Sustainability Focus Topic
Room: 5 & 6 - Session SU+AC+MI+MS-TuM

Critical Materials and Energy Sustainability
Moderators: Erik B. Svedberg, The National Academies, Robert Lad, University of Maine

8:00am **SU+AC+MI+MS-TuM1 How Critical Materials Affect Emerging Technologies**, ***Alexander King***, The Ames Laboratory **INVITED**

We live in a golden age for the development of technologies that have potential for clean and efficient production, storage or use of energy. Many, if not all of these technologies, however, depend on the properties of specific materials that may have low availability, or produce environmental challenges of their own during their production. We will look at the impact of materials supply challenges on the adoption of some recent clean energy technologies, consider possible impacts on some emerging technologies, and describe what efforts must be undertaken to ensure that fragile materials supply-chains do not prevent the adoption of technologies that promote a sustainable energy future.

9:20am **SU+AC+MI+MS-TuM5 The Role of Oxidation and Charging Rates on Li Electrochemical Deposition in Solid State Batteries**, ***Alexander Yulaev***, University of Maryland, *V. Oleshko*, NIST, *P. Haney*, NIST Center for Nanoscale Science and Technology, *A.A. Talin*, Sandia National Laboratories, *M.S. Leite*, University of Maryland, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

The recent progress in all-solid-state Li-ion batteries (SSLIBs) allowed a significant reduction of overall dimensions of stand-alone medical and micro-electronic devices. Owing to their compatibility with microfabrication process, high specific power, energy densities, and reduced safety risks of the thermal runaway, SSLIBs are likely to compete with their liquid counterparts in the near future. However, the large-scale implementation of SSLIBs requires further characterization during their fabrication and operation. Particularly, spatially resolved *in-operando* techniques probing electrochemical processes at the interfaces are needed. In the present work, we quantify the effects of oxidizing environment and charging rates on a lithium plating morphology using UHV electron microscopy and spectroscopy in correlation with electrochemical characterization. To conduct these measurements, we fabricate a model thin-film planar battery with $LiCoO_2$ cathode, LiPON electrolyte, and an ultra-thin carbon anode. Our experimental data reveal a strong dependence of plated Li morphology on presence of oxidation species at the surface and a gas phase. Under UHV conditions a linear correlation between the nucleation density of lithium clusters and a charging rate is observed. We show that the 2D nucleation model adequately describes the obtained dependence. The plated lithium morphology drastically changes from the in-plane clusters to out-of-plane whisker growth when ~10^{-7} Pa of oxygen is admitted to the UHV chamber. The in-plane cluster growth resumes when oxygen pressure increases from 10^{-7} to 10^{-5} Pa. We envision that our findings will contribute to whisker-free safer SSLIB performance under realistic operating conditions.

9:40am **SU+AC+MI+MS-TuM6 Unique Super-Ionicity Achieved on the Nanoscale with Applications in Next-Generation Lithium Ion Batteries**, ***Progna Banerjee***, *D. Dumett Torres*, *P. Jain*, University of Illinois at Urbana-Champaign

Lithium-ion (Li-ion) batteries have been dominating the global market for consumer electronics and power vehicles. However, significant safety concerns arise from degradation reactions (reduction/decomposition) of the electrolyte during cycling, potentially causing dendrite formation resulting in leakage and fires. A potential solution is the replacement of the flammable organic electrolyte with an inorganic solid electrolyte with superior electrochemical, mechanical and thermal stability, absence of leakage, long shelf-life, enhanced electrochemical stability and the possibility of battery miniaturization.

A promising candidate for these solid electrolytes are super—ionic materials which exhibit high ionic conductivities matching those of liquid electrolytes. In these materials, past a phase transition, one sub-lattice (often the cationic) melts, resulting in a disordered cation network, wherein cations can transport in a manner reminiscent of that of a liquid. Known superionic materials, such as AgI, Cu_2Se etc. in their bulk form, display this phase transition at high temperatures and/or pressures, making them unsuitable for many applications. In our recent study, we examined Cu_2Se nanocrystals (NCs) prepared from their magic-sized CdSe counterparts using a synthetic topotactic method called cation exchange. In these NCs, the superionic disordered "liquid-like" behavior was observed under ambient conditions. Larger NCs prepared under similar conditions interestingly display ordered layers of Cu^+ ions and vacancies similar to bulk solid. We investigate the origin of this nanoscale effect using arguments based on lattice strain, cationic occupancies obtained from crystallography, and density functional theory (DFT) calculations.

We are extending this work to investigate the possible mechanism of ionic transport in these NCs using a.c. impedance measurements. We are investigating size and dimensionality effects on the transport behavior of cations and the superionic phase transition. We will also investigate the effect of cation vacancies in terms of their profile and density on the phase transition behavior and ionic conductance. This study will pave the way to fundamental understanding on ion transport behavior in solids, and applications as solid-state electrolytes, thermoelectrics and ultrafast electronic switches.

11:00am **SU+AC+MI+MS-TuM10 Electric Cell Potential Driving Changes in Perovskite Surface Termination and Enabling Catalysis**, ***Monika Backhaus***, Corning, *L. Gregoratti*, *M. Amati*, Elettra-Sincrotrone Trieste, Italy **INVITED**

Dynamic segregation processes in perovskite electrodes have been studied in operando in electrochemical model cells with thin zirconia electrolyte and mixed perovskite catalyst by spatially resolved scanning photoelectron microscopy (SPEM) in combination with impedance spectroscopy and gas analysis in the goal to gain better understanding of electrode surface chemistry and its key drivers. We focused on the oxygen reduction reaction at perovskite electrodes and electrochemically driven reactions, such as redox reactions in chemical reactors or sensors. The current overview summarizes our synchrotron in-operando surface spectroscopy in various technical areas.

Our electrochemical cells are built of a thin zirconia electrolyte and mixed perovskite catalyst. They were studied by SPEM at the Elettra synchrotron. The experimental set up allowed operating temperatures up to 700C, mixtures of unreactive or reactive gases at chamber pressure up to 10^{-5} mbar and local pressure above the sample of 1mbar (gas jet). Electrochemical measurements, such as monitoring of i-V behavior or impedance were realized simultaneously.

The surface termination of (La,Sr)MnO_3 (LSM) electrodes was studied as a function of cell potential, oxygen partial pressure and temperature. The surface chemistry reversibly changed with applied potential, exhibiting Mn-termination in highly oxygen-rich environment and increasing strontium segregation in oxygen-poor environment and under reducing cell potential. Cathode termination changed not only with applied cell potential, but also with cell current. LSM cathode pump cells operating at high current densities preserved an "oxygen-rich" surface chemistry under high cell potential, while low current cells exhibited large changes in surface chemistry.

The response of perovskite electrodes to reactive gas environment was also investigated. Model cells with LSM electrodes were studied in oxygen-propene gas mixtures at different cell potentials under oxygen flux at 400-600°C. Oxygen ion flux and cell potential, both were found to drive dynamic changes of catalyst and electrolyte surface chemistry, including redox reaction, surface segregation and long range surface diffusion. Strongly positive cell potential drove an interaction of hydrocarbon with the mixed oxide catalyst surface, yielding adsorbed carboneous species with epoxy-type bonding at a strongly Sr-enriched surface. The carboneous surface complexes reversibly formed and decomposed with cell potential, suggesting it to play the role of an intermediate in an oxide-electro-catalyzed partial oxidation of propene.

11:40am **SU+AC+MI+MS-TuM12 Possibilities of Hydrogen Energy Utilization in Kazakhstan: Preparation of TiCrMn Hydrogen Storage Alloys and Investigation of Their Absorption Properties**, ***Saule Zholdayakova***, *H.-H. Uchida*, *Y. Matsumura*, Tokai University, Japan

The society of Kazakhstan has been becoming strongly dependent on fossil fuels, which results in facing serious environmental problems. Kazakhstan is a Central Asian country with rich natural resources, such as Mn, Cr and Ti and energy self-sufficiency is 200% including exportation. Most of the consumption is fossil resources, mainly dependent on coal. The power configuration of Kazakhstan is 70% coal, 19% natural gas, 1% oil, and 10% hydraulic power. With a background of rich production of fossil fuels, Kazakhstan exports most of its oil and domestically dependent on coal. By 2020, Kazakhstan government planning to reduce the amount of green house gas produces by 15% of that in 1992. For these reasons, the development of renewable energy is significant. In this study we focus on the application of hydrogen as an energy carrier for spreading renewable energy, especially hydrogen energy to solve the environmental problems in Kazakhstan. Hydrogen has more energy per unit of mass, flexible storage options, and it is clean energy. Hydrogen can be stored as a gas, a liquid and as a solid. The

other side, for realization hydrogen energy system we need to think more concretely about a manufacture of hydrogen, storage, transportation and utilization. The main manufacture method for hydrogen is electrolysis. The electricity consumption per capita is 5000 kWh/year. If hydrogen energy become a conductor of energy, 1.13m^3/year of water will necessary to source of hydrogen. After utilizing renewable energy for product hydrogen from water, storage, transport and change to electric power. In the end of consumption, we get the same amount of water. In this study, especially conditions necessary for the renewable energy in Kazakhstan are summarized and trained to preparing hydrogen storage ally using the metals of Mn, Cr and Ti available in Kazakhstan.

Tuesday Afternoon, October 31, 2017

Sustainability Focus Topic
Room: 5 & 6 - Session SU+2D+MS+NS-TuA

Membranes, Thin Films, and Sensors

Moderators: Keith Brown, Boston University, Roya Maboudian, University of California at Berkeley

2:20pm **SU+2D+MS+NS-TuA1 Protecting Food and Water Quality: Considerations for Materials Innovation**, ***Susan Duncan***, Virginia Polytechnic Institute and State University **INVITED**

Innovation in materials and membranes provides opportunity for enhancing water and food safety, diversifying and expanding water and food sources, protecting nutrient quality and bio-availability, and improving human health and well-being. Food and water are transitioned from their original sources into resources for animal feed and human food through production, processing, packaging, and distribution/retail stages. Throughout these stages, membranes and materials for physical and chemical separations, microbiological control, analysis and measurement, capture and containment are required.

