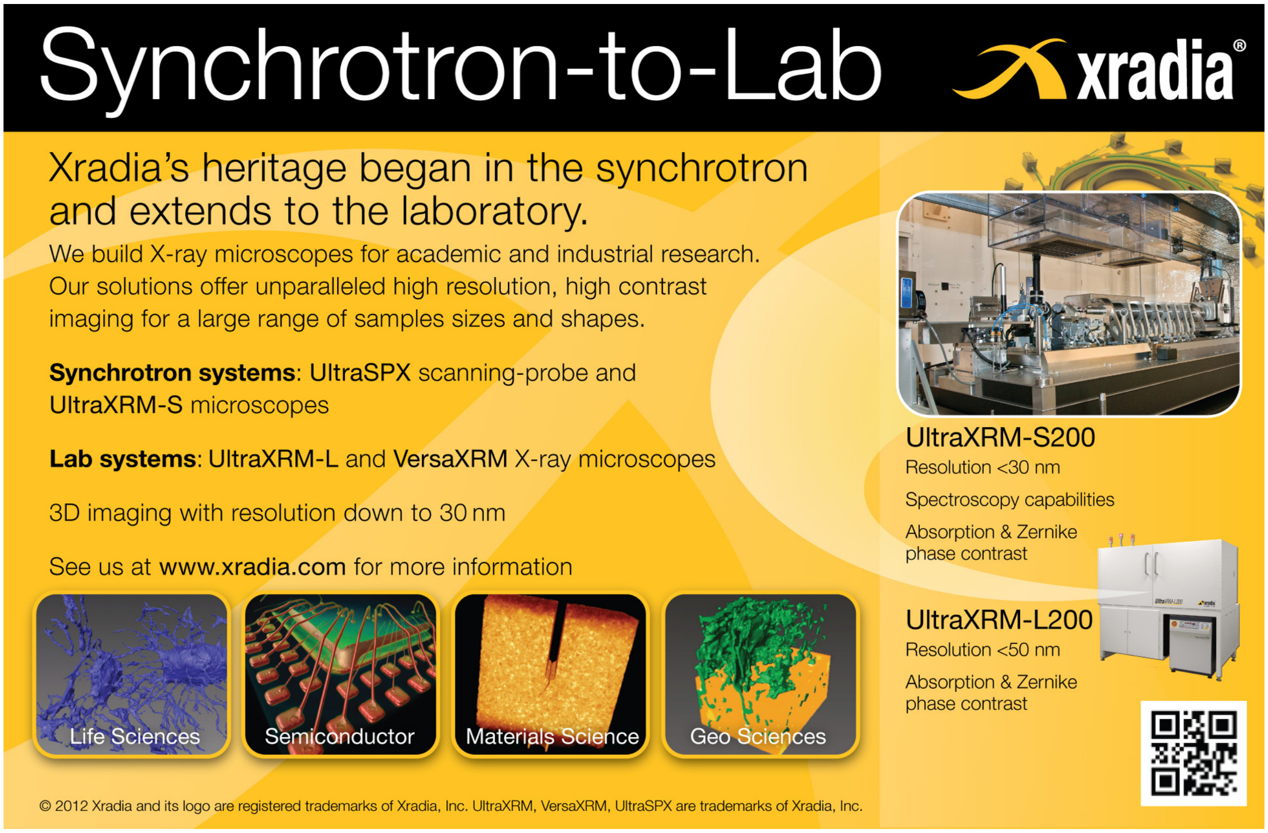
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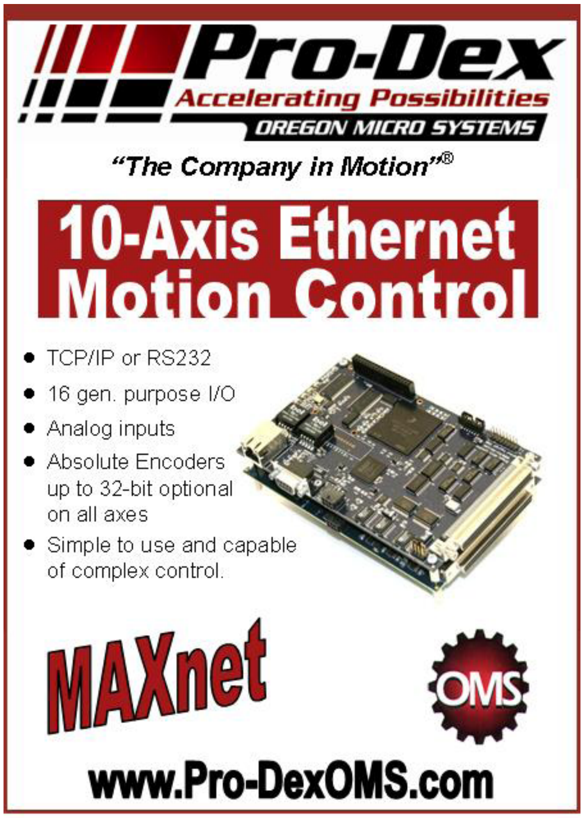
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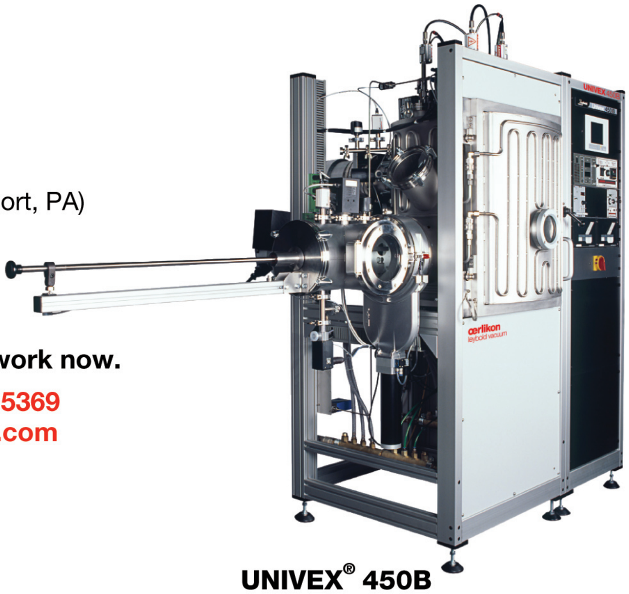

