

Tuesday Morning, October 19, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+SS-TuM

In Situ Spectroscopy – Interfacial Chemistry/Catalysis

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-TuM1 Oxidation and Reduction of Pd(100) and Supported Pd Nanoparticle Model Catalysts**, *R. Westerstrom, S. Blomberg, N. Martin, J. Gustafson, E. Lundgren, J.N. Andersen, M.E. Messing, K. Deppert*, Lund University, Sweden, *H. Bluhm*, Lawrence Berkeley National Laboratory, *O. Balmes, R. van Rijn*, ESRF Grenoble, France

Using *in situ* high pressure X-ray photoelectron spectroscopy, we study the oxidation and reduction by O₂ and CO in the mbar pressure regime of Pd(100) and Pd nanoparticles of 15 or 35 nm diameter supported on a SiO_x substrate. We find the oxidation behavior of these model catalysts to be qualitatively similar, with an ultra-thin surface oxide forming prior to the onset of bulk PdO formation. However, the Pd nano particles are observed to bulk oxidize at sample temperatures 40 degrees lower than Pd(100). For the PdO surface, we identify a core level shift of the Pd 3d and O 1s levels of -0.3 and -1.3 eV, respectively, relative to the corresponding levels in bulk PdO. In a CO atmosphere, the Pd 3d shift changes by +0.55 eV due to CO adsorption, and CO adsorbed on the oxide can be identified in the C1s. Also the reduction by CO is similar between the single crystal and the nanoparticle samples, but after the complete removal of the oxide, the nanoparticles incorporate carbon to form a Pd carbide. This is not observed for the single crystal sample.

8:20am **IS+SS-TuM2 In-situ XPS Studies of CO₂ Captured by Aqueous Monoethanolamine (MEA) Solutions**, *T. Lewis, A. Chaudhuri*, University of California, Irvine, *M. Faubel*, Max-Planck Institut fur Dynamik und Selbstorganisation, Germany, *B. Winter*, Helmholtz-Zentrum Berlin fur Materialien und Energie, Germany, *J.C. Hemminger*, University of California, Irvine

XPS on a micro liquid jet has been used to study solutions of monoethanolamine (MEA), which is commonly used in gas stream scrubbing for carbon dioxide capture. It is likely that interactions between CO₂ and the aqueous MEA solution at the gas/liquid interface are important to this process, yet there is little information available concerning the spatial distribution of species at the interface of such solutions. In the present work, aqueous solutions of MEA with a range of pH values as well as solutions of MEA reacted with CO₂ have been measured using tunable synchrotron radiation from the BESSY facility in Berlin, where the photoelectron kinetic energy can be varied to obtain depth dependent composition information. N1s photoemission spectra allow for the identification of protonated versus unprotonated MEA by the different binding energies of the two species, and likewise, C1s spectra allow for the determination of CO₂-reacted versus unreacted MEA. Depth profiling reveals that deprotonated MEA is more surface active than both protonated MEA and the CO₂-reacted species. The mechanism of the reaction of CO₂ with aqueous solutions of monoethanolamine will be discussed in light of our results.

8:40am **IS+SS-TuM3 Photoelectron Spectroscopy Under Humid Conditions**, *H. Bluhm*, Lawrence Berkeley National Laboratory **INVITED**

The interaction of water with surfaces plays a major role in many processes in the environment, atmosphere and technology. Weathering of rocks, adhesion between surfaces, and ionic conductance along surfaces are among many phenomena that are governed by the adsorption of molecularly thin water layers under ambient humidities. The properties of these thin water films, in particular their thickness, structure and hydrogen-bonding to the substrate as well as within the water film are up to now not very well understood. Ambient pressure photoelectron spectroscopy (APXPS) is a promising technique for the investigation of the properties of thin water films. We will discuss the basics of APXPS as well as the particular challenges that are posed by investigations in water vapor at Torr pressures, as well as show examples of the application of APXPS to the study of water films on metals and oxides.

9:20am **IS+SS-TuM5 Chemistry of Aminoacids at the Water – Metal Interfaces under UHV and AP Conditions**, *A. Shavorskiy*, Lawrence Berkeley National Laboratory, *T. Eralp*, The University of Reading, UK, *F. Aksoy, Z. Liu, H. Bluhm*, Lawrence Berkeley National Laboratory, *A. Cornish, D. Watson*, The University of Reading, UK, *K. Schulte, J.N. Andersen*, Lund University, Sweden, *G. Held*, The University of Reading, UK

Many important catalytic reactions take place at the interface between a solid catalyst and a solution, in particular aqueous solutions play a crucial role in all biological systems. The presence of the solvent at the solution-catalyst interface can dramatically change the chemical surface properties and, therefore, the entire catalytic process. Although surface science has been very successful in studying gas-surface reactions, most UHV-based surface science techniques cannot be applied to the co-adsorption of solvent and reactant molecules of important reaction systems because the solvent desorption temperature in UHV is too low to allow co-adsorption at realistic reaction temperatures. In order to keep significant amounts of water adsorbed near room temperature pressures of up to 1 mbar are needed for most metals. Recently, ambient pressure X-ray photoelectron spectroscopy (APPEs), has become available for studying these systems at close-to-real conditions [Bluh09].

For the experiments reported here we chose to study the influence of water on the adsorption of glycine and alanine on Pt[111] and Pt[110] in UHV and on Cu[110] at near-ambient pressure. The comparison between results obtained in UHV and at AP allows us to reveal importance of the reaction conditions (in particular reaction pressure and temperature) on the chemical composition and stability of the molecular adlayers on metals. It also bridges the pressure gap in studies of such kind of bio-related systems. Our results show an absence of any noticeable changes in the chemical composition of the aminoacids on Pt[111] and Pt[110] when co-adsorbed with water in UHV. On the other hand we observed clear decrease of the amino acid desorption temperature and a change of the desorption pathway (compared to UHV [Barl05]) on Cu[110] when the H₂O pressure is increased above 10⁻⁵ mbar. Two possible mechanisms of lowering the stability of the amino acids in the presence of water are discussed: (a) oxidation of the amino acid by OH or O or (b) hydrogenation of the anionic amino acid followed by desorption of the less stable intact form [Jone06].

[Bluh09] H. Bluhm, J. El. Spec. Rel. Phen., doi:10.1016/j.elspec.2009.08.006, 2009.

[Jone06] G. Jones et al Surf. Sci. 600 (2006) 1924.

[Barl05] S. M. Barlow et al Surf. Sci 590 (2005) 243.

[Ande07] K. Andersson et al. J. Phys. Chem. C 111 (2007) 14493.