Synergistic partnerships, among scientific disciplines and between private-public entities, encourage innovation in the design and applications of materials and membranes for discoveries and advancements in water and food processing and packaging. The objective of this discussion is to showcase the engagement of chemists, engineers, and food scientists in approaching and resolving challenges relating to water and food processing, safety, and quality and the relationship to the consumer. Three featured examples, relating to membranes and materials, include:

Aquaculture: Recirculating water for the purpose of raising fish has high economic and global impact by increasing sustainable supply of high quality food proteins for feeding the growing global population. Challenges include the need for removing biosolids, small molecular weight molecules, and bacteria that influence fish health and quality of the fish as a food source.

Water Safety from Source and Supplier to the Consumer: Protecting public health is the primary role of water treatment. Changes in water disinfectant treatment, e.g. chlorine to chloramine, affect material stability, safety and performance and can lead to significant economic impacts and consumer concerns.

Food Packaging Functionality: Protecting food and beverage freshness from processing to purchase requires understanding of the food system, the process, and storage conditions. Innovative materials that interfere with light energy can protect beverage and food quality for retaining freshness and nutrient retention for enhancing human health.

Expanding our scientific continuum from molecule to materials through process, package and consumer perspective enriches and guides scientific discovery.

3:00pm **SU+2D+MS+NS-TuA3 Real-time Detection of Water Contaminants Using a Graphene-based Field-Effect Transistor Sensing Platform**, ***Junhong Chen***, University of Wisconsin - Milwaukee **INVITED**

The National Academy of Engineering identified "providing access to clean water" as one of the top 10 grand challenges for engineering in the 21st century. A central requirement for safe drinking water is the availability of low-cost and real-time water quality monitoring. Current detection methods for critical analytes in water are often too expensive or unsuitable for in-situ and real-time detection (*an unmet need*). As a result, there is a lack of water quality monitoring along the water distribution line and at the point of use, which is inadequate because of potential deterioration in water quality within water distribution systems (e.g., Flint Water Crisis). This talk will unveil a powerful approach to real-time water sensors through a graphene-based field-effect transistor platform. The working principle of the sensor is that the conductivity of 2D nanomaterial channel (usually measured in resistance) changes upon binding of chemical or biological species to molecular probes anchored on the graphene surface. As such, the presence and the concentration of analytes, such as heavy metals, bacteria, and nutrients, can be rapidly determined by measuring the sensor resistance change. The talk will introduce the performance of the sensor for detection of various water contaminants and focus on the molecular engineering aspects of the sensor device through both theoretical and experimental approaches. The talk will end with a brief introduction on the translation of the platform technology from concept to prototype product through partnership with industries.

5:00pm **SU+2D+MS+NS-TuA9 Nanocellulose Thin Films and Nanocellulose Aerogels**, ***Kenneth Carter***, University of Massachusetts - Amherst, *A. Chang*, *K.L. Martin*, *Y. Li*, University of Massachusetts – Amherst **INVITED**

Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. We have developed a new method for the preparation of well-dispersed cellulose nanofibrils and nanocrystals. Advantageously, the method does not require the use of harsh acids and excludes the use of catalytic oxidants such as 2,2,6,6-tetramethyl-1-piperidine-N-oxy (TEMPO) . Furthermore, the nanofibrils and nanocrystals produced by the method are easily re-dispersible and give stable aqueous dispersions. Transparent, robust nanocellulose thin films were prepared with outstanding anti-fogging properties. Most recently, nanocellulose was used to prepare aerogel/foam materials using a new fabrication method. The aerogels are mechanically stable and robust. Our new aerogel fabrication process obviates the need to use freeze-drying or low pressure solvent removal. We will present data on new nanocellulose aerogels with densities ranging from 5-100 mg/cm^3.

5:40pm **SU+2D+MS+NS-TuA11 Fabrication and Characterization of Thermal Treated Si/Si+Ge Thin Films For Energy Harvesting**, *S. Budak*, *Z. Xiao*, ***Michael Howard***, *B. Rodgers*, *M. Alim*, Alabama A&M University

Thermoelectric thin film devices were prepared from the alternating nanolayers of Si and Si+Ge to form the Si/Si+Ge thin films structures using DC/RF magnetron sputtering system. Fabricated thermoelectric devices were treated at different temperatures for an hour for each case to form quantum (nano) structures in the alternating nanolayers of Si and Si+Ge to increase both the Seebeck coefficients and the electrical conductivity and decrease the thermal conductivity. The prepared Si/Si+Ge thin film thermoelectric devices were characterized using the Seebeck coefficient measurement; the four probe van der Pauw resistivity measurement and the laser thermal conductivity systems for in-plane geometries. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). Thermal treatment showed positive effects on the thermoelectric properties of Si/Si+Gethin films on the selected temperatures. The findings will be presented during the meeting.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

6:00pm **SU+2D+MS+NS-TuA12 Thermoelectric Properties of Bi_2Te_3/Sb_2Te_3 Thin Films Annealed at Different Temperatures**, *S. Budak*, *Z. Xiao*, *M. Howard*, ***Breonna Rodgers***, *M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from Bi_2Te_3/Sb_2Te_3 thin films using DC/RF magnetron sputtering system. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM/EDS).

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

Sustainability Focus Topic
Room: 5 & 6 - Session SU+AS+EM+MS-WeM

Piezoelectrics, Thermoelectrics, and Superconductors
Moderators: George Nolas, University of South Florida, Kimberly Cook-Chennault, Rutgers University

8:20am **SU+AS+EM+MS-WeM2 Investigation into Novel p-type Thermoelectric Materials**, ***Dean Hobbis***, *K. Wei*, *G.S. Nolas*, University of South Florida

Novel thermoelectric materials are in high demand due to the ability to directly convert waste heat into electrical power, a process that has limitless applications both privately and commercially. Currently n-type thermoelectric materials have been more vastly studied than p-type and have been optimized to higher Figures of Merit (ZT). A thermoelectric module requires both n-type and p-type materials, therefore the efficiency of the module is characterized by the combination of ZT values. This means the optimization of p-type thermoelectric materials is extremely important to the commercial viability of thermoelectric technology. Furthermore, the particular synthesis method is also of importance for applications in industry. In skutterudites, for example, methods of fractional filling are typically used to improve thermoelectric efficiency by promoting phonon scattering to reduce thermal conductivity in the material, but most of the elements used as filler are electron donors. Nevertheless, Br is an electron acceptor when used as a filling atom [1]. In quaternary chalcogenides, thermal conductivity can be intrinsically low due to the crystal structure so methods to improve electrical transport is often employed through alloying and substitution on different atomic sites. Certain antimonides also possess intrinsically low thermal conductivity. Furthermore, differing processing conditions can influence the transport properties significantly, resulting in different ZT values. In this talk we present our latest work on these material systems, including new data that shows substantial improvement In ZT with composition and processing conditions.

[1] Nolas et al. *Mat. Res. Soc. Symp.* 626, **2001**, Z10.1.1

8:40am **SU+AS+EM+MS-WeM3 Thermoelectrics for Sustainable Energy Harvesting**, ***Mary Anne White***, Dalhousie University, Canada **INVITED**

Thermoelectrics can convert heat to power. The key to this process is the combined electrical (high electrical conductivity and Seebeck coefficient) and thermal (low thermal conductivity) properties. Although thermoelectrics have been used commercially for more than 50 years, new materials with higher efficiency could make their use more widespread. A large fraction of energy consumed is actually wasted as heat, so efficient conversion of this waste heat to useable power would be a great advantage to humanity. After a general introduction to thermoelectrics, this presentation will focus on improvement of thermoelectrics via sustainable approaches, including consideration of sustainability of the elements, and recent work focusing on elements with high availability.

9:20am **SU+AS+EM+MS-WeM5 Toward a Greener World: The (Re)search for Lead-Free Piezoelectrics**, ***Xiaoli Tan***, Iowa State University **INVITED**

Piezoelectricity refers to the linear coupling, in the direct effect, between mechanical stress and electric displacement, and in the converse effect, between mechanical strain and applied electric field. The proportionality constants are the piezoelectric coefficients which are equivalent between the direct and the converse effects. For the past six decades ceramics based on $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) perovskite oxides have been the workhorse of piezoelectric technology due to their excellent properties, ease of processing, and low cost. The high piezoelectric performance of PZT is primarily resulted from the intrinsic lattice distortion and the ferroelectric domain switching. However, environmental concerns with lead have stimulated worldwide intensive efforts in the search for lead-free piezoelectric ceramics.

The research efforts on lead-free piezoelectric ceramics have been largely concentrated on three solid solution families: $BaTiO_3$-based, $(K_{0.5}Na_{0.5})NbO_3$-based, and $(Bi_{1/2}Na_{1/2})TiO_3$-based compositions. $BaTiO_3$-based ceramics exhibit excellent piezoelectric coefficients, but their applications are limited by their low Curie points (~100 ºC). $(K_{0.5}Na_{0.5})NbO_3$-based compositions possess high piezoelectric coefficients and relatively high Curie points (> 200 ºC), but have stringent requirements on the processing conditions. $(Bi_{1/2}Na_{1/2})TiO_3$-based polycrystalline ceramics develop giant electrostrains (up to 0.70%), but usually require a very high electric field.

In this presentation, an overview of the recent development in the search and research on lead-free piezoelectric ceramics will be given. Their chemical compositions, structure evolutions, and mechanisms for property optimization will be discussed. In addition, two specific investigations will be presented. The first one is on the microstructural response to poling electric fields in the $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ solid solution. With the *in situ* transmission electron microscopy technique, it is directly observed that poling fields can either destroy or create morphotropic phase boundaries and the associated strong piezoelectric property. The second investigation is on the development of a giant electrostrain of 0.70% at 50 kV/cm at room temperature in $\{[Bi_{1/2}(Na_{0.84}K_{0.16})_{1/2}]_{0.96}Sr_{0.04}\}(Ti_{0.975}Nb_{0.025})O_3$. This polycrystalline ceramic with randomly oriented grains is even better than some single crystals in terms of some electromechanical properties. *In situ* transmission electron microscopy examination indicates that the giant electrostrain is originated from the reversible phase transitions under applied electric fields.