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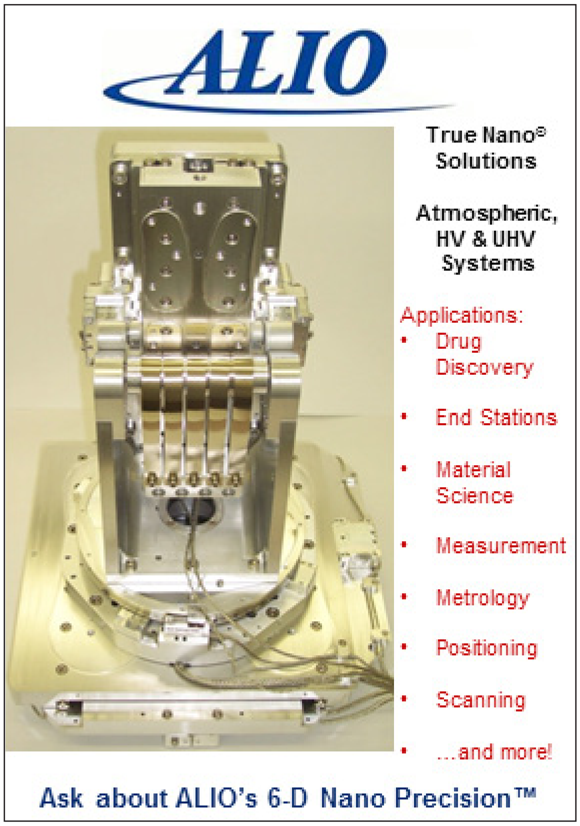