9:40am **IS+SS-TuM6 In-situ Ambient Pressure XPS Observations of Reversible Charge Storage in Ni Electrodes**, *A.H. McDaniel, F. El Gabaly*, Sandia National Laboratories, *M. Grass, Z. Liu*, Lawrence Berkeley National Laboratory, *K.F. McCarty*, Sandia National Laboratories, *H. Bluhm*, Lawrence Berkeley National Laboratory

Electrochemical technologies will be increasingly used to supply energy to the world without contributing to climate change. These technologies can store and convert energy with unsurpassed efficiencies through, for example, the charging and discharging of batteries or the inter-conversion of electrical and chemical energy via fuel cell and electrolyzer. Perhaps the most important phenomena to understand in electrochemical energy storage/conversion is how electric charge is transferred across interfaces and subsequently stored in material phases and/or double layers. Currently, detailed knowledge is lacking of critical pathways such as which chemical reactions are responsible for charge transfer, what species are involved, and where charge transfer reactions occur in heterogeneous devices. These limitations arise in no small degree from the physical complexities of these devices, which consist of a variety of electrified materials undergoing chemical reactions. Lacking this knowledge, development proceeds largely using engineering approaches.

To help answer these questions we have spectroscopically characterized electrochemical charge-transfer and storage as it occurs. This is accomplished by primarily using a new diagnostic based on synchrotron X-ray spectroscopies that we have been developing at the Advanced Light Source (ALS, LBNL, Berkeley, CA). Photoelectrons are used as a contactless probe for the direct measurement of the electric inner potential everywhere in a Ni-YSZ based electrochemical cell operating at near ambient pressure. This information, in addition to space-resolved chemical characterization of the surface species showing phase changes relevant to Ni-metal-hydride batteries, will be discussed. The experimental configuration consists of a thin-film Ni electrode that is electrochemically modified by injection of O₂⁻ ions. During an applied bias, charge is stored

in the electrode by the conversion of the Ni to NiOOH. This leads to dramatic changes in the XPS spectra as well as the existence of a constant discharge potential plateau resulting from the equilibrium of NiOOH with two other phases, Ni and H₂O. Thus, our approach has the ability to identify the phases that store charge, which are only stable under electrical bias. This rich data will provide new understanding on how electrochemically driven phases form.

10:40am **IS+SS-TuM9 Hard X-ray Photoelectron Spectroscopy: an Effective Probe for Electronic Structure in Materials Science, W. Drube**, Deutsches Elektronen-Synchrotron DESY, Germany **INVITED**

The use of hard X-ray excitation in the range from about 2 to 15 keV for photoelectron spectroscopy (HAXPES) is a rapidly emerging technique at synchrotron sources worldwide since it significantly widens the range of applications, in particular in the study of complex materials and buried nano-structures or interfaces. Due to the increased electron inelastic mean free paths, it becomes possible to probe chemical composition and electronic structure in the bulk of materials with considerable sensitivity, down to typically 10-20 nm at 10 keV kinetic energy. This not only is essential in the study of complex correlated materials which often exhibit a modified surface electronic structure but also is very relevant for technologically interesting multi-layered materials with buried interfaces. As an additional benefit, "as-grown" materials can be measured without need for prior surface treatment.

A drawback is the rapidly decreasing photoelectric cross section in the hard X-ray range, especially for shallow core levels and valence states, and - until recently - the limited availability of suitable high-voltage electron spectrometers. The latter are available meanwhile and the high X-ray flux at undulator beamlines has been shown to effectively compensate the cross section decrease. In addition, the X-ray tunability over a large energy range not only allows to significantly vary the electron probing depths and the photoelectric cross sections, but also enables the study of resonance phenomena at deep inner-shell thresholds. Further, the excitation of X-ray standing wave fields within single crystals or multi-layered structures can be effectively used to correlate geometric and electronic structure information.

In the past five years, HAXPES activities at synchrotron laboratories worldwide have increased dramatically and the trend continues as new instruments are currently being built and planned. A brief overview is given on the current activities worldwide, both on instrumental developments and results obtained. At DESY, HAXPES experiments routinely use a dedicated spectrometer at an X-ray wiggler with moderate energy resolution (~0.5 eV), well suited for many core level studies. Very recently, high-resolution studies also became possible at DESY with the availability of PETRA III, a new storage ring source providing the highest X-ray brilliance.

11:20am **IS+SS-TuM11 Novel Applications in Surface Science – In situ Sample Analysis in Extreme Environments, A. Thissen**, SPECS Surface Nano Analysis GmbH, Germany

Modern devices are often only functional in environments far away from ultrahigh vacuum, still being the standard operation conditions for all Surface Science techniques. In parallel the importance of surfaces for the correct device operation is continuously increasing due to miniaturization down to the nanoscale. To contribute to advanced materials analysis in future means using Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Also extremely low or high temperatures might be necessary. In past all standard Surface Science Techniques did not work under these *extreme* environments. This work summarizes and presents existing solutions nowadays and future development routes to new instruments and materials analysis methods being functional under these working conditions. Opportunities and limits will be discussed, from the perspective of a supplier of scientific instruments. Finally applications, examples and results from existing *In situ* methods like high pressure treatments cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy Systems (NAP-PES or HP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in highest or lowest temperatures, high magnetic fields and static or dynamic potentials will be demonstrated.

Tuesday Afternoon, October 19, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+SS-TuA

In Situ Microscopy/Spectroscopy – Interfacial Chemistry/Catalysis

Moderator: S. Kodambaka, University of California Los Angeles

2:00pm **IS+SS-TuA1 In-situ LEEM Study of Ceria Growth on Cu(111)**, J.T. Sadowski, S.D. Senanayake, F. Yang, Y.M. Choi, Brookhaven National Laboratory, J.I. Flege, J. Falta, B. Menkens, University of Bremen, Germany, J.A. Rodriguez, J. Hrbek, Brookhaven National Laboratory

The use of CeO₂-based materials in catalysis has attracted considerable attention in recent years. Ceria has shown great potential as a novel reducible oxide support with unique oxygen storage capacity (OSC) [1]. Ceria can accommodate a large number of oxygen vacancies and the oxidation states of the Ce cation can be switched readily between Ce³⁺ and Ce⁴⁺ depending on the ambient conditions. Hence ceria can actively participate in redox chemical reactions.

The formation of well-ordered, flat CeO₂ films is required in order to minimize substrate effects in surface chemistry of ceria. An earlier successful approach to this problem involved growth of ceria films on Ru(0001) [2]. More recently, CeO₂(111) was grown on a Cu(111) substrate [3]. High activity of ceria-based model catalysts was demonstrated on the inverse catalyst [4, 5] with ceria nanoparticles supported on noble metal substrates. Overall, there is still little known about the mechanism for the growth of ceria film on metal surfaces, its structure and stoichiometry.