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11:20am **SU+AS+EM+MS-WeM11 Thermal Annealing Effects on the Thermoelectric Properties of Si/Si+Sb Thin Films**, ***Satilmis Budak***, *Z. Xiao*, *M. Curley*, *M. Howard*, *B. Rodgers*, *M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from multi-nanolayered Si/Si+Sbthin films using DC/RF magnetron sputtering system. Thermoelectric devices were annealed at different temperatures to form quantum (nano) structures in the multilayer thin films to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The prepared devices were characterized using Seebeck coefficient measurement; four probe van der Pauw measurement resistivity and the laser thermal conductivity systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS).

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

11:40am **SU+AS+EM+MS-WeM12 Critical Current by Design**, ***George Crabtree***, *U. Welp*, Argonne National Laboratory, *K. Kihlstrom*, University of Illinois at Chicago, *A. Koshelev*, Argonne National Laboratory, *A. Glatz*, Northern Illinois University, *I. Sadovskyy*, *W.K. Kwok*, Argonne National Laboratory **INVITED**

We introduce a new approach for rational design of superconducting critical currents, using time-dependent Ginzburg-Landau simulation to predict the critical current produced by an arbitrary mixed pinning landscape. Time dependent Ginzburg-Landau simulations automatically take into account vortex flexibility, the variation of coherence length with temperature and field, the mutual interaction of vortices and the interaction of vortices and defects. Core pinning by an arbitrary mixed pinning landscape is included by lowering the superconducting condensation energy at points, along lines and within finite nanoscale regions corresponding to specific pinning defects. We show results for several real-world cases that verify predictive ability, outline a program for unfolding the interaction of multiple pinning defects and for maximizing the critical current in targeted temperature and field ranges

Vortices in High Performance High Temperature Superconductors, W. K. Kwok et al., Reports on Progress in Physics. 79, 116501 (2016)

Toward Superconducting Critical Current by Design, Ivan A. Sadovskyy et al, Advanced Materials 28(23), 4593-4600 (2016)

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, as part of the Center for Emergent Superconductivity Energy Frontier Research Center and by the Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Science.

Manufacturing Science and Technology Group
Room: 5 & 6 - Session MS+AS-WeA

Advanced Surface, Interface, and Structural Characterization for High Volume Manufacturing

Moderator: Alain C. Diebold, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute

2:20pm **MS+AS-WeA1 The Cornell High Energy Synchrotron Source Upgrade: Current and Future Capabilities for Thin-film Research**, ***Arthur Woll***, Cornell University **INVITED**

In early 2019, the Cornell High Energy Synchrotron Source (CHESS) will complete its most significant upgrade since its construction in 1980. CHESS was originally constructed as a dual-purpose machine, serving as both an x-ray source as well as a particle physics experiment. Since 2008, CHESS has operated as one of only five dedicated high energy synchrotron sources in the world, and one of only two in the U.S.. The upgrade will result in a dramatically improved source, will include six new undulator-fed experimental stations, and represents a unique opportunity to increase and improve access to hard x-ray synchrotron light.

CHESS's history and mission emphasize the importance of deep collaboration with user communities to identify critical areas of instrumentation and methodological development. In particular CHESS has a long history of serving and advancing research on thin films and interfaces – in areas spanning both basic and applied research. CHESS currently hosts active user communities engaged in many of the most promising areas of thin-film research – including organic electronic thin films, high-K dielectrics and other complex oxides, dichalcogenides, and III-V nitrides. Particular research tools include ex-situ characterization such as grazing incidence small- and wide-angle scattering (GISAXS and GIWAXS), fast pole-figure analysis, automated x-ray reflectivity. Specialized equipment for in-situ measurements include chambers for in-situ thermal annealing and solvent annealing, and support for user-supplied UHV chambers for studying in situ thin-film growth and surface science. We will present several examples of recent user science as well as ongoing and proposed CHESS-based developments for thin-film research to motivate a discussion among the thin-film community of the most promising and critical areas for future capabilities of CHESS.

3:00pm **MS+AS-WeA3 Using Synchrotron XRD Techniques to Impact Microelectronics Manufacturing Technologies**, ***Jean Jordan-Sweet***, *C. Lavoie*, IBM T.J. Watson Research Center, *A.V. Carr*, IBM Research, Albany, NY, *N. Breil*, IBM SRDC, East Fishkill; now with Applied Materials Inc., *M.M. Frank*, IBM T.J. Watson Research Center **INVITED**

Since the early 1980s IBM has maintained a strong effort in synchrotron-based research. While our involvement with these facilities has been multi-faceted, we have leveraged our impact through two main avenues: the development of unique instrumentation and the nurturing of mutually beneficial collaborations with academia.

I will present examples of how synchrotron-based XRD studies have impacted our heavily materials- and process-centric technologies, preceded by a description of the instrumentation and techniques that were developed and applied in these examples. Much of our success in supporting IBM technology has been based on the use of *in-situ* XRD, electrical resistance, and optical light scattering measurements during the rapid thermal annealing of thin films or arrays of features. This instrumentation was developed at the NSLS (Brookhaven National Laboratory) [1], and has been redesigned, automated and recently installed at the Canadian Light Source. A second technique that is crucial for understanding the microstructure of thin polycrystalline films on single-crystal substrates is the measurement of texture. With the use of a linear or area detector, many high-resolution pole figures covering a large range of d-spacing can be obtained simultaneously [2]. Understanding and controlling film texture is critical to controlling phase transformations in thin films and to stabilizing and enhancing thermal processing windows during device manufacturing [3].

The first example is a long-term effort to understand the effects of materials and processing on the formation of low-resistance contacts to the gate, source and drain of CMOS devices. It has spanned three materials sets and many generations of chips. The culmination of this knowledge lies in a valuable database containing structure, roughness and resistance information from many thousands of anneals on key samples. With these measurements, IBM was able to extend the manufacturing lifetime of C54-$TiSi_2$, stabilize the NiSi process, and recently resolve a Ni "fang" defect [4] related to the IBM Power8® processor. The second example illustrates how the same techniques are helping us develop advanced memory devices based on ferroelectric hafnium oxide, which are intended to be used for neuromorphic computing.

1] G.B. Stephenson et al., Rev. Sci. Instrum. 60, 1537, 1989; L.A. Clevenger et al., J. Mater. Res. 10, 2355 (1995); J.L. Jordan-Sweet, IBM J. Res. Develop. 44, 457 (2000).

2] S. Gaudet et al., J. Vac. Sci. Technol. A 31(2), 021505 (2013).

3] B. DeSchutter et al., Appl. Phys. Rev. 3, 031302, 2016; C. Lavoie et al., ECS Transactions (accepted).

4] N. Breil et al., Microelectron. Eng. 137, 79 (2015).

4:20pm **MS+AS-WeA7 Development of Ultra-thin ALD Grown high-k Dielectrics and Interconnect Diffusion Barrier Layers aided by Advanced X-ray Structural Analysis for sub 10nm Nodes**, ***Steven Consiglio***, *K. Tapily, R.D. Clark, C.S. Wajda, K.-H. Yu, T. Hakamata, G.J. Leusink*, TEL Technology Center, America, LLC, *S. Dey, A.C. Diebold*, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute **INVITED**

As the semiconductor industry develops processes and integration schemes for the 10nm technology node and beyond, conventional scaling of existing materials is no longer sufficient to enable further device scaling. New materials in the form of ultra-thin films need to be introduced and evaluated at an ever-increasing pace and conventional inline wafer metrology systems do not offer the needed flexibility and capabilities to probe the physical/chemical/structural properties of such extremely scaled layers of increasing complexity.

In this regard, we have investigated the properties of ultra-thin high-k dielectrics and interconnect (both Cu and Ru) diffusion barriers using advanced synchrotron X-ray structural analysis. Some key examples will be illustrated including analysis of higher-k phase stabilization and texturing in thin dielectrics on Si and high mobility substrates, ferroelectric phase stabilization for negative differential capacitance dielectrics, and the evaluation of diffusion barrier performance by using an in-situ ramp anneal method for both Cu and Ru which is a potential Cu interconnect replacement metal.

References:

S. Consiglio et al., *J. Electrochem. Soc*., **159**(6), G80-G88 (2012).

K. Tapily et al., *ECS Trans.*, **45**(3), 411-420 (2012).

R. Vasić et al., *J. Appl. Phys*., **113**, 234101 (2013).

S. Consiglio et al., *J. Vac. Sci. Technol. B,* **32**(3), 03D122 (2014).

K. Tapily et al., *ECS J. Solid State Sci. Technol.*, **4**(2), N1-N5 (2015).

S. Consiglio et al., *ECS J. Solid State Sci. Technol.*, **5**(9), P509-P513 (2016).

S. Dey et al., *J. Appl. Phys*., **120**, 125304 (2016).

S. Dey et al., *J. Vac. Sci. Technol. A*, **35**(3), 03E109 (2017).

5:00pm **MS+AS-WeA9 Stress Control of rf Sputter Deposition of Piezoelectric $Sc_{0.12}Al_{0.88}N$**, ***Michael Henry***, *R.P. Timon, T.R. Young, E.A. Douglas, B. Griffin*, Sandia National Laboratories

Substitution of Al by Sc has been predicted and demonstrated to improve the piezoelectric response with applications in radio frequency (RF) filter technologies. Although cosputtering has achieved Sc incorporation in excess of 20%, industrial processes require single target sputtering and is currently limited. However, the major concern with sputter deposition of ScAl is the control over growth of inclusions while simultaneously controlling film stress for suspended MEMS structures. Our work on 12% Sc suggests, with a direct relationship between the inclusion occurrences and compressive film stress, deposition control can suppress the inclusion growth by increasing the compressive stress. Too much compressive stress can prevent suspension of MEMS devices due to Euler buckling.