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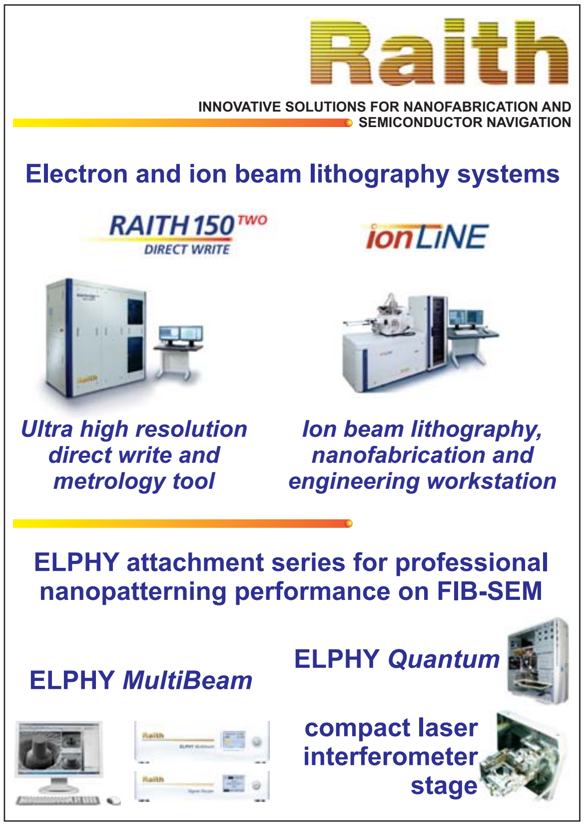

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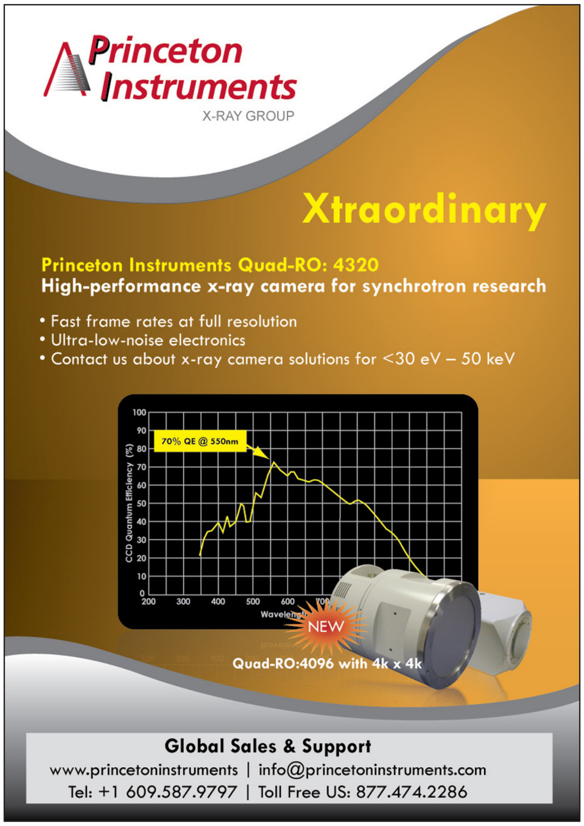

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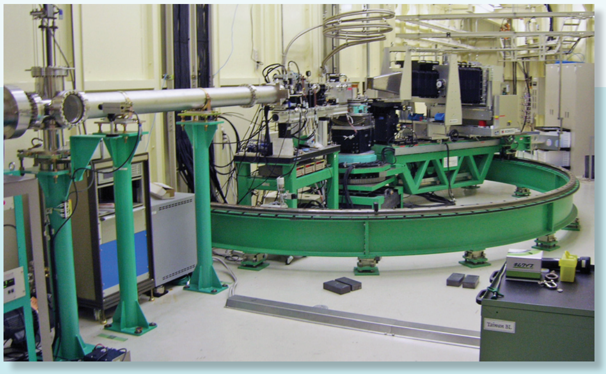
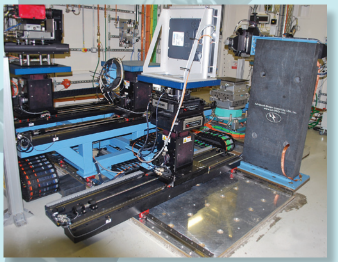
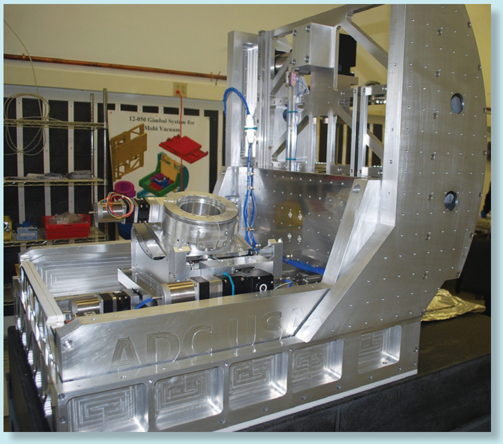
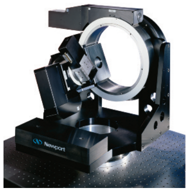


