

Tuesday Morning, October 30, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+SS+EN-TuM

In Situ Spectroscopic Studies of Catalysis and Gas-Solid Reactions

Moderator: B. Roldan Cuenya, University of Central Florida

8:00am **IS+AS+SS+EN-TuM1 Ambient Pressure XPS for Alternative Energy Research and Environmental Science, H. Bluhm**, Lawrence Berkeley National Laboratory **INVITED**

Solid/vapor and liquid/vapor interfaces play a major role in many processes in the environment and technology. Examples include heterogeneous catalysis, fuel cell technology, aerosol chemistry, and weathering of minerals and rocks. The measurement of these interfaces under realistic conditions of gas pressure and temperature has gained increasing importance over the last decades. Ambient pressure photoelectron spectroscopy (APXPS) is a promising technique for the investigation of liquid and solid surfaces in the presence of gases at pressures in the Torr range. The heart of an APXPS instrument is a differentially pumped electrostatic lens system that separates the sample, which is in a gas atmosphere at pressures of up to 5 Torr, from the electron spectrometer, which is kept in vacuum. This talk will discuss the history and basics of APXPS and show examples of the application of APXPS to the study of aqueous solution, metal oxides, soot, and fuel cell electrodes under reaction conditions.

8:40am **IS+AS+SS+EN-TuM3 In Situ Soft X-ray Photon-in/Photon-out Spectroscopy of Photo-electrochemical Reactions of Hematite in Water Splitting, J.H. Guo**, Lawrence Berkeley National Laboratory, *A. Braun*, Empa, Swiss Federal Laboratories for Materials Science and Technology, *K. Sivula*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *D. Bora*, Lawrence Berkeley National Laboratory, *J.F. Zhu*, *L. Zhang*, University of Science and Technology of China, *M. Grätzel*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *E.C. Constable*, University of Basel, Switzerland

Hydrogen fuel generation by solar water splitting in photoelectrochemical cells (PEC) is one of the first steps in artificial photosynthesis and an essential part of the holy grail of solar energy conversion. Iron oxide, literally "rust", is an interesting PEC photoanode material because of its affordability, good stability, good spectral match of the solar spectrum, and yet controversial because of its poor electronic structure. At present, iron oxide is taking center stage as prospective PEC