This work will describe the RF sputtering deposition and major parameter control over the deposition of $Sc_{0.12}Al_{0.88}N$. We will continue to show a multistep deposition which begins with a process of high compressive stress suppressing the inclusions and then drive the film back towards lower compressive stress levels such that an inclusion free low compressive stress film is deposited such that suspended resonators can be formed. To detail piezoelectric film properties, both top metal and top/bottom metal resonators are demonstrated from 500 MHz to 2 GHz.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+MN+MS+SS-WeA

Nanopatterning, Nanofabrication and 3D Nanomanufacturing

Moderator: Brian Borovsky, St. Olaf College

2:20pm **NS+MN+MS+SS-WeA1 Site-controlled Si Nanodot Formation for a RT-SET via Ion Beam Mixing and Phase Separation**, ***Xiaomo Xu****, *G. Hlawacek, D. Wolf, T. Prüfer, R. Hübner, L. Bischoff,* Helmholtz Zentrum Dresden-Rossendorf, Germany, *M. Perego,* Institute for Microelectronics and Microsystems (IMM-CNR), France, *A. Gharbi*, Laboratoire d'électronique des technologies de l'information (CEA-Leti), France, *H.-J. Engelmann, S. Facsko, K.-H. Heinig, J. von Borany*, Helmholtz Zentrum Dresden-Rossendorf, Germany

The increased use of personal computing devices and the Internet of Things (IoT) is accompanied by a demand for a computation unit with extra low energy dissipation. The Single Electron Transistor (SET), which uses a Coulomb island to manipulate the movement of single electrons, is a candidate device for future low-power electronics. However, so far its development is hindered by low-temperature requirements and the absence of CMOS compatibility. By combining advanced top-down lithography with bottom-up self-assembly of Si nano dots (NDs) we will overcome this barrier.

In this work, Si NDs – suitable as RT Coulomb islands – are formed via ion beam mixing followed by thermally stimulated phase separation. Broad-beam Si^+ and Ne^+ beams followed by a rapid thermal annealing (RTA) treatment were utilized to create a layer of NDs, which are subsequently visualized by Energy-Filtered Transmission Electron Microscopy (EFTEM). The conditions for ND formation, namely the dependence on ion type, primary energy, irradiation fluence, layer thickness and thermal budget during RTA, are optimized based on an extensive survey of this multidimensional parameter space. The presented work is guided by TRIDYN simulations of the Si excess in a SiO_2 layer due to ion beam mixing and 3D Kinetic Monte-Carlo (3DkMC) simulation for the phase separation during the thermal treatment. To tailor towards a single Si ND, the focused Ne+ beam from the Helium Ion Microscope (HIM) is utilized to create user defined patterns of NDs in planar layer stacks. This allows to achieve a mixing volume small enough for restricted Ostwald ripening and successful single ND formation. The existence of the formation of spatially controlled single NDs with a diameter of only 2.2 nm is confirmed by comparing the EFTEM Si plasmon-loss intensity with simulated plasmon loss images.

In the future – by combining conventional lithography, direct self-assembly (DSA) and ion beam mixing – nanopillars with a single embedded ND will be integrated in a CMOS-compatible way. EFTEM and electrical characterization techniques will be used for realizing this novel pathway towards a room-temperature SET device.

2:40pm **NS+MN+MS+SS-WeA2 Scanning Tunneling Microscope Fabrication of Atomically Precise Devices**, ***Richard Silver****,* NIST, *X. Wang,* University of Maryland, College Park, *P. Namboodiri, J. Wyrick, S.W. Schmucker, M.D. Stewart, R. Murray, J.A. Hagmann, C. Richter*, NIST

Atomically precise device fabrication is a technique that enables a new class of atom-based electronic structures with applications ranging from novel low dimensional materials to devices for quantum information processing. Deterministic placement of individual dopant atoms in the Si lattice is achieved using hydrogen-based scanning probe lithography. Controlling the position and electronic or quantum state of deterministically placed atoms in a solid state environment enables novel devices such as single atom transistors and solid state qubits.

However, fabricating functional atom-based devices is particularly challenging because of the need for exceptional ultra-high vacuum, near perfect atomic order, and low temperature epitaxial silicon overgrowth. This, coupled with sensitivity of atomic positional accuracy to thermal processing, and variability in scanning tunneling microscope patterning conditions, make exquisite control of process conditions essential.

In this presentation, we will focus on measurements and characterization of ultra-thin, atomically abrupt, highly doped low-dimensional devices and strategies for contacting these devices. We will describe our methods to align and contact buried devices and address significant challenges in making robust electrical contact to buried devices. We will present low-temperature electrical measurement results from atomically abrupt wires and tunnel junctions with coplanar gates. We have studied the effects of process conditions on device dimensionality and electrical performance in the context of extensive analysis of delta layer formation with optimized locking layer epitaxial growth techniques to enhance the confinement of Phosphorus dopant atoms. Low temperature transport measurements are used to investigate materials properties, effects from atomic imperfection and quantum transport phenomena.

3:00pm **NS+MN+MS+SS-WeA3 Contacting Buried Atomic-Precision Devices in Si using Kelvin Probe and Optical Microscopy**, ***Jonathan Wyrick****, P. Namboodiri, X. Wang, R. Murray, J.A. Hagmann, K. Li, S.W. Schmucker, M.D. Stewart, C. Richter, R.M. Silver*, NIST

STM based hydrogen lithography has proven to be a viable route to fabrication of atomic-precision planar electronic devices. These devices are realized by a patterning step followed by dopant deposition and incorporation, and ultimately encapsulation with epitaxial Si. Atomically precise tunnel junctions, SETs, and Quantum Dots are examples of components that can be fabricated using hydrogen lithography.

The strength of this technique is the ability to control the lateral placement of phosphorus atoms in a single atomic layer of Si with sub-nanometer precision. At the same time, it presents challenges that must be overcome if devices are to be interfaced to the outside world. Locating and then fabricating aligned electrical contacts to buried devices is non-trivial, and becomes easier as the size of buried features is increased, but this is done at the expense of increased writing times and exposure to potential contamination.

We present a strategy for contacting buried devices aimed at minimizing the write-times associated with STM based fabrication by maximizing the positional accuracy with which we can locate subsurface structures. This is done by employing STM fabricated fiducials, AFM topography scans, Kelvin Probe Microscopy, and dark field optical microscopy. The data from each technique can be aligned and corrected for distortions, allowing us to determine buried device locations to better than 200nm accuracy.

3:20pm **NS+MN+MS+SS-WeA4 Quantifying Liquid Transport and Patterning using Atomic Force Microscopy**, *N. Farmakidis,* ***Keith Brown***, Boston University

Atomic force microscopy (AFM) provides unique insight into the nanoscale properties of materials. It has been challenging, however, to use AFM to study soft materials such as liquids or gels because of their tendency to flow in response to stress. Here, we propose an AFM-based technique for quantitatively analyzing the transport of soft materials from an AFM probe to a surface. Specifically, we present a method for loading an AFM probe with a single 0.3 to 30 pL droplet of liquid, and subsequently measuring the mass of this liquid by observing the change in the vibrational resonance frequency of the cantilever. Using this approach, the mass of this liquid was detected with pg-scale precision using a commercial AFM system. Additionally, sub-fL droplets of liquid were transferred from the probe to a surface with agreement found between the real-time change in mass of the liquid-loaded probe and the volume of the feature written on the surface. To demonstrate the utility of this approach in studying nanoscale capillary and transport phenomena, we experimentally determine that the quantity of liquid transported from the tip to a surface in a given patterning operation scales as the mass of liquid on the probe to the 1.35 power. In addition to providing new avenues for studying the dynamics of soft materials on the nanoscale, this method can improve nanopatterning of soft materials by providing *in situ* feedback.

4:20pm **NS+MN+MS+SS-WeA7 Positioning and Manipulating Single Dopant Atoms Inside Silicon**, ***Andrew Lupini****, B.M. Hudak, J. Song,* Oak Ridge National Laboratory, *H.R. Sims,* Vanderbilt University, *M.C. Troparevsky,* Oak Ridge National Laboratory, *S.T. Pantelides,* Vanderbilt University, *P.C. Snijders*, Oak Ridge National Laboratory **INVITED**

The ability to controllably position single atoms inside materials could enable production of a new generation of atomically precise artificial materials with direct relevance for many areas of technology. For example, spins from individual donors in a semiconductor comprise one of the most promising architectures for quantum computing. However, fabrication of the 'qubits' that would make up a quantum computer is still unreliable and many fundamental materials science questions remain unanswered. Perhaps the key technical difficulty is the task of accurately positioning single atom dopants inside a solid with control, or at least understanding, of their local environment.

Silicon is the ideal substrate to explore such ideas because of the ability to obtain isotopically purified samples (a "spin-vacuum") and compatibility with existing electronic components and manufacturing technologies. Group V elements are promising candidates for use as single-atom qubit dopants in Si, and it has recently been argued that bismuth could be an excellent dopant for such applications, because of its anomalously high spin-orbit coupling.

*** NSTD Student Award Finalist**

Bi, in particular, has a large atomic number relative to Si, making it an ideal candidate to study using *Z*-contrast scanning transmission electron microscope (STEM). However, both precise doping and the imaging of single dopant atoms present many scientific challenges. For example, Bi is not very soluble in Si, meaning that the dopant atoms tend to migrate out of position during sample growth.

Here we will show examples of sample growth including novel nanostructures and single atom dopants. We will show dopant atoms imaged inside Si samples, and demonstrate electron-beam directed movement of single dopants.