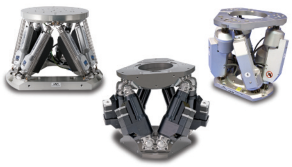




Turnkey System



Simple 3-circle



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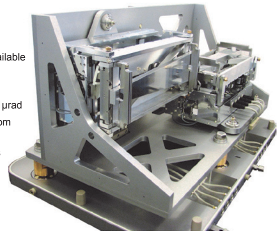

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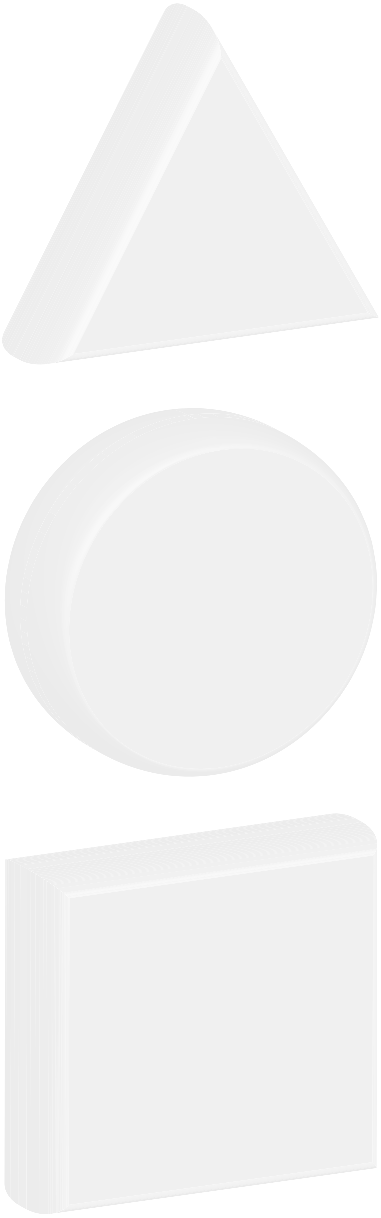


2012
Users Meeting

GENERAL
INFORMATION

Practical Matters

Locations

General sessions will be held in the lecture hall on the first floor of the APS conference center, Bldg. 402. Vendor exhibits will be in the center's lower level and the atrium on the main level. Workshop locations are listed on the Comprehensive Program and posted at the registration desk. .

Meals

The conference fee includes a continental breakfast and coffee breaks each day and the poster session reception. Buffet lunches will be served Monday through Wednesday in the tent on the patio on the lower level of the conference center. If you pre-ordered lunches on your registration form, you will receive your tickets when you receive your meeting materials. (A limited number of extra lunch tickets are available for purchase at the registration desk.) Banquet tickets are nonrefundable. The Argonne cafeteria and Argonne Guest House restaurant are both open for lunch; the Guest House restaurant it is open for dinner. The Beanline coffee shop in the Building 401 lobby will be open for its usual hours of 2:30 to 4:30 pm. The 401 Grill will be closed throughout the meeting. A list of nearby restaurants is available on the APS home page (www.aps.anl.gov) under the side heading Visitor Information.

Telephones and Messages

Messages for you can be left at the registration desk; the telephone numbers there are 630.252.9580 and 630.252.9581. The messages will be posted on a bulletin board by the entrance to the lecture hall. If you need to make a telephone call, a pay phone is located downstairs near the restrooms at the back of the gallery. If you need to send or receive a fax, a fax machine is located in the APS User Office (Bldg. 401, Rm. B1154). The number of this machine is 630.252.9250.