In the present work the growth of thin ceria films on Cu(111) has been investigated *in-situ* by means of low-energy electron microscopy (LEEM). Ce was deposited from an e-beam evaporator onto Cu(111) under O₂ atmosphere (5x10⁻⁷ Torr). Real-time observation of the film growth revealed that at relatively high substrate temperature (above 800K) flat, highly crystalline, epitaxial CeO_x(111) film has been formed. In this presentation we will discuss in detail the mechanism of the nucleation and growth, and the atomistic structure of the CeO_x film on Cu(111) under varying growth conditions and Cu(111) oxidation state.

[1] A. Trovarelli, *Catalysis by Ceria and Related Metals*, Imperial College Press, London, 2002.

[2] D. R. Mullins, P. V. Radulovic, S. H. Overbury, *Surf. Sci.* **429**, 186 (1999).

[3] V. Matolin, J. Libra, I. Matolinova, V. Nehasil, L. Sedlacek, F. Sutara, *Appl. Surf. Sci.* **254**, 153 (2007).

[4] J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, and M. Pérez, *Science*, **318**, 1757 (2007).

[5] J. A. Rodriguez, J. Hrbek, *Surf. Sci.*, **604**, 241 (2010).

The authors are thankful to the US Department of Energy (Chemical Sciences Division, contract no. DE-AC02-98CH10886) for financial support. Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract no. DE-AC02-98CH10886.

2:20pm **IS+SS-TuA2 Quantitative Speciation of Zn(II) During the Solution Synthesis of ZnO Nanowires Using In-Situ XANES Spectroscopy**, K.M. McPeak, Drexel University, M. Becker, B.A. Bunker, University of Notre Dame, J.B. Baxter, Drexel University

Low temperature, aqueous solution synthesis is widely used to deposit ZnO nanowire arrays for applications such as dye sensitized solar cells. Zinc nitrate and hexamethylenetetramine (HMTA) are the most common precursors for the solution synthesis of ZnO nanowires; but after ten years of using this chemistry, the underlying mechanisms of the reaction remain unclear. We report on the in-situ x-ray absorption spectroscopy of ZnO

nanowire growth from HMTA and zinc nitrate precursors. Time-resolved, in-situ x-ray absorption near-edge structure (XANES) spectra, at the Zn K-edge, give detailed information about the local structure of both Zn(II) in solution and the solid phases formed throughout the reaction. A principal component analysis (PCA) algorithm was employed to determine the number and type of probable species present during the growth of ZnO nanowires under real reaction conditions, with temperatures up to 90 °C and concentrations ranging from 4 – 25 mM. Only two species were present for ZnO nanowire growth at all concentrations and temperatures studied: [Zn(6H₂O)]²⁺ and ZnO_(s). The proportions of these Zn species as a function of reaction time were determined quantitatively by least-squares fitting (LSF) the experimental time-dependent XANES spectra with linear combinations of the principal component spectra. PCA and target testing conclusively refute previous theories that ZnO nanowire growth from HMTA and zinc nitrate precursors occurs due to the thermal decomposition of an intermediate zinc-amine or zinc-HMTA complex. Additionally, XANES analysis shows that no zinc hydroxide intermediates exist above the detection limit of 0.05 mM. Beyond the focused investigation of ZnO, this study also establishes in-situ XANES spectroscopy, in combination with PCA and LSF, as an excellent quantitative tool to understand the solution synthesis of semiconductor nanostructures and thin films.

2:40pm **IS+SS-TuA3 X-ray Spectromicroscopy of Organic and Inorganic Nanostructures**, S.G. Urquhart, University of Saskatchewan, Canada

INVITED

Understanding the composition and structure of complex surfaces is essential for many scientific questions, from understanding processes in surface corrosion to the development of organic electronic devices. X-ray Spectromicroscopy provides surface sensitive chemical speciation with high lateral spatial resolution, by combining the chemical sensitivity of X-ray absorption and photoemission spectroscopy with the high spatial resolution of X-ray microscopy. This presentation will discuss x-ray spectromicroscopy studies to study phase segregation in mixed Langmuir Blodgett thin films as well as efforts to develop a new zone-plate based surface sensitive spectromicroscopy.

1.) We have used surface sensitive X-ray Photoelectron Emission Microscopy (X-PEEM) to study the mechanisms of phase separation and growth in mixed Langmuir Blodgett thin films.[1,2] Here, the chemical sensitivity of x-ray absorption spectroscopy provides spatially resolved composition information to complement the morphology information provided by AFM.

2.) We are developing of a new form of new surface sensitive x-ray microscopy, based on electron-yield detection in a scanning zone plate microscope. Preliminary results from the development of this new method will be presented.

References:

1.) Christensen et al., *J. Electron Spectrosc. and Rel. Phenom.* (2008) **162**, 107-114.

2.) S.E. Qaqish, *Langmuir* (2009) **25**, 7401-7409.

Research supported by NSERC (Canada) and performed at the Canadian Light Source (CLS) and the Advanced Light Source (ALS). The CLS is supported by NSERC, NRC, CIHR, U. Saskatchewan, and the ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

4:00pm **IS+SS-TuA7 The Use of in-situ Spectro-Electrochemical Tools on the Way to R&D of Rechargeable Li and Mg Batteries**, D.A. Aurbach, Bar-Ilan University, Israel

INVITED

The performance of high energy density rechargeable Li and Li ion batteries depends on passivation phenomena. On thermodynamic basis, both the negative electrodes: Li metal or lithiated carbonaceous materials and the positive electrodes: lithiated transition metal oxides are reactive with the electrolyte solutions that are relevant to these systems (polar-aprotic solvents and Li salts).

Thereby, it is highly important to understand the complicated surface chemistry that characterizes all kinds of rechargeable Li batteries. Based on understanding the correlation between surface phenomena, performance and safety features, it is possible to optimize electrolyte solutions in which irreversible phenomena and electrodes capacity fading will be minimized. Consequently, it was highly important to develop specific spectroscopic and microscopic tools that can be used in conjunction with electrochemical techniques and can be specifically suitable for such highly reactive systems. In this talk we demonstrate the development and use of *in-situ* FTIR spectroscopy for mapping the complicated surface reaction of Li metal electrodes in most relevant electrolyte solutions. Especially important was an approach based on internal reflection modes. The use of *in-situ* Raman spectroscopy for understanding lithiation processes of graphite in ionic liquids will be demonstrated. Application of spectroscopy enables to follow detrimental processes such as co-intercalation of the solvents' cations together with Li insertion, what interferes badly with the passivation phenomena, on which the reversibility and stability of Li-graphite anodes depend. The same techniques were applied to non-aqueous electrochemistry of magnesium, in the framework of R&D of rechargeable Mg batteries. The use of EQCM was helpful in characterizing passivation free Mg electrodes, in ethereal solutions with contain magnesium organo-chloro-aluminate complex electrolytes. Highly useful for the study of surface phenomena related to Li batteries were *in-situ* AFM measurements, with which it was possible to follow delicate phenomena related to surface films formation, exfoliation of Li-graphite electrodes and break down and repair of passivation phenomena on both Li metal and Li graphite electrodes. The study of Mg anodes was nicely promoted by the use of *in-situ* STM measurements. This technique was very suitable for characterization of Mg anodes in passivation free electrolyte solutions. New directions for development of *in-situ* techniques suitable for highly reactive electrochemical systems, will be discussed.