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5:00pm **NS+MN+MS+SS-WeA9 Characterization of Butyl Tin Photoresists for Nanoscale Patterning**, *J.T. Diulus, R.T. Frederick,* Oregon State University, *M. Li,* Rutgers University, *D. Hutchison, M.R. Olsen, I. Lyubinetsky, L. Árnadóttir,* Oregon State University, *E.L. Garfunkel,* Rutgers University, *M. Nyman,* Oregon State University, *H. Ogasawara,* SLAC National Accelerator Laboratory, ***Gregory Herman***, Oregon State University

Inorganic photoresists are of interest for nanomanufacturing due the potential for high resolution patterning with low line edge roughness, while having high sensitivity to extreme ultraviolet (EUV) radiation. The combination of high absorption coefficient elements and radiation sensitive ligands can improve inorganic photoresist sensitivity while providing high contrast. Inorganic clusters are ideal candidates for photoresists since they have nanometer particle sizes with high particle size uniformity, and the ligand chemistries can be tuned for radiation induced chemistries that control relative solubility differences. In this presentation, characterization of a promising inorganic cluster-based EUV photoresist will be presented, where the goal of the studies is to better understand patterning mechanisms. In these studies, we are investigating butyl tin Keggin cluster that has recently been synthesized, and has shown promising properties as an inorganic photoresist. Key to these clusters, for application as an EUV photoresist, are the high EUV absorption coefficient for Sn, and the radiation sensitive carbon-tin bond. Removal of the organic ligand changes the polarity of the film, which provides the necessary solubility contrast for nanopatterning. We have used temperature programed desorption, electron stimulated desorption, and ambient pressure X-ray photoelectron spectroscopy to characterize both thermal and radiation induced processes in thin films formed from these clusters. We have found that butyl group desorption occurs through both thermal and radiation induced processes, and have determined both the carbon-tin bond strength and electron desorption cross-sections. Studies performed in different ambient conditions, and photon energies, have shown large effects on the radiation induced chemistries, where a significant enhancement in carbon decay was observed for O_2 pressures up to 1 torr. These studies provide a means to better understand the radiation induced processes that result in the solubility contrast of these materials, and may guide in the development of improved EUV photoresists for nanolithography.

5:20pm **NS+MN+MS+SS-WeA10 Impact of Polymer Templated Annealing on Gold Nanowires**, ***Tyler Westover***, *R.F. Davis, B. Uptrey, J. Harb, A. Woolley, S. Noyce*, Brigham Young University

The formation of gold nanowires using bottom up nanofabrication has resulted in wires of small dimension or high conductivity, but not both. We form nanowires on DNA origami through directed assembly of nanoparticles or nanorods followed by electrochemical plating. These metal deposition processes result in non-ideal microstructure and correspondingly low conductivities. To remedy this we have sought to reduce the grain boundary density and surface roughness through annealing. However annealing causes the wires to coalesce into beads. We have found that through the use of a polymer the wires can be templated to retain their overall morphology, while improving surface roughness, throughout a low temperature anneal. We have measured these wires to have less than 1kOhm resistances by electron beam lithography, in a two point configuration. Using electron beam induced deposition we have successfully made four point contacts to measure the change in resistance due to annealing. We will present results on polymer templating, showing that the wires maintain their overall morphology with improved conductivities during low temp (200° C) annealing.

5:40pm **NS+MN+MS+SS-WeA11 Dynamic Growth of Nanopores on Graphene via Helium Ion Microscope**, *S. Kim,* ***Anton Ievlev****, M.J. Burch, I. Vlassiouk, A. Belianinov, S.V. Kalinin, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Controlling atomic-to-nanoscale defect formation on graphene is of significance as defects can modify properties as well as functionality of graphene. Especially, controlled formation of nanopores in graphene can be used for energy harvesting/storage, analysis of biomolecules and the separation of gases or liquids. Nanopores can be fabricated either by using high energy focused electron beam or by focused helium ion beam with high precision. However, focused electron beam has very low throughput to form nanopores despite its superiority in pore size control. On the contrary, focused helium ion beam has much higher throughput in nanofabrication with its capability to form sub-5nm pores. In this study, we utilized the focused helium ion microscope to fabricate nanopores on graphene and demonstrated atomic scale control in growth of nanopores by helium ion irradiation. We demonstrated the size control of nanopores down to ~ 3nm in a diameter. Formation and growth kinetics of nanopores by different helium ion irradiation conditions were explored and analyzed using the image data analytics. Also, Raman spectroscopic measurements was performed to demonstrate the effect of a helium ion dose on the change of initial defect density on graphene which leads to different behaviors and growth kinetics of nanopore formation.

This work was supported by the Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

Manufacturing Science and Technology Group
Room: 5 & 6 - Session MS-ThM

Additive and Other Novel Manufacturing Techniques

Moderator: Vincent Smentkowski, General Electric Global Research Center

8:00am **MS-ThM1 Thermal Spray for Additive Manufacturing**, *A. Agarwal*, ***Cheng Zhang***, Florida International University **INVITED**

Additive manufacturing is gaining popularity in the commercial domain due to engineering and economic advantages over conventional manufacturing, such as reduced material wastage, lightweight components, and rapid manufacturing to near net shapes. Thermal spray processes are promising for additive manufacturing of metals, ceramics as well as polymers. Thermal spray is a wide range of manufacturing processes in which material in the form of particles/wire is sprayed and deposited at elevated temperatures to form coatings and free-standing 3D structures. These processes include plasma spray, flame spray, detonation gun, high-velocity oxyfuel spray, wire arc spray and cold gas spray. Thermal spray allows rapid processing of near net shape structures at bulk scale with complex shapes, contours, and variable thickness. Thermal spray techniques enable manufacturing of composite materials and functional gradient structures. While thermal sprayed coatings have diverse applications in wear resistance, biomedical implants, thermal barrier, corrosion protection, direct write sensors, fuel cells, etc., free-standing 3D structures fabricated by thermal spray are not as extensively used. This talk will present an overview of the state of the art of additive manufacturing via thermal spray techniques. The challenges and potential solutions will be described. A Novel in situ characterization techniques will be discussed that provide insight into processing-structure-property correlations in bulk 3D components fabricated by thermal spray. This will enable development of bulk components with predictable properties by thermal spray techniques.

8:40am **MS-ThM3 Eliminating Excess Flow during Active Brazing through Surface Preparation with ALD**, ***Ronald Goeke***, *C.A. Walker, P. Sarobol, P.T. Vianco*, Sandia National Laboratories

Active brazing is a permanent metallurgical joining method in which highly reactive brazing filler metals are utilized to directly braze metals to nonmetals. Due to limitations of the active brazing filler metal spreading adequately over a nonmetal surface, the filler metal must be preplaced between the two faying surfaces of the brazement. When heated the liquid filler metal is normally contained within the brazement by capillary attraction. Chemical reactions at the brazement faying surfaces often lead to excessive braze filler metal flow, rendering the brazed assembly useless. Conformal coatings nanometers thick, deposited by atomic layer deposition (ALD) onto the metal surfaces, modify the surface chemistry to eliminate excessive filler metal flow. Unlike other means used to prevent excessive filler metal flow, the thin ALD coating does not hinder next assembly processes, does not require post-braze cleaning or alter the base material mechanical properties.

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9:00am **MS-ThM4 Analysis of Textile Surface Characteristics for Direct Write Printing of Ink-based Textile Electronics**, ***Jesse Jur***, *R. Bhakta, H. Shahariar, H. Soewardiman*, North Carolina State University

Direct write printing is studied as a method for producing large-area electronics directly onto flexible textile substrates. This process delivers viscous conductive particle inks in the range of 1 - 20 kilo-cps to a surface via a pressure-backed nozzle, making it a process that has key similarities and differences to traditional screen-printing and ink-jet printing. In this work, key correlations are defined between the print head speed and viscosity on the ability to design electronic device structures on textile substrates. For standard surface printing on the textile, sheet resistance values ranges from 5 - 16 mOhms/sq for Ag and Ag/AgCl inks. In addition, the ability to design devices through the bulk of the textile is explored. Ink penetration is shown to vary between to 100 microns into the textile structure based on the hydrophobic characteristic of the textile substrate, ink viscosity and the delivery pressure of the ink. Such penetration is shown to fabricate multi-layered printed structures on the surface and back of the textile. Device applications range from printed/flexible heaters, antennas, circuit boards, and dry electrodes for biopotential monitoring.

9:20am **MS-ThM5 Three-Dimensional Silicon Mesostructures for Bioelectric Interfaces**, ***Yuanwen Jiang****, *B. Tian*, The University of Chicago

Silicon-based materials exhibit biocompatibility, biodegradability as well as a spectrum of important electrical, optical, thermal and mechanical properties, leading to their potential applications in biophysical or biomedical research. However, existing forms of silicon (Si) materials have been primarily focused on one-dimensional (1D) nanowires and two-dimensional (2D) membranes. Si with three-dimensional (3D) mesoscale features has been an emerging class of materials with potentially unique physical properties. Here, we incorporated new design elements in the traditional chemical vapor deposition (CVD) method to prepare various forms of 3D Si mesostructures and studied their functional biointerfaces with cellular components. In the first example, an anisotropic Si mesostructure, fabricated from atomic gold-enabled 3D lithography, displayed enhanced mesoscale interfacial interactions with extracellular matrix network. This topographically-enabled adhesive biointerface could be exploited for building tight junctions between bioelectronics devices and biological tissues. Another Si mesostructure with multi-scale structural and chemical heterogeneities, was adopted to establish a remotely-controlled lipid-supported bioelectric interface. We further adapted the bioelectric interface into the non-genetic optical modulation of single dorsal root ganglia neuron electrophysiology dynamics. Our results suggest that the dimensional extension of existing forms of Si could open up new opportunities in the research of biomaterials manufacturing and application.

9:40am **MS-ThM6 Microplasma Sputtering for 3D Printing of Metallic Microstructures**, ***Yosef Kornbluth***, Massachusetts Institute of Technology, *R. Matthews, L. Parameswaran, L. Racz*, MIT Lincoln Laboratory, *L. Velásquez-García*, Massachusetts Institute of Technology

Additive manufacturing technologies promise to transform the development and production of agile microsystems, but are limited by the ability to print microelectronics-quality interconnects. State of the art 3D printing techniques for conductors cannot yet deliver the feature resolution and electrical conductivity required for high performance microcircuits, and have materials and substrate constraints and post-processing requirements. We develop a novel microplasma sputtering system that has the potential to provide direct-write capability of quality metal interconnects on non-standard substrates for integrated circuits, with future extensibility to dielectrics and semiconductors. The microplasma is generated at atmospheric pressure, obviating the need for a vacuum. By manipulating the metal at the atomic level, we retain the resistivity of bulk metal, and by sputtering the metal, we eliminate the need for post-processing or lithographic patterning.