Transportation

Conference staff can make limousine reservations for you during the meeting as long as you make your request before 1:00 pm on Wednesday.

ATM

An automated teller machine is located in Bldg. 233, behind the Argonne cafeteria. This machine accepts the following cards: American Express, Discover/Novus, The Exchange, Master Card, Plus, Visa, and 24 Access.

Computer Access

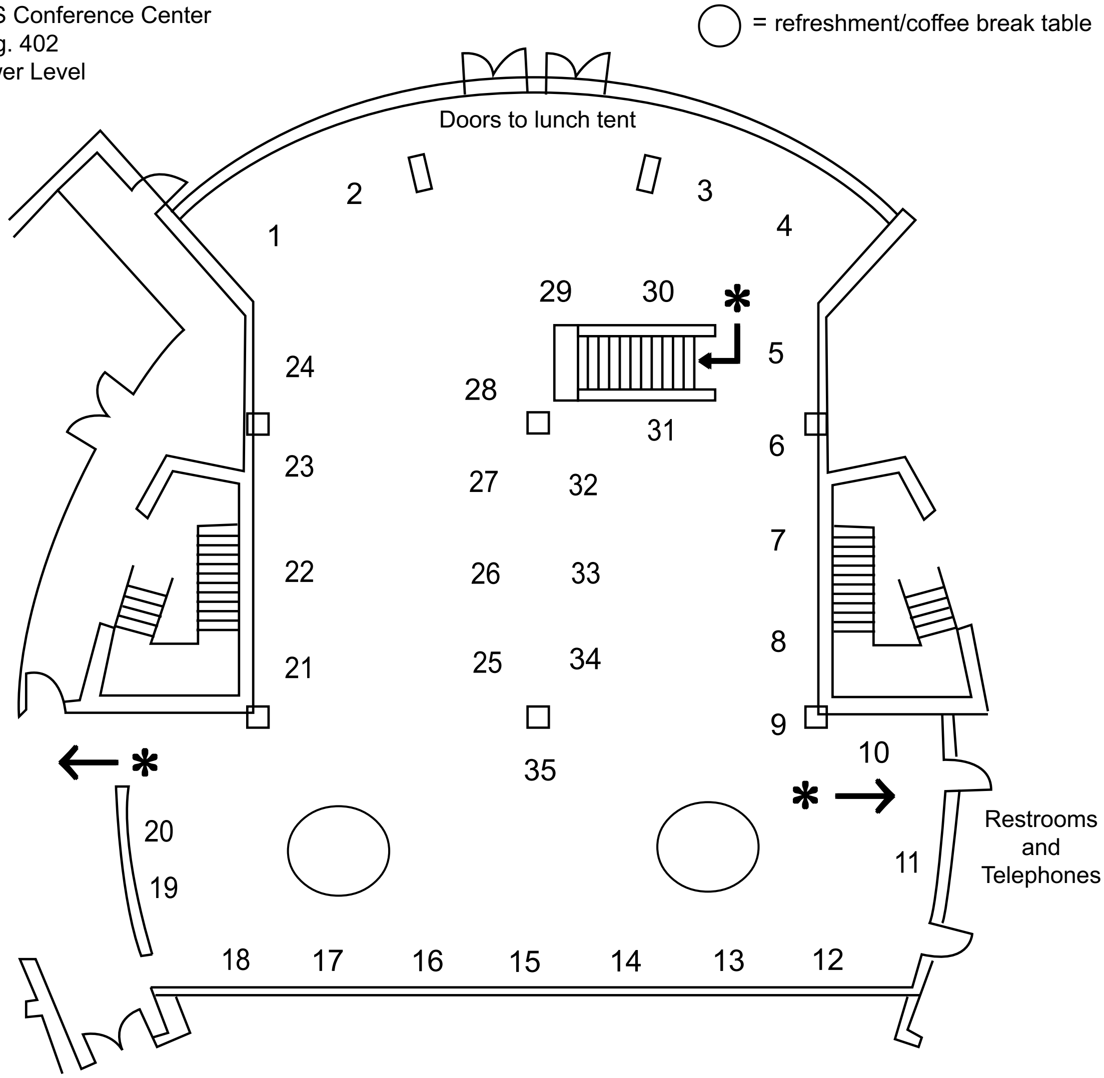
Public computer terminals are available in the Bldg. 401 atrium behind the silver wall. Wireless access is also available in the Conference Center.