4:40pm IS+SS-TuA9 Electrochemistry Platforms for In Situ Transmission Electron Microscopy of Li-ion Batteries. *A. Subramanian, J.P. Sullivan, J. Huang, M.J. Shaw, N. Hudak*, Sandia National Laboratories, *Y. Zhan, J. Lou*, Rice University

Nanoscale materials offer a number of potential advantages for Li-ion batteries: examples include low-cost LiFePO₄ nanoparticle cathodes that exhibit good rate performance despite having low electrical conductivity and high-capacity conversion anodes that have high cycle life despite large volume changes per cycle, e.g. Si nanowires. However, one of the challenges with the use of nanoscale materials is their electrochemical characterization, particularly assessing structural changes in nanoscale particles, or reaction product layer interfaces, such as the solid-electrolyte-interphase (SEI). This requires tools with atomic to nanoscale spatial resolution. To meet this need, we have developed a micro-electromechanical systems (MEMS)-based platform for performing electrochemical measurements using volatile electrolytes inside a transmission electron microscope (TEM). This platform uses flip-chip assembly with special alignment features and multiple buried electrode configurations. The nanoscale materials of interest are assembled into the viewing area using dielectrophoresis (DEP). This permits the incorporation of a diverse array of nanoscale particles, including the co-assembly of anode materials in proximity to cathode materials. As an initial realization of the MEMS-based platform, we have developed an unsealed platform that permits *in situ* TEM electrochemistry using ionic liquid electrolytes or *ex situ* electrochemistry and TEM imaging using conventional battery electrolytes. We have demonstrated these approaches using β -MnO₂ nanowire cathodes that were individually assembled using DEP. These wires were lithiated over a range of potentials, in ethylene carbonate-based electrolytes with lithium metal as a counter electrode, in order to produce a range of lithium content. Using TEM and solid-state electrical characterization, we observed that lithiation introduces increasing lattice disorder particularly at the nanowire surfaces; yet, the wires remain β -phase. The electrical measurements revealed a monotonic decrease in electrical conductivity with increasing lithium content, consistent with electronic localization at defects or an increased band gap. From these results, we conclude that *in situ* TEM characterization tools will enable important mechanistic understanding of Li-ion battery materials. This work was supported by LDRD and EFRC projects and was performed, in part, at CINT, a U.S. DOE, Office of Basic Energy Sciences user facility. Sandia is a multiprogram laboratory operated by Sandia Corp., a wholly owned subsidiary of Lockheed Martin Company, for the U.S. DOE's NNSA under contract DE-AC04-94AL85000.

5:00pm IS+SS-TuA10 In-Situ Heating, Imaging, and Analysis of Nanoparticles Using SEM, STEM, and XPS. *J.L. Sturgeon*, RJ Lee Group, Inc., *Z. Liu*, University of Pittsburgh, *K.L. Bunker, T.L. Lersch, J. Mastovich, B.R. Strohmaier*, RJ Lee Group, Inc., *J.C. Yang*, University of Pittsburgh

Use of an *in-situ*, semiconductor-based heating stage in high-resolution scanning electron microscope (SEM) and scanning transmission electron microscope (STEM) instruments permits rapid, but controlled, temperature changes and the ability to collect images and videos in real time with minimal drift. A Protochips Aduro™ system utilized on a Hitachi S-5500 SEM/STEM allows analysis at elevated temperatures coupled with low voltage SEM/STEM imaging. Catalyst nanoparticles consisting of an iron core surrounded by a carbon shell have been studied using this technology. Elevated temperatures result in a variety of changes to the core-shell structure as well as migration and agglomeration of the iron nanoparticles. X-ray photoelectron spectroscopy (XPS) was also used to study the surface chemistry of these materials before and after heating. These experiments give critical insights into the kinetics of reaction of the iron nanoparticles. Additional analysis at higher accelerating voltages is possible using a dedicated STEM instrument. Other applications using elevated heating of nanoparticles will be discussed.

5:20pm IS+SS-TuA11 Understanding the Role of Fe Catalyst in Carbon Nanotube Growth Using Atomic-Scale (S)TEM. *A. Mkhoyan, M.J. Behr, E.S. Aydil*, University of Minnesota

Wednesday Morning, October 20, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+AS+NS+MI-WeM

In Situ Microscopy/Spectroscopy – In Situ Nanoscale Processes

Moderator: A. Mkhoyan, University of Minnesota

8:00am **IS+AS+NS+MI-WeM1 Low-dimensional Superconductivity of Pb Nanostructures**, J. Kim, H. Nam, G.A. Fiete, C.K. Shih, The University of Texas at Austin

The influence of low-dimensional geometries on superconductivity is an important issue to study because in low dimensions it is key to understanding coherence and robustness of the superconducting state in quantum-mechanically confined geometries. The lateral size dependence of superconductivity on 2 dimensional Pb islands is studied by using *in-situ* low temperature Scanning Tunneling Microscopy/Spectroscopy (STM/S). The superconducting transition temperature (T_c) of each island is obtained by fitting the STS data with a BCS-like density of states. It is found that superconductivity shows a clear dependence on the Pb island lateral size even when it is larger than the bulk coherence length (~80nm), and it is also found that T_c drops very quickly below a certain lateral size. In addition, an intriguing lateral proximity effect is observed at the interface of different local superconducting regions of Pb islands. Current imaging tunneling spectroscopy (CITS) is used to visualize this proximity effect in real space.