We have modeled and constructed a first-generation system that incorporates continuous material feed and focusing with electrostatic fields. The microplasma head has a grounded central target wire, surrounded by two pairs of electrodes evenly distributed around the target: two opposing electrodes biased at a positive voltage to form the plasma, and two biased at a negative voltage to focus the plasma. Electrostatic fields guide the ionized fraction of the working gas towards a localized spot on the substrate. The directed ions collide with other gas atoms and, crucially, with sputtered metal atoms from the target. The net force of these collisions drags the metal atoms towards the substrate. This indirect electrostatic focusing mitigates the inherent spread of the sputtered material caused by collisions at atmospheric pressure, and enables fine feature definition. By focusing the sputtered material, we achieve imprints significantly narrower than the cathode, avoiding the need to machine target electrodes as small as the desired feature size.

Multi-physics COMSOL simulations predict that features orders of magnitude narrower than the target-wire cross section can be printed if the electric fields are set appropriately. We present findings from our COMSOL simulations and experimental confirmation of key findings.

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*** National Student Award Finalist**

Manufacturing Science and Technology Group
Room: 18 - Session MS-ThA

Working with Government Labs and User Facilities
Moderators: Bridget Rogers, Vanderbilt University, Mikel Holcomb, West Virginia University

2:20pm **MS-ThA1 Tackling Fundamental and Applied Problems Using EMSL Capabilities - Examples of Applying Surface and Interface Sensitive Tools to Biological Systems**, *C.R. Anderton, D.R. Baer, M.H. Engelhard,* ***Scott Lea***, Pacific Northwest National Laboratory

Tackling many of the most difficult and pressing scientific challenges of today requires an array of advanced instrumentation and expertise. The Environmental Molecular Sciences Laboratory (EMSL) is a US Department of Energy national scientific user facility with a wide range of advanced research capabilities that provides access to users with specialized research needs. EMSL's mission is to lead molecular-level discoveries for the Department of Energy and its Office of Biological and Environmental Research that translate to predictive understanding and accelerated solutions for national biological, energy, and environmental challenges. To achieve this goal, EMSL science is focused into four Science themes: atmospheric aerosol systems, biological dynamics and design, terrestrial and subsurface ecosystems, and molecular transformations (www.emsl.pnnl.gov). Dynamic processes that occur at interfaces underpin research in these science focus areas. EMSL provides an array of unique and advanced capabilities to facilitate interfacial research, including state of the art spectroscopy, microscopy, magnetic resonance, and computational capabilities. EMSL has also made significant strides in the development of *in situ* capabilities designed to interrogate these interfaces in real-time and in a variety of environments. By providing integrated experimental and computational resources for discovery and technological innovation in molecular sciences, EMSL particularly encourages endeavors that utilize multiple capabilities. This talk will focus attention on the application of several surface sensitive and interface tools to biological systems. Like other DOE national user facilities, access to EMSL capabilities is through a proposal and peer review process and can be no-cost for work to be disseminated to the scientific community through open literature publication. Numerous national scientific user facilities are making efforts to increase industrial utilization, and EMSL has recently taken steps to facilitate access to its capabilities for industrial users.

2:40pm **MS-ThA2 Opportunities for Users at the Center for Nanoscale Materials**, ***Kathleen Carrado Gregar***, Argonne National Laboratory

The Center for Nanoscale Materials (CNM) at Argonne National Laboratory is a premier user facility providing expertise, instrumentation, and infrastructure for interdisciplinary nanoscience and nanotechnology research. Academic, industrial, and international researchers can access the center through its user program for both nonproprietary (at no cost) and proprietary research. As a Department of Energy (DOE) funded research center, the CNM is at the forefront of discovery science that addresses national grand challenges encompassing the topics of energy, information, materials and the environment. The scientific strategy of the CNM is consolidated under the following three crosscutting and interdependent scientific themes. Collectively, they aim at the discovery and hierarchical integration of materials across different length scales, at the extremes of temporal, spatial, and energy resolutions: (a) Quantum materials and phenomena (b) Manipulating nanoscale interactions, and (c) Synthesis of nano-architectures for energy, information and functionality. Embedded within these three themes and supporting them are the vector capabilities of X-ray microscopy, electron microscopy, and computational materials science.

Unique capabilities at CNM include a premier clean room with advanced lithography and deposition capabilities, expansive synthesis and nanofabrication resources, a hard x-ray nanoprobe at the Advanced Photon Source synchrotron, myriad scanning probes including low temperature, ultrahigh vacuum STMs, TEMs with in situ holders and chromatic aberration-correction, a 30 TFlop supercomputer, and ultrafast optical probes. A key CNM asset includes outstanding staff with expertise in synthesis, nanophotonics, scanning probe and electron microscopy, nanofabrication, and theory, simulation and modeling. Core technological materials range from 2D layered materials to nanocrystalline diamond. All capabilities and expertise are available through peer-reviewed user proposals; access is free of charge for non-proprietary research. CNM is one of DOE's premier Nanoscale Science Research Centers serving as the basis for a national program encompassing new science, new tools, and new computing capabilities for research at the nanoscale (https://nsrcportal.sandia.gov). Recent staff and user research highlights will be presented, painting a picture of present and future nanoscience and nanotechnology at the CNM (www.anl.gov/cnm).

The Center for Nanoscale Materials, an Office of Science user facility, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC-02-06CH11357.

3:00pm **MS-ThA3 The CNST NanoFab at NIST:** ***Nanofabrication for US Commerce****, V.K. Luciani,* ***Chen Zhang***, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The NIST Center for Nanoscale Science and Technology (CNST) supports the U.S. nanotechnology enterprise from discovery to production. As part of the CNST, the shared-use NanoFab provides its users rapid access to a comprehensive suite of tools and processes for nanoscale fabrication and measurement. The CNST NanoFab at NIST is part of the Department of Commerce and therefore puts a high priority on operating a business friendly, easily accessible facility. The same rates are applied to all users, whether from industry, academia or NIST. Applications are accepted at any time and are reviewed and processed every week. Also, NIST does not claim any inherent rights to inventions made in the course of a NanoFab project. Your intellectual property rights are not affected. The NanoFab features a large, dedicated facility, with tools operated within an ISO 5 (class 100), 750 m^2 (8,000 ft^2) cleanroom and in adjacent laboratories that have superior air quality along with temperature, humidity, and vibration control. Over 80 major process tools are available, including but not limited to e-beam lithography, 5x reduction stepper photolithography, nano-imprint lithography, laser writing for mask generation, scanning and transmission electron microscopy, three Focused Ion Beam (FIB) systems, metal deposition, plasma etching, chemical vapor deposition, atomic layer deposition, deep silicon etching, ion beam etching and a soft-lithography lab. The NanoFab staff consists of scientists, engineers and technicians that specialize in all areas of nanofabrication and provide training and ongoing technical assistance to users. Our goal is to be a catalyst to our users' success and to help nurture nanotechnology commerce in the Unites States. Project applications and instructions are easily available on the web at www.nist.gov/cnst/nanofab. Users inside NIST and from all around the country are provided on-line access to tool schedules and the tool reservation system. From physicists, engineers and biologists to medical researchers, users find common ground at the nanoscale in the CNST NanoFab.

3:20pm **MS-ThA4 Research Opportunities at the Cornell NanoScale Science and Technology Facility**, ***Michael Skvarla***, Cornell NanoScale Science and Technology Facility

The Cornell NanoScale Science and Technology Facility (CNF) is a member of NNCI, a network of open-access facilities partially subsidized by the US National Science Foundation to provide researchers with rapid, affordable, shared access to advanced nanofabrication tools and associated staff expertise. Hundreds of researchers worldwide (from academia, industry, and government) utilize CNF to make structures and systems from the nanometer scale to the centimeter scale. CNF offers extensive capabilities in electron-beam lithography, stepper photolithography, soft lithography, and direct-write tools for rapid prototype development, along with the flexibility to accommodate diverse projects and to deposit, grow, and etch a wide variety of materials. CNF's technical staff is dedicated full-time to user support, providing one-on-one help with process development, tool training, and troubleshooting. They can offer expertise in a wide range of fabrication topics, including electronics, photonics, magnetics, MEMS, materials, basic studies in chemistry and nanostructure physics, fluidics, and the life sciences and bioengineering (more than 30% of CNF's users now focus on biology). All researchers are welcome and all reasonable interactions are possible; no experience in nanofabrication is necessary. A central part of CNF's mission is education and outreach, with a special interest in assisting users from "non-traditional" fields seeking assistance to implement nanofabrication techniques for the first time. CNF's user program is designed to provide the most rapid possible access (typically 2 weeks) with the lowest possible barriers to entry (users retain full control of their IP, with no entanglement by CNF or Cornell University). Projects range from extensive, long-term device development to short-term use of specific tools, advanced capabilities, or singular staff expertise.

This talk will explore the CNF tool set, areas of expertise, types of services and advice available, and examples of ongoing work with the hope of stimulating ideas and possibilities.

We invite you to explore the CNF and NNCI and discuss ways we can help bring your research visions to fruition. As a first step, CNF's User Program Managers will at no cost provide detailed processing advice and cost estimates for potential new projects. The CNF technical staff meets every

Wednesday afternoon for conference calls where we welcome questions about any topic related to nanofabrication. Visit cnf.cornell.edu to contact us and get started.

4:00pm **MS-ThA6 Shyne - Allowing Users to Leverage $800 Million in Nanotechnology Research, Education, Infrastructure & Facilities at Northwestern and the University of Chicago**, ***Peter Duda***, University of Chicago, *B. Meyers*, Northwestern University

Welcome to the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource, an NSF-NNCI program! SHyNE is a new national resource that provides academic, small business and industry researchers access to cutting-edge nanotechnology facilities and expertise. In addition to traditional nanotechnology tools, SHyNE ensures the integration of soft (biological) nanostructures with the backbone of enabling hard materials, for applications such as microfluidic modules for bio-sensors and synthetic scaffolds for tissue regeneration, among others.

SHyNE streamlines our nanotechnology facilities, providing unique and integrated capabilities for internal Northwestern and UChicago researchers as well as external users, especially small and medium enterprises and startup companies. SHyNE further cements our leadership in nanotechnology and related advanced materials research, education and outreach.SHyNE deepens existing collaborations between Northwestern and UChicago and is expected to draw a variety of researchers from the Chicago area, the greater Midwest and nationally. SHyNE also offers regional colleges and public institutions, including museums, the opportunity to access research and training instrumentation under one umbrella. Through this program and the combined capabilities of the SHyNE facilities, we will connect state-of-the-art research facilities to academic, government and commercial programs across the Midwest, which in turn will lead to life-enhancing breakthroughs. As one of the 16 members of the nanotechnology network, SHyNE will benefit from and contribute to the vast resources of national collaboration of world-class peer institutions.