To use your laptop computer on the APS wireless networks, complete the following steps:

1. Open the wireless connection on your computer (either the 401 or 402 networks).
2. Read and accept the Argonne internet access policy, which will appear as a Web page on your desktop. After you click "accept," a registration Web page will appear.
3. The registration web page asks you for the following information:
    a. First and last name
    b. E-mail address
    c. Building and room where you will be located (use 402 conference center)
    d. Phone number where you can be reached on site (use 630-252-9090)
    e. Name of person you are visiting or conference you are attending
    f. Home institution
    g. Do you need to send e-mail directly to an off-site server?
    h. What is the duration of this registration? (You'll be given choices.)

If you have problems, please contact someone in the APS User Office (B1154, located immediately off the Conference Center atrium).

Exhibitor Locations – 2012 APS/CNM/EMC Users Meeting
Argonne National Laboratory



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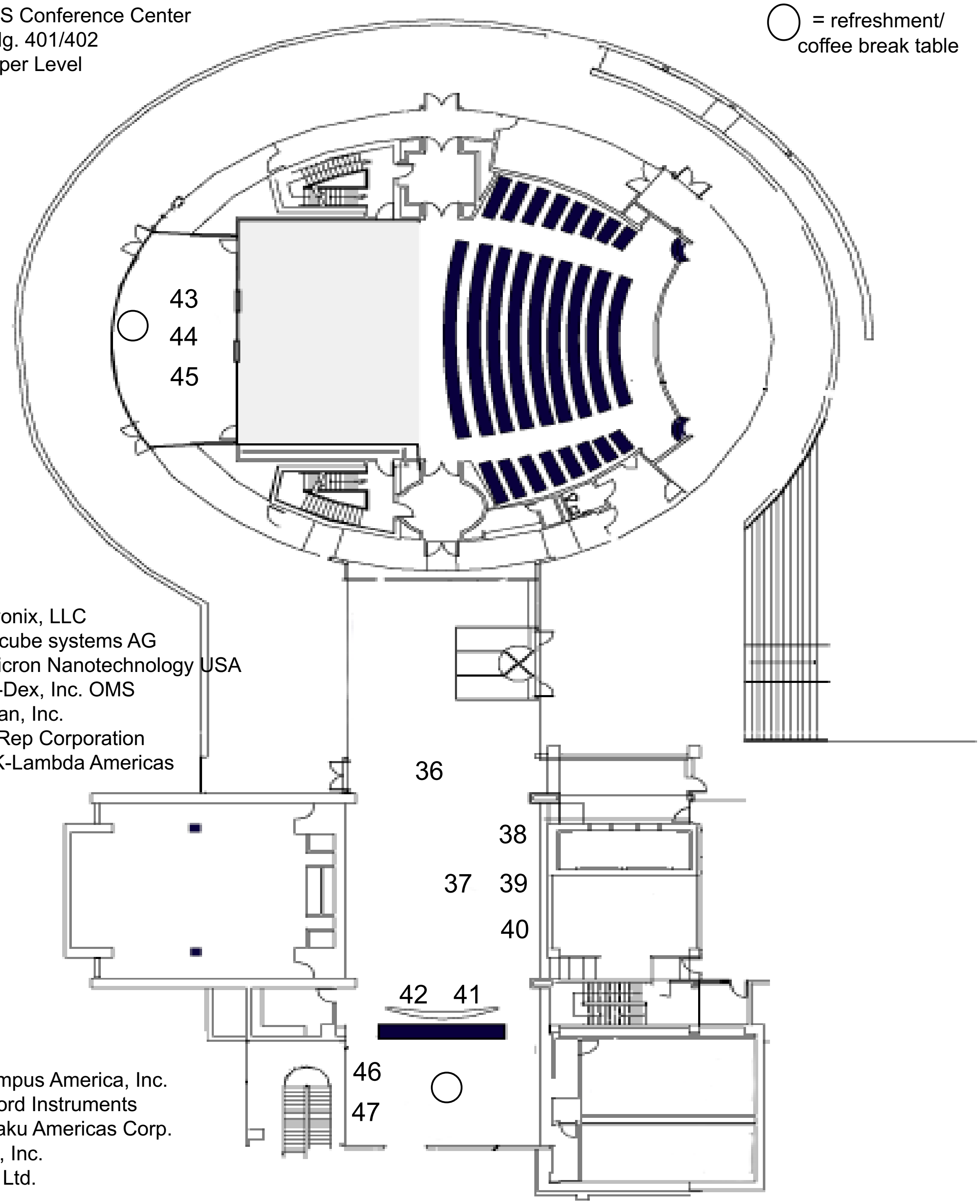
* UPSTAIRS/ATRIUM EXHIBITORS PLUS REFRESHMENT TABLES