8:20am **IS+AS+NS+MI-WeM2 Enabling the Measurement of In-Situ, Site-Specific Mineral Transformation Rates in Supercritical CO₂ through Development of a High Pressure AFM**, S. Lea, Pacific Northwest National Laboratory, S.R. Higgins, Wright State University, K.G. Knauss, Lawrence Berkeley National Laboratory, K.M. Rosso, Pacific Northwest National Laboratory

Capture and storage of carbon dioxide in deep geologic formations represents one promising scenario for minimizing the impacts of greenhouse gases on global warming. At issue is the ability to demonstrate that CO₂ will remain stored in the geological formation over the long-term and so knowledge of mineral-fluid transformation rates is critical for this determination. The majority of previous research on mineral-fluid interactions has focused primarily on the reactivity of minerals in aqueous solutions containing CO₂. However, caprock integrity would be dictated primarily by mineral interaction with supercritical CO₂ (scCO₂) as the buoyant phase slowly displaces or desiccates residual aqueous solution at these surfaces. Many of the mechanisms of mineral interfacial reactions with hydrated or water-saturated CO₂ are unknown and there are unique challenges to obtain kinetic and thermodynamic data for mineral transformation reactions in these fluids.

A high-pressure atomic force microscope (AFM) is currently under development that will enable *in-situ* site-specific measurements of metal carbonate nucleation and growth rates on mineral surfaces in contact with scCO₂ fluids. This apparatus is based on the hydrothermal AFM that was developed by Higgins et al.¹, but includes some enhancements and is designed to handle pressures up to 1500 psi. The noise in our optically-based cantilever deflection detection scheme is subject to perturbations in the density (and therefore index of refraction) of the compressible supercritical fluid. Consequently, variations in temperature and pressure within the fluid cell can have a significant impact in our ability to discern atomic steps on mineral surfaces. We demonstrate with our test fluid cell that the equivalent rms noise in the deflection signal is similar to (and in some cases less than) the equivalent noise for an AFM in its 'standard configuration' under controlled pressures of ~80 bar and temperatures of 60-80 °C and therefore *in-situ* atomic scale imaging of mineral surfaces in scCO₂ should be possible. This talk will also focus on recent progress in the development of this instrumentation, which will enable a unique platform for elucidating the role of water in mineral transformations, providing a means for determining effective kinetic constants.

1. Higgins, S. R.; Eggleston, C. M.; Knauss, K. G.; Boro, C. O., A hydrothermal atomic force microscope for imaging in aqueous solution up to 150°C. *Review of Scientific Instruments* **1998**, 69 (8), 2994-2998.

8:40am **IS+AS+NS+MI-WeM3 Au on VLS-grown Si Nanowires: Spreading of the Liquid Metal Seed**, E. Dailey, P. Madras, J. Drucker, Arizona State University **INVITED**

In situ TEM shows that liquid AuSi spreads from the seed along the NW sidewalls to form a thin liquid sheath for some growth conditions. The thin

liquid film phase separates to form small solid Au clusters when the NW is cooled below the solidus temperature. Quantitative composition maps show that the Au composition is highest near the NW tip. The thickness and length that the liquid film spreads from the seed is growth condition and NW diameter dependent and represents a steady state during growth. These observations can be related to the spreading thermodynamics of liquid droplets along cylinders. Growth conditions for which the liquid AuSi spreads from the seed stabilize 'vertical' growth along <111> by lowering the surface energy of the high-energy {112} bounding facets. In contrast, the NWs kink toward <112> when grown using conditions that favor growth with Au-free sidewalls since these NWs are bound by facets that are found on the Si equilibrium crystal shape.

9:20am **IS+AS+NS+MI-WeM5 Advanced Study of Nanoscale Mechanisms: Plans for In-Situ TEM Microreactor, Gas Cell, and Multi-Beam Irradiation Experiments**, B.G. Clark, K. Hattar, Sandia National Laboratories, D. Nackashi, J. Damiano, S. Mick, Protochips, Inc., B.L. Doyle, Sandia National Laboratories

Over the years, in-situ TEM experiments have allowed for observation of material mechanisms at high resolution and in real time; a feat often not possible with any other experimental technique. With increasing demand for understanding nanoscale material mechanisms, both with growth in the applications of nanomaterials and in the development of predictive materials models based on experimental observation, the realm of in-situ TEM experiments has continued to expand. Highlighted in this presentation will be the development of three, exciting new capabilities for in-situ TEM experiments at Sandia National Labs.

The first part of the talk will focus on the development of two new in-situ TEM stages. Expanding on the success of static and single inlet-outlet liquid cells, we are designing a new in-situ TEM microreactor liquid cell with the capability to mix fluids in controlled temperature regimes, to view reactions as a function of time, and to capture and analyze reaction products. Research programs using this stage will pursue studies of self-assembly, directed assembly, and nanoparticle formation and growth. In addition, for observation of advanced degradation of materials in the presence of gases and/or vapor, a new in-situ TEM gas cell stage is being developed. This stage will have the capability to study a variety of gas-solid and vapor-solid interactions, such as corrosion, oxidation, and hydriding, with accurate control over temperature and pressure. Envisioned research will include understanding environmental degradation of materials during storage of spent nuclear fuels, an issue of critical importance for the future of nuclear energy.

The second part of the talk will highlight the development of a new, triple-ion-beam in-situ irradiation TEM. By combining expertise in in-situ TEM experiments with expertise in ion beam studies, planning is currently underway that would culminate in the construction of an instrument capable of studying the effects of bombardment by up to three ion beams simultaneously within the TEM. This unique, triple-ion-beam capability would enable advanced experiments such as real-time studies of neutron induced damage and transmutation in a fission/fusion reactor by combining Fe, He, and H ions.

*This work is supported by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:40am **IS+AS+NS+MI-WeM6 In Situ TEM Investigation into the Thermal Stability of Nanograined FCC Metals and Alloys**, K. Hattar, B.G. Clark, Sandia National Laboratories, J. Kacher, University of Illinois at Urbana-Champaign, J.A. Knapp, D.M. Follstaedt, L.N. Brewer, Sandia National Laboratories, I.M. Robertson, University of Illinois at Urbana-Champaign

Nanostructured materials often display very unique properties related to their far-from-equilibrium nature. Due to these unique structures, many of these materials transform into other, more stable microstructures with minimal thermal excitation. This work will highlight examples of the unexpected routes taken during the microstructural evolution of pulsed-laser deposited (PLD) free-standing face-centered cubic (FCC) thin films as a function of deposition condition and annealing temperatures. A direct comparison between the grain growth dynamics observed during *in situ* TEM annealing experiments in PLD films of high-purity aluminum, copper, gold and nickel films, as well as aluminum-alumina alloys shows a multitude of kinetics. For high-purity systems film thickness, void density, grain size distribution, and deposition temperature were found to be the

primary factors observed controlling the rate, extent, and nature of the grain growth. The growth dynamics ranged from nearly classical normal grain growth to abnormal grain growth resulting in a bimodal grain size distribution. The grain growth rate was found to be highly dependent on the materials system despite all of the films being nanograined FCC metals produced by similar PLD parameters. The investigation of the aluminum-alumina alloys produced under various compositions and deposition parameters suggests that particle pinning can be used to maintain nanostructured films, even after annealing treatments at high homologous temperatures.