We wholeheartedly welcome you to use our facilities under the guidance and instruction of our talented staff, discover our unique instrumentation and capabilities, and find out more what SHyNE can do for you!

4:20pm **MS-ThA7 Science Opportunities with Soft X-Rays for Users at the Advanced Light Sources**, ***Zahid Hussain***, Advanced Light Source, Lawrence Berkeley National Laboratory

Sharper and sharper experimental tools are often crucial for understanding of novel physical phenomena and making new discoveries. Today in condensed matter physics we are experiencing need for revolutionary new instrumentation for understanding interplay of many degrees of freedom interacting at different energy, length and time scales. These interactions lead to new phases of matter and emergent phenomena such as high temperature superconductors, topological insulators and thermoelectric materials, to name a few. The primary focus of my talk is to present the science opportunity, through various examples, upon the necessity for advanced techniques and instrumentation to elucidate the application of soft x-ray synchrotron radiation for unraveling the emergent phenomena in quantum materials and energy related challenges.

4:40pm **MS-ThA8 Research Opportunities and How to Become a User at the Center for Functional Nanomaterials**, ***Samuel Tenney***, Brookhaven National Laboratory

The Center for Functional Nanomaterials (CFN) is a Department of Energy (DOE) Nanoscale Science Research Center located at Brookhaven National Laboratory. The CFN is a state of the art user facility for both proprietary and nonpropietary research with currently more than 500 users per year from industry, academia, and other government labs that publish well over 300 papers per year. The CFN is comprised of 5 research groups (interface science and catalysis, soft and bio materials, electronic nanomaterials, electron microscopy, and theory and computation) that are centered around the 3 strategic themes of the CFN including the study of Nanomaterials in Operando Conditions, Nano-architectures for Energy Solutions, and Self-assembled Nanomaterials by Design. The CFN has a very strong synergy with the National Synchrotron Light Source II (NSLS-II) and currently partners in the operation of 3 endstations that are used for the characterization of nanomaterials. The CFN houses a state-of-the-art cleanroom with world record 1 nanometer lithography capabilities among others. The CFN has over 50 staff members with expertise in a wide variety of areas related to nanoscale science that are dedicated to user support and the development and fostering of an extensive user community. Since its inception the CFN was designed with the idea of housing a complete suite of equipment, techniques, and technical staff to tackle the biggest challenges at the forefront of nanoscale science and technology all under one roof. We will also present how to become a user and discuss the process of applying for time to use the CFN's resources.

5:00pm **MS-ThA9 Opportunities at the Center for Nanophase Materials Sciences**, ***Arthur Baddorf***, Oak Ridge National Laboratory

The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is a DOE Office of Science User Facility that provides a national and international user community access to expertise and equipment for a broad range of nanoscience research, including nanomaterials synthesis, nanofabrication, imaging/microscopy/characterization, and theory/modeling/simulation. CNMS also acts as gateway for the nanoscience community to benefit from ORNL's neutron sources (SNS and HFIR) and computational resources. CNMS facilities are accessible based on peer-reviewed proposals and are offered at no cost to users who intend to publish their results.

In addition to a broad assortment of nanomaterials characterization tools, the CNMS has particular expertise in the following capabilities:

• Nanofabrication - The CNMS Nanofabrication Research Laboratory houses 10,000 ft2 of class 100/1000 clean room space for material modification using advanced lithographic, etching, thin-film deposition, and characterization tools.

• Bio-Inspired Nanomaterials - The CNMS offers capabilities to manipulate and image hydrated biological samples, and to create inorganic nanostructures of biological interest.

• Inorganic and Hybrid Nanomaterials Synthesis - Synthesis of nanostructures and thin films are performed by CVD and PLD with real-time diagnostics, including 2D layered materials, carbon nanostructures, oxide films, as well as hybrid organic/inorganic perovskite films, with wet/dry assembly of these materials into optoelectronic device architectures.

• Macromolecular Nanomaterials Synthesis - Laboratories include a wide range of polymer synthesis capabilities with special emphasis on selective deuteration and ionic polymerization

• Chemical Imaging – In addition to elemental distribution, bonding and chemical configuration is obtained using energy and mass spectroscopies.

• Electron and Atom Probe Microscopy - Sub-Ångstrom electron microscopy and spectroscopy, soft-matter TEM, and atom probe and electron tomographies are available.

• Scanning Probe Microscopy - Scanning tunneling and atomic force microscopies and spectroscopies in a range of environments for mapping of physical and electronic structure, electronic and ionic transport, spin, thermovoltage, electromechanics, magnetism, and dissipation.

• Nanomaterials Theory Institute - The NTI provides and advances capabilities for theory and high-performance simulation to enable fundamental understanding of physical and chemical properties of nanoscale materials.

5:20pm **MS-ThA10 Research Opportunities at the National High Magnetic Field Laboratory**, ***Eric Palm***, National High Magnetic Field Laboratory

The National High Magnetic Field Laboratory (MagLab) is the largest and highest powered magnet lab in the world. With more than 1700 users annually making use of its facilities it is a unique laboratory for basic research on topics as varied as materials, energy and life. This presentation will focus on those research capabilities as well as the technical challenges involved in creating the worlds highest magnetic fields for research.

Manufacturing Science and Technology Group
Room: Central Hall - Session MS-ThP

Topics in Manufacturing Science and Technology

MS-ThP1 Influence of Strain Rate on Deformation Behaviour of an AX52 Alloy Prepared by ECAP, ***Kristyna Halmesova***, Comtes Fht, Czech Republic, *Z. Trojanova*, Charles University, Prague, Czech Republic, *J. Dzugan*, Comtes Fht, Czech Republic, *P. Minarik*, Charles University, Prague, Czech Republic

Cast magnesium alloy AX52 (nominal composition Mg-5Al-2Ca in wt.%) was processed by equal channel angular pressing (ECAP) using A route and 1-8 passes. The microstructure and texture of samples have been assessed using electron backscatter diffraction and X-ray diffraction. The differences in grain size measured by these techniques allow for an understanding of microstructural evolution. Samples were tested in tension at room temperature initial strain rates in the interval from 1×10^{-3} to 1×10^{2} s^{-1}. The results reveal a significant strain rate sensitivity, which is affected by the ECAP processing. Deformation at higher strain rates became to be unstable. Deformation mechanisms operating at various strain rates are discussed in connection with microstructure and texture.

MS-ThP4 Material Characterization of Tungsten Dispenser Cathodes, ***Briana Fees***, San Jose State University and Coherent Inc

Barium impregnated tungsten dispenser cathodes are a critical component in the production of ion plasma lasers. As the emission source for the generation of plasma, the final processing, i.e. activation, of the cathode plays a crucial role in the emission of electrons as well as the lifetime of the laser. This activation process serves two primary purposes; the first being outgassing of impurities, adsorbed and absorbed during cathode processing and atmospheric exposure; the second being conversion of the impregnated barium oxide into free barium on the surface of the cathode, as the barium is the actual ion source. The objective of this work is to perform a full characterization of key process indicators which most influence activation. Preliminary results show a large variance in the resistance of cathode lots indicating a need for unique processing.

Applied Surface Science Division
Room: 13 - Session AS+MS-FrM

Unlocking the Sample History: Forensics and Failure Analysis

Moderators: Karen Gaskell, University of Maryland, College Park, Matthew Linford, Brigham Young University

8:20am **AS+MS-FrM1** ***In Situ*** **Diagnostics of the Coupled Mechanical and Electrochemical Degradation of High Capacity Electrode Materials in Lithium Ion Batteries**, ***Xingcheng Xiao***, General Motors R&D Center **INVITED**

Higher capacity in electrode materials (such as Silicon) is always accompanied by higher volume expansion. Most of the efforts to date in Si based electrodes have been focused on architectural design to avoid Si cracking. To achieve high current efficiency and long cycle life, the solid-electrolyte interface (SEI) must be mechanically and chemically stable despite the large volume-change. In this presentation, I will show you a comprehensive set of *in-situ* diagnostic techniques we developed to understand the coupled mechanical/chemical degradation of SEI layers during cycling. Based on the learning from the in-situ diagnostics, I will discuss some coating design strategies to achieve high cycle efficiency and extend the cycle life of high energy density batteries for electrical vehicle applications.

9:00am **AS+MS-FrM3 A Novel Approach to Characterizing the Silicon Anode Electrolyte Interface in Lithium Ion Batteries**, ***Caleb Stetson***, Colorado School of Mines, National Renewable Energy Laboratory, *C.S. Jiang, S. Harvey, K. Wood, G. Teeter, C. Ban, M. Al-Jassim*, National Renewable Energy Laboratory, *S. Pylypenko*, Colorado School of Mines

As the Lithium-ion battery (LIB) technology sector continues to develop, advances increasingly rely on innovative battery materials, particularly anode materials. Silicon has arisen as a frontier in anode material research mainly due to its high theoretical lithium capacity and the extensive knowledge regarding its processing and fabrication.

One of the principal challenges associated with the development of LIBs is the lack of understanding of the solid electrolyte interphase (SEI) layer that forms between the organic electrolyte and anode during the initial cycling of the battery. Formed from electrolyte decomposition products, this layer must be electronically insulating while still being permeable to lithium ions to allow for charge transport. This balance between differing properties is often difficult to maintain: if the SEI grows too thick, it loses its permeability to lithium; if it becomes too thin, the electronic resistance cannot be maintained and current will flow between the two electrodes. Measuring spatial variation in resistivity within this layer and correlating these data with chemical composition is of upmost importance to understanding SEI performance.