Exhibitor Locations – 2012 APS/CNM/EMC Users Meeting
Argonne National Laboratory

APS Conference Center
Bldg. 401/402
Upper Level

○ = refreshment/
coffee break table



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37. attocube systems AG
38. Omicron Nanotechnology USA
39. Pro-Dex, Inc. OMS
40. Gatan, Inc.
41. TecRep Corporation
42. TDK-Lambda Americas

43. Olympus America, Inc.
44. Oxford Instruments
45. Rigaku Americas Corp.
46. TMI, Inc.
47. IDT Ltd.

Additional exhibitors on the Gallery level.

2012 APS/CNM/EMC Users Meeting - Schedule at a Glance

Monday May 7th

8:45-12:20	**Combined Plenary Session *(Lect. Hall)***					
	8:45- 8:55	**Peter Eng**, APSUO Chair, Welcome				
	8:55 -9:25	**Eric Isaacs**, ANL Director, Welcome from the Laboratory and Introduction of The Honorable Judy Biggert				
	9:25 -9:45	**The Honorable Judy Biggert,** U.S. Representative, 13th Congressional District of Illinois				
	9:45 - 9:50	**Peter Eng**, APSUO Chair, Introduction of Keynote				
	9:50 - 10:30	**Richard Harris,** Science Desk Correspondent for NPR				
	10:30 - 11:00	**Coffee Break *(Gallery and Atrium)***				
	11:00 - 11:20	**Brian Stephenson**, Director, APS				
	11:20 - 11:40	**Amanda Petford-Long**, Director, CNM				
	11:40 - 12:00	**Dean Miller**, Director, EMC				
	12:00 - 12:20	**Tony Lanzirotti,** NUFO Report, The University of Chicago, CARS				
	12:20 - 1:30	**Lunch (Tent) + Postdoc Luncheon (A1100)**				
1:30 - 5:30	**Parallel Plenary Sessions**					
	APS *(Lecture Hall)*		**CNM *(Bldg. 402, E1100-1200)***		**EMC *(Bldg. 401, A1100)***	
	1:30 - 2:10	Keynote: Alexis Templeton	1:30 - 2:15	Keynote: Caroline Ross	1:30 - 2:00	Ted Norris
	2:10 - 2:30	Damian Ekiert: 2012 Franklin Awar	2:15 - 2:45	Horacio Espinosa	2:00 - 2:30	J. G. Wen
	2:30 - 3:10	Linda Young	2:45 - 3:15	Esmeralda Yitamben	2:30 - 3:15	Keynote: David McComb
	3:10 - 3:40	Coffee Break	3:15 - 3:40	Coffee Break	3:15 - 3:40	Coffee Break
	3:40 - 4:20	Mike Gillan	3:40 - 4:10	Paul Evans	3:40 - 4:00	Yuyuan Lin
	4:20 - 4:40	Ahmet Uysal	4:10 - 4:40	Pingshan Wang	4:00 - 4:30	Marquis Kirk
	4:40 - 5:30	George Srajer	4:40 - 4:55	Pongsakorn Kanjanaboos	4:30 - 5:00	Renu Sharma
5:30 - 8:30	**Social Event: Dinner and Video/Music Event (Tent and Lect. Hall)**					