In addition to investigating the grain growth dynamics and the resulting grain size distribution, the variety of internal microstructures formed from thermal annealing were evaluated. These structures ranged from intergranular voids to stacking-fault tetrahedra. An unexpected, metastable hexagonal-closed packed phase was indentified in the high-purity nickel films. These *in situ* TEM observations have provided key insight into the microstructural evolution of nanograined free-standing metal films and the defect structure present in the grains resulting from various growth dynamics, in addition to suggesting multiple methods to tailor the structure and the resulting properties of nanostructured free-standing films.

*This work is supported by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy both at Sandia and under grant DE-FG02-07ER46443. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **IS+AS+NS+MI-WeM9 In Situ TEM Studies of Nanomagnetism and Thermal Transport, J. Cumings, University of Maryland**

INVITED

The transmission electron microscope is a powerful tool for many areas of nanoscience. The combination of high spatial resolution and high time resolution, giving video-rate imaging, makes it uniquely capable of many types of studies of phenomena in-situ during imaging. Here I will present two areas where we have made recent advances. In nanomagnetic structures, it is possible to image in real-time the reversal process of coupled systems called artificial spin ice. These systems exhibit frustration, leaving disorder in their lowest energy magnetic configurations. I will present studies showing the magnetic reversal processes for these structures, revealing that microscopically correlated events lead to avalanche phenomena. A second topic that I will present is electron thermal microscopy of carbon nanotubes. Here, a new technique will be introduced that allows thermal imaging with nanoscale spatial resolution. This technique has been used to study the thermal transport through carbon nanotubes, and I will present results showing that thermal contact resistance can limit the thermal transport in nanotubes. I will show that this contact resistance can be tuned by two orders of magnitude by appropriately controlling the fabrication of the contacts. Together these results serve to demonstrate the capabilities of studies utilizing in-situ transmission electron microscopy.

11:20am **IS+AS+NS+MI-WeM11 In-situ Infrared Transmission Analysis of Atomic Layer Deposition Reactions on Polymer Films and Fibers, G.N. Parsons, B. Gong, J.S. Jur, C. Oldham, K. Lee, North Carolina State University**

Many new product applications related to packaging, filtration, protection and others offer substantial opportunities and raise new demands for polymer/inorganic thin film integration and surface modification. In-situ transmission infrared spectroscopy can provide critical insight into reaction mechanisms that proceed during inorganic film deposition on organics. We are particularly interested in low-temperature atomic layer deposition (ALD) which ideally proceeds through a binary sequence of self-limiting surface reactions to form highly conformal and uniform films on high surface area structures. In-situ IR spectroscopy allows us to probe and identify specific polymer/precursor reaction mechanisms that occur during precursor and reactant exposure. Typical atomic layer deposition precursors and reactants include trimethylaluminum (TMA), diethyl zinc (DEZ) and water, and polymer materials studied to date include polypropylene, polyamide-6, polyesters (such as polybutylene terephthalate), cellulose, polyvinyl alcohol and others. We have investigated deposition reactions on planar polymer sheets as well as micro- and nano-scale polymer fibers.

In-situ IR transmission data demonstrates that typical non-reactive materials such as polypropylene will take up precursors with minimal precursor/polymer reaction, resulting in subsurface alumina nucleation. Polymers with more reactive backbone or side chain groups, such as cellulose, polyvinyl alcohol or polyamide-6 react readily with the precursor. For example, when polyamide-6 is exposed to TMA, N-H and C-O stretching modes decrease markedly, indicating that TMA attacks the

electrophilic carbon atom in the carbonyl group leading to methyl insertion and formation of C-O-Al- and C-CH₃ bonds. Electron micrograph images of polyamide fibers after TMA exposure confirms significant extent of reaction. Deposition on cellulose cotton fibers, however, shows primarily surface adsorption, resulting in true ALD growth and highly conformal film coatings by TEM. We will show details of the in-situ transmission ALD reactor, and illustrate how the tool is especially amenable and adaptable to in-situ surface reaction analysis on polymer fiber networks.

Wednesday Afternoon, October 20, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+BI+AS-WeA

In Situ Microscopy/Spectroscopy – Biological Interfaces

Moderator: M. Grunze, University of Heidelberg, Germany

2:00pm **IS+BI+AS-WeA1 Adsorption and Phase Transition of Liposomes via Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy**, M.R. Hernandez, T.C. Ng, E.N. Towns, B.C. Walsh, D.P. Land, University of California at Davis

Liposomes are becoming increasingly prevalent as an important part of drug delivery systems in modern medicine, however a better understanding of the physical characteristics is needed. In this study we present our results on the stability and adsorption of liposomes formulated from dipalmitoylphosphatidylcholine (DPPC) via attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The phase transition temperature of liposome formulations of pure DPPC, DPPC and cholesterol, and DPPC, cholesterol, and 1,2-Distearoyl-phosphatidylethanolamine-methyl-polyethyleneglycol-2000 (DSPE-mPEG2000) is determined using a temperature dependant study (25°C to 50°C) and been found to occur abruptly around 41°C for pure DPPC liposomes and exhibit gradual temperature changes from 35°C to 43°C for the other two liposome formulations. We have studied the adsorption characteristics of different formulations of liposomes with both hydrophobic and hydrophilic surfaces created by different self-assembled monolayers, and will present a new method for studying an *in vitro* way of studying the adsorption of different formulations of liposomes onto a surface of immobilized proteins. Knowing the stability of liposomes and liposome-protein adsorption characteristics allows for a better understanding of their use and design of future formulations in drug delivery systems.

2:20pm **IS+BI+AS-WeA2 Synchrotron Based Infrared Imaging at the Diffraction Limit**, J. Nasse, University of Wisconsin-Milwaukee, C. Gohr, A. Rosenthal, Medical College of Wisconsin, C. Hirschmugl, University of Wisconsin-Milwaukee

A new mid-infrared beamline (IRENI) extracting a large horizontal swath of radiation (320 hor. x 25 vert. mrad²) to homogeneously illuminate a commercial IR microscope equipped with an infrared Focal Plane Array (FPA) detector has recently been commissioned at the Synchrotron Radiation Center in Stoughton, WI. This new facility provides the opportunity to obtain chemical images with diffraction-limited resolution, for all wavelengths in the mid-IR concurrently, in minutes. The design of this facility and an initial application will be presented.