The SEI forms on the anode surface with thickness in the nanometer regime, which poses a challenge for finding the buried interface of the SEI with the Si anode. In order to locate and measure electronic properties at this interface, our group has utilized a scanning spreading resistance microscopy (SSRM) probe and scanner head to measure resistivity with nanometer-scale resolution. This system is installed in an argon glove box to minimize sample exposure to oxygen and humidity. The SSRM probe features a doped diamond-coated silicon probe that is both electronically conductive and wear resistant. The application of a sample-probe bias voltage while varying the force exerted on the probe in AFM contact mode allows for measurement of resistivity laterally and vertically.

Measurements of resistance vs. depth for SEIs demonstrate strong trends of resistance decrease as the probe penetrates deeper levels of the SEI. Several techniques are utilized to investigate the chemical composition at different depths of the SEI, including Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). Combining resistance and chemical speciation data originating from specific depths provides an interesting basis for the study of SEIs and the evolution of Si anodes under different cycling conditions with distinct electrolyte solutions.

9:20am **AS+MS-FrM4 In situ Liquid SIMS Investigation of Ion Solvation in Electrolytes for Lithium Ion Batteries**, ***Zihua Zhu***, *Y. Zhang, Z. Xu, M. Su, C. Wang, X.F. Yu, J.G. Wang*, Pacific Northwest National Laboratory

Ion-solvent interactions are of great fundamental and practical importance. However, many mysteries have long been existing in this field. For example, for the electrolytes used for Li ion batteries, preferential solvation and coordination number of a Li^+ ion are two interesting questions in hot debates so far. A major reason for above situation is lacking of reliable analysis techniques that can provide direct molecular information to elucidate ion-solvent interactions. In this work, in situ liquid SIMS was used to examine salt ion-solvent molecule interactions in several representative electrolytes used for Li ion batteries. Our data of the $LiPF_6$ in EC: DMC electrolyte show very strong molecular evidence that EC is preferentially solvated with Li^+, supporting previous ESI-MS and NMR results, but against recent Raman results. In addition, our data suggest that although the coordination number of a Li^+ ion can be as high as six in bulk electrolytes, three of them may be more stable than the remaining ones. In addition, it was observed that Li^+ and FSI^- ions tend to well-separated in 1.0 M LiFSI in DME electrolyte, consistent with our MD simulation results. As a comparison, many ion clusters were observed in the same concentration of $LiPF_6$ in EC: DMC electrolyte. The above findings suggest that in situ liquid SIMS can provide key evidence for better understanding of the ion-solvent interactions in the electrolytes for Li ion batteries.

9:40am **AS+MS-FrM5 Determining Bulk and Interface Chemical Damage Regimes in XPS Depth Profiling using Cluster Ion Beams**, ***Benjamin Schmidt***, *J. Newman, J.F. Moulder, J.E. Mann*, Physical Electronics

The development of gas cluster ion beams (GCIB) has provided fresh opportunities to study materials that exhibit chemical changes under monatomic argon ion bombardment during XPS surface cleaning or depth profiling. This is especially important as mixed inorganic/organic structures are increasingly used in applications such as OLED display devices and medical implants.

Several variables are available to fine tune cluster energy and size, which provides high levels of control to the user, but can present an overwhelming parameter space for practical use. For example, previous studies have shown that there is a relationship between the GCIB energy/atom and observed chemical changes. In the case of depth profiling bulk HfO_2, Barlow [1] observed that no change in Hf 4f peaks was detected for argon GCIB settings of 6 eV/atom, whereas a decrease to 2 eV/atom was required to minimize indium reduction in InAs. In a similar study on HfO_2, we observe similar results. By varying beam conditions, no Hf 4f reduction is observed at nominal 5.6 eV/atom, but is seen with an nominal 8 eV/atom beam. We discuss bulk and interface effects under these various conditions. For example, while no peak shape changes were observed in bulk HfO_2 at 5.6 eV/atom, reduced Hf oxide species are observed near the Si substrate, broadening the measured HfO_2/Si interface. We have investigated several other material systems, including polymers and Ti compounds, to provide guidance on general user settings.

[1] AJ Barlow, JF Portoles, PJ Cumpson. Observed damage during Argon gas cluster depth profiles of compound semiconductors. J App Phys 116, 054908 (2014)

10:00am **AS+MS-FrM6 In Situ Studies on Radiation Resistance of Nanoporous Metals**, ***Jin Li****, Texas A&M University, *C. Fan*, Purdue University, *Y. Chen*, Los Alamos National Laboratory, *X. Zhang*, Purdue University

High energy particle radiation induces severe microstructural damage in metallic materials. Void swelling is a general consequence of radiation damage and can drastically degrade the mechanical integrity of irradiated materials. Nanoporous (NP) materials have great potentials to alleviate irradiation-induced damage due to their giant surface-to-volume ratio. Here we show, by using in situ Kr ion irradiation of nanoporous Au in a transmission electron microscope, nanopores shrink during radiation, and their shrinkage rate is pore size dependent. In addition, from temperature-dependent studies, we found that both defect density and nanopores evolve with radiation temperature. Higher temperature results in lower defect density and reduced shrinkage rate of nanopores. The sink strength of nanopores as a function of temperature is estimated. Moreover, NP Au exhibits significantly enhanced swelling resistance compared to coarse-grained Au.

*** ASSD Student Award Finalist**

This study sheds light on the design of radiation-tolerant nanoporous metallic materials.

10:20am **AS+MS-FrM7 Surface Analysis in the World of Fine Art**, ***Thomas Beebe, Jr.***, *Z. Voras, C. Goodwin, K. deGhetaldi, B. Baade, J. Mass*, University of Delaware **INVITED**

Connections between the science of surface analysis and the science of cultural heritage, such as it is, have been neither historically strong nor particularly productive, unfortunately for both fields. We are developing new collaborations aimed at changing this. Not all cultural heritage conservators adopt a scientific approach, and not all of those that do are willing to expand their scientific approaches to include surface-sensitive techniques such as XPS and TOF-SIMS, in many cases because their backgrounds have not led them to know about such methods. To be fair, we surface scientists don't have all the answers and often can't get them. Not all surface scientists are interested in pushing the boundaries of their sample types into such unconventional realms, and not all of those that are interested have the patience to develop the new sample-handling and sample-preparation techniques applicable to XPS and TOF-SIMS analysis, not to mention dealing with the ultra-small sample sizes of such precious works of art. This presentation will draw upon several recent examples from the speaker's research team to show how XPS and TOF-SIMS can be used to shed some light on mechanisms of chemical and physical degradation, proposed and applied methods of stopping such degradation, and proposed and applied methods of repairing such degradation. The examples will come from a range of paintings and other art objects spanning from the Italian Renaissance to the post-Modern era.

11:00am **AS+MS-FrM9 Surface Characterization of Acrylic Artists' Paints After Wet Cleaning with Water-in-Oil Microemulsions.**, ***Michael Clark***, *M. Keefe*, The Dow Chemical Company, *T. Learner*, The Getty Conservation Institute, *B. Ormsby*, Tate, UK, *A. Phenix*, The Getty Conservation Institute, *E. Willneff*, University of Leeds, UK

This paper reports on developments from collaboration between The Dow Chemical Company, Tate and the Getty Conservation Institute to improve cleaning systems for unvarnished modern painted surfaces. Increased use of new artistic paints since the 1950s has created a need for new cleaning approaches as traditional wet and dry cleaning systems have been found to be unsuitable in many cases.

This body of research has focused on the development of improved wet cleaning systems for artists' acrylic emulsion paints. The present study describes novel microemulsion systems based on water and mineral spirits, each formulated with different anionic or non-ionic surfactants. For this application, water-in-oil microemulsions were designed to capture the positive aspects of water-based cleaning systems (good pick-up and dispersion of soils; control over the conductivity and pH) while limiting, to a degree, the risks associated with exposure to aqueous cleaners. These notable cleaning solutions have been found to be very effective at removing surface soiling on acrylic paintings and other water sensitive works of art. A range of spectroscopic techniques have been employed to characterize the paint surface for changes induced treatment with different cleaning solutions. TOF-SIMS and XPS results show that trace amounts of surfactant residues from cleaning formulations remain on paint surfaces in some cases. Amounts vary depending on the surfactant type, inherent surfactant solubility, in addition to the clearance steps undertaken.

11:20am **AS+MS-FrM10 Surface and Depth Profiling of Soft Organic Thin Films. X-Ray Photoelectron Spectroscopy Study**, ***Tatyana Bendikov***, Weizmann Institute of Science, Israel, *S.J. Hutton*, Kratos Analytical Ltd, United Kingdom of Great Britain and Northern Ireland, *R. Balgley, G. de Ruiter, M. Lahav, M.E. Van der Boom*, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials and thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. In general, XPS is limited to probe the top <15 nm of a sample, and for thicker structures a digging-like etching process is needed.

Recent advances in depth profiling of organic and biological materials are based on sputtering with large Argon ion clusters (Ar_n^+).[1] Unlike monoatomic ions (Ar^+), large cluster ions do not penetrate deeply into the material, therefore sputter material from the near-surface region only, leaving the subsurface layers undisturbed and undestroyed.

Here we present two examples of successful XPS depth profiling of composite metal-organic architectures self assembled on the pyridine terminated silicon/ ITO substrates. The samples consist of four main components: metal complexes ($[M(mbpy\text{-}py)_3][PF_6]_2$, M = Ru (**1**) or Os (**2**); $Pd(PhCN)_2Cl_2$ (**3**) and (1,4-bis[2-(4-pyridyl)ethenyl]benzene, **BPEB**, (**4**) spacer molecules.

The first system was prepared by sequential immersion of the substrate in solution **1** (alternating with solution **3**) (4 layers) followed by **2** (alternating with **3**) (4 layers). Each layer is ~ 6 nm thick, thus the consequent total thickness of the organic film reaches 40-50 nm.[2]

In the second example molecular assemblies consist of different layers of metal complexes **1** and **2**, separated by repetitive spacers **4** alternated with **3**. Total thickness of the analyzed **[Ru-BPEB$_{12}$-Os]** assembly is ~20 nm.[3]

1. P. J. Cumpson et. al., *Surf. Interface Anal.*, **2013**,45, 1859-1868.

2. G. de Ruiter et. al., *J. Am. Chem. Soc*., **2013**, 135, 16533-16544.

3. R. Balgley et. al., *J. Am. Chem. Soc.*, **2016**,138, 16398-16406.

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