Tuesday May 8th

9:00 - 4:40	**Cross-facility Thematic Workshops**					
	Operando Characterization of Energy Systems *(Bldg. 401, Room A1100)*		**Probing the Interface between Biological Systems and the Environment *(Bldg. 402, Rooms E1100/E1200)***		**Imaging at All Length and Time Scales *(APS 402 Lecture Hall)***	
	8:50 - 9:00	Welcome & Intro. Remarks	8:45 - 9:00	Welcome & Intro. Remarks	8:45 - 9:00	Welcome & Intro. Remarks
	9:00 - 9:40	Dean Miller	9:00 - 9:40	Matthew Marshall	9:00 - 9:40	Shengnian Luo
	9:40 - 10:20	Thomas Hansen	9:40 - 10:20	Catherine Murphy	9:40-10:20	Xianghui Xiao
	10:20 - 10:50	**Coffee Break**	**10:20 - 10:50**	**Coffee Break**	**10:20 - 10:50**	**Coffee Break**
	10:50 - 11:30	Haimei Zheng	10:50 - 11:30	Jason Unrine	10:50 - 11:30	Wilson K.S. Chiu
	11:30 - 12:10	Shen Dillon	11:30 - 12:10	Ka Yee Lee	11:30 - 12:10	Peter Sutter
	12:10 - 1:30	**Lunch *(Tent)***	**12:10 - 1:30**	**Lunch *(Tent)***	**12:10 - 1:30**	**Lunch *(Tent)***
	1:30 - 2:10	Ralph Nuzzo	1:30 - 2:10	Ryan Tappero	1:30 - 2:10	Phillip First
	2:10 - 2:50	John L. Fulton	2:10 - 2:50	Maxim I. Boyanov	2:10 - 2:50	Paul Kotula
	2:50 - 3:20	**Coffee Break**	**2:50 - 3:20**	**Coffee Break**	**2:50 - 3:20**	**Coffee Break**
	3:20 - 4:00	Héctor D. Abruña	3:20 - 4:00	Mark Jensen	3:20 - 4:00	Geoff Campbell
	4:00 - 4:40	Mariana Bertoni	4:00 - 4:40	Chantel C. Tester	4:00 - 4:40	Christian Kisielowski
4:40 - 7:00	**Poster Session and Reception (TCS--bus transportation provided between APS, Guest House, and TCS)**					
7:00 -9:00	**APS Partner User Council Meeting and Dinner (Argonne Guest House Dining Room)**					

Wednesday May 9th

12:00 - 2:00	**CNM Users Executive Committee Meeting (C4200, Building 401)**					
12:10 - 1:30	**APSUO's Steering Committee Lunch (Bldg. 401, Fifth Floor Gallery)**					
Full and Half Day Workshops	**Parallel Facility-specific Workshops**					
	APS Workshop Locations		**CNM Workshop Location**		**EMC Workshop Location**	
	APS WK1	Bldg. 401, Room A1100	**CNM WK7**	Bldg. 401, Room A5000	**EMC WK8**	Bldg. 402, Room E1100
	APS WK2	Bldg. 440, Room A105/106				
	APS WK3	APS 402 Lecture Hall				
	APS WK4	Bldg. 402, Room E1200				
	APS WK5	Bldg. 460 (Guest House) Conf. A				
	APS WK6	Bldg. 460 (Guest House) Conf. A				

Thursday May 10th

8:30 - 5:30	**CNM Short Courses *(CNM Building 440)***		
Full and Half Day Courses	**Short Course A**	Functional Imaging with Ambient Atomic Force Microscopy	Rm. A105/106
	Short Course B	Confocal Raman Microscopy	Rm. B108
	Short Course C	Practical Methods for Fabricating Nanostructures and Devices	Upstairs Gallery
	Short Course D	High-performance Computing Techniques for Materials Modeling and Nanophotonics	Rm. A201

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