IRENI combines a bright IR synchrotron source to an FTIR microscope with a multi-element detector for wide-field imaging as opposed to the common dual-aperture geometry with raster scanning that is available at most synchrotron IR beamlines. The swath of radiation from the SRC is extracted as 12 beams and recombined into a 3 x 4 bundle of beams that is refocused onto a sample plane of an infrared microscope illuminating 40 x 60 micron² sample area. The sampled spatial resolution is defined by both the magnification after the sample and the FPA pixel size. Here, a 74x Schwarzschild objective achieves effective geometric pixel sizes of 0.54 x 0.54 micron², which is approximately $\lambda/4$ for even the shortest wavelength of 2 μ m. This spatial oversampling provides adequate information to obtain concurrent, diffraction-limited images across the entire spectral range. In addition, the spectral quality is excellent, since the high density, stable, broadband flux from the synchrotron achieves high quality spectra for 0.54 x 0.54 micron²/pixel using similar measuring times as table-top instruments that image 5.5 x 5.5 micron²/pixel.

The presence of calcium-containing crystals, including calcium pyrophosphate dihydrate (CPPD) and hydroxyapatite-like basic calcium phosphate (BCP), in synovial fluids plays a major role in cartilage degeneration in osteoarthritis. Models of calcium crystal formation tend to produce small, sparse crystals embedded in debris enriched in proteins, lipids, and carbohydrates, which interfere with many identification techniques. Synchrotron FTIR imaging circumvents difficulties in identifying these crystals and also allows for characterization of the surrounding matrix. We present results from well-characterized models of calcium crystal formation that demonstrate our ability to both identify crystals *in vitro* and characterize the matrix surrounding these crystals.

This work has been done with support from an NSF Major Research Instrumentation grant (DMR-0619759) and the Synchrotron Radiation Center, which is also supported by NSF (DMR-0537588).

2:40pm **IS+BI+AS-WeA3 Proteins and Lipids at Liquid/Solid Interfaces: *In situ* Studies by Neutron Reflectometry and Infrared Spectroscopy**, M. Strobl, M. Kreuzer, University of Heidelberg, Germany, M. Reinhardt, R. Steitz, Helmholtz Zentrum Berlin, Germany, M. Grunze, R. Dahint, University of Heidelberg, Germany **INVITED**

Proteins and lipids at liquid/solid interfaces are of crucial importance in the design of biofunctional interfaces. For example, adsorbed protein layers determine the biocompatibility of implants and may control bacterial adhesion. Upon surface contact, proteins commonly undergo structural changes, which will alter their activity and biological function. In combination with lipids, proteins are valuable model systems to mimic cell membrane function. Thus, in order to improve our understanding of biofunctional interfaces, a strong need exists to develop surface analytical tools, which facilitate *in situ* characterization on a molecular level.

Due to its *in situ* capability, non-destructive character and the short wavelength of neutron beams, neutron reflectometry offers a very attractive approach to the analysis of layer structures on the nanometer scale. It provides detailed information on the amount of adsorbed species as well as on the thickness, density and hydration of the adsorbate. In combination with surface sensitive infrared spectroscopy (ATR-FTIR), additional information is obtained on specific molecular groups of the adsorbate as well as on molecule conformation.

We will report on the set-up of a new time-of-flight neutron reflectometer at the Helmholtz Center Berlin, which is especially adapted to biological samples and, for the first time, facilitates simultaneous *in situ* ATR-FTIR characterization. Dedicated sample environments have been developed to study biological films as a function of applied pressure, shearing forces and temperature. As a potential application, we discuss the phase behavior and stability of immobilized oligolamellar lipid bilayer films under load and shear, which are important in bio-lubrication and the search for advanced implant materials, such as artificial joints. A second example will focus on the impact of surface chemistry and structure on the activity of immobilized proteins.

4:00pm **IS+BI+AS-WeA7 Biological Imaging with Coherent X-rays: The Lens-less Approach to High Resolution**, A. Beerlink, Universität Göttingen, Germany **INVITED**

Understanding molecular functions in complex environments such as biological cells or novel composite materials are a prerequisite for the advancement of nano and biomedical sciences. They require a combination of high spatial resolution, quantitative contrast and

full compatibility with environmental conditions, such as aqueous media. To this end, the potential of x-ray imaging is not yet fully developed, but currently undergoes rapid progress. While classical x-ray microscopy based on Fresnel zone plates has matured and provides useful structural information in a growing range of applications, this technique is severely limited by the nanostructuring process of the lenses. In

recent years, novel lens-less approaches for imaging have emerged, where the object functions are reconstructed from the measured intensities

either in the far-field regime, or under near-field conditions (propagation imaging). We present experiments using x-ray quasi point sources to illuminate the sample in combination with digital recording of the resulting diffraction patterns. One focus is the applicability towards biological samples, for which the imaging properties of the different coherent microscopy approaches will be compared. In this context, recent results obtained with ultrabright femtosecond pulses provided by the free electron laser FLASH will be presented and accessible information complementary to synchrotron imaging will be discussed.

4:40pm **IS+BI+AS-WeA9 Dielectric Constant and Polarization of Biomolecules Determined by Torsional Resonance Nanoimpedance Microscopy**, K. Kathan-Galipeau, S.U. Nanayakkara, P.A. O'Brien, B.M. Discher, D.A. Bonnell, University of Pennsylvania

We have developed a new technique, torsional resonance nanoimpedance microscopy (TR-NIM), that allows for the measurement of frequency-dependent local transport properties on soft materials. AFM measurements at torsional resonances provide a key advantage: the ability to achieve low-force scanning while maintaining the tip in the near-field. As a result, it is possible to measure impedance between the tip and sample without damaging the sample.

This technique has been used to determine the resistance, capacitance, and dielectric properties of a novel class of biomolecules. These redox active molecules, known as maquettes, consist of dimers and tetramers of alpha helix polypeptides and provide a convenient functional alternative to natural

proteins. Maquettes are capable of binding a range of cofactors; this study examines the properties of iron and zinc porphyrins. Maquettes serve as a benchmark for integrating electronics with biologically inspired materials that possess unique characteristics, such as electron-transfer capability, the possibility of gating redox activity, optoelectronic functionality, and nanometer size.

In order to determine the behavior of these functional biomolecules on electrodes, PDMS stamping was used to create stripes that alternate between maquettes and bare graphite. Stamping also allowed us to control the assembly of the redox-active maquettes from multilayers to horizontally oriented monolayers (maquettes laying down) and vertically oriented monolayers (maquettes standing up) by varying the stamping time and the concentration of the maquettes in organic solvents.

Interestingly, we observe that the resistance decreases with increased height of maquettes, which is explained in terms of the configurations of the molecules on the electrode. The dependence of local impedance on exposure to optical radiation revealed an increase in capacitance and decrease in resistance when the maquettes are exposed to 425 nm light. This is true for both zinc and iron porphyrin cofactors. We attribute the decrease in resistance to photoactivated current. The increase in capacitance is due to an increase in the polarizability of the maquettes.

5:00pm **IS+BI+AS-WeA10 Dynamic Observation of Phospholipid Model Cell Membranes and Particles by STM and Vibrational Spectroscopy.** *T. Yamada*, RIKEN, Japan, *S. Matsunaga*, The University of Tokyo, Japan, *T. Kobayashi*, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Scanning tunneling microscopy (STM) and other surface-scientific techniques can be utilized to explore the microscopic dynamics of biological molecules in the context that the techniques are applicable for solid surfaces immersed in aqueous solutions. We devised STM and vibrational spectroscopies to make usable for molecular monolayers at solid-liquid interface. We attempted to observe phospholipid layers formed on octanethiol-terminated gold (111) single-crystalline substrates placed in aqueous buffer solutions (in situ STM). By in situ STM we could observe dihexanoyl-*sn*-glycero-3-phosphocholine (DHPC), a relatively short kind of lipid, forming a fluidic monolayer. A crystalline phase of this monolayer was observed by applying an electrode potential compatible with the membrane potentials of real cells. Furthermore, mixed lipid layers have been examined by STM [1]. We found some nanometer-scale raft structures (phase-separated domains), which are functionally characteristic for real cell membranes. We also studied phospholipid particles suspended in buffer solutions. Suspensions were prepared from a phosphocholine (PC) and an ethanolamine (PE), consisting of nanometer-scale phospholipid particles with narrow size distribution. In situ STM revealed particles with a diameter ~ 10 nm (named "minimal lipid particles (MLP)"), forming a monolayer along the Au(111). It is known that some categories of antibiotics selectively attack lipids contained in germ cell membranes and disintegrate the whole cells. We chose "duramycin", a 19-residued peptide antibiotic, which specifically binds PE. When the total concentration of phospholipid was controlled between 100 μM and 500 μM , a layer of MLP was discerned. During STM scanning, 7 μM of duramycin solution was added into the suspension, and the PC+PE MLP became fragile and seemed to be scratched by the tip, ending up with a widespread multilayer. This sort of highly leveraged effect of duramycin is characteristic in the action of antibiotics [2]. These works demonstrated the advantage of STM in monitoring the live nanometer-scale reactions of biological entities, which have not been recognized experimentally so far. We expect more application of STM in physiological investigation in cell biology.

[1] S. Matsunaga et al., *Electrochem. Commn.* **9** (2007) 645.

[2] S. Matsunaga et al., *Langmuir* **25** (2009) 8200.

5:20pm **IS+BI+AS-WeA11 Rapid In-Situ Assessment for Microbes on Simultaneously Prepared Plate with Substrate and Zirconium Based Thin Film Metallic Glasses (TFMGs).** *P.T. Chiang*, I-Shou Univ./Fooyin Univ. Hospital, Taiwan, Republic of China, *G.J. Chen*, *H.H. Liu*, *Y.H. Shih*, I-Shou Univ., Taiwan, Republic of China, *J.P. Chu*, National Taiwan Univ. of Science and Technology, Taiwan, Republic of China, *J.S.C. Jang*, National Central Univ., Taiwan, Republic of China

ZrAlNiCuSi TFMGs could modify the stainless steel's surface with high hardness, scratch-adhesion capabilities. Zr-based TFMGs' smooth surface could decrease and prolong the lag phase of microbes' growth for at least 24 hours.

The actual numbers of pathogenic bacteria might be underestimated by conventional methods due to sublethal injury, malnutrient's and other physiological factors which reduce bacterial viability. Moreover, these methods would limit the real-time quantitative detection and easily cause contaminations with bias.

Rapid comparisons in the same culture condition are obtained on a simultaneously prepared plate with substrate and Zr based TFMGs. By utilization of GFP plasmid (pGLO) into HB101 with 10mM arabinose induction, we could measure the intensity of green fluorescence by LAS-3000 fluorescent detector to setup the real-time monitor system for observation of bacterial growth on TFMGs' surface.

This integrated method was time-saving, cost-effective and simple. The serially rapid in situ monitor of the microbial growth will emerge as a novel tool to realize the TFMGs or other materials' antimicrobial properties.

Thursday Afternoon Poster Sessions

In Situ Microscopy and Spectroscopy Topical Conference

Room: Southwest Exhibit Hall - Session IS-ThP

In Situ Microscopy and Spectroscopy Topical Conference Poster Session

IS-ThP2 Surface Studies of Ionic Liquids and Their Interaction with Water and CO₂. *A.M. Margarella, T.M. McIntire, M.H. Cheng*, University of California, Irvine, *H. Bluhm, Z. Lui*, Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California, Irvine

Ionic liquids are substances composed entirely of ions which have a low melting point, typically below 100° C, and other unique properties such as very low vapor pressure. These properties, in addition to ionic conductivity, make them useful as solvents for a number of applications, such as gas separation and solar cells. Using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS), the surface composition of different room temperature ionic liquids has been investigated. AP-XPS offers the advantage of doing photoelectron spectroscopy under higher pressures, up to a few torr, so the sample can be exposed to a variety of chemical environments. The AP-XPS used in these experiments is at the Advanced Light Source synchrotron facility. Utilizing synchrotron radiation, depth profiles of the elements in the compounds can be obtained by varying the photoelectron kinetic energy. We first investigated the surface composition of imidazolium halides under humid conditions; our results indicate that with added water vapor in the chamber, up to 15% relative humidity, the surface composition does change slightly. Higher relative humidity environments are currently being explored. The effect of water vapor on the surface of ionic liquids is important because many ionic liquids are hygroscopic, and when using them in applications, it is difficult to keep them dry. Using AP-XPS, we are also exploring the effect of CO₂ on the depth profiles of the ionic liquids. Ionic liquids have the potential to be used for CO₂ capture because the solubility for CO₂ is generally high and, when compared to other absorbents, the ease of recovery is straight-forward. For this application, the surface plays an important role in this process because the surface of the ionic liquid is the first part that interacts with the gas stream containing CO₂. Depending on the nature of the ionic liquid, it can either dissolve the CO₂ or react with it to form a carbamate. Additionally, we will investigate the role of water on the interaction with CO₂. Near Edge X-ray Absorption Fine Spectroscopy (NEXAFS) will also be used to study these interactions. By combining the surface science techniques XPS and NEXAFS, we can understand the role of different ionic liquids in capturing CO₂.

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Zhan, Y.: IS+SS-TuA9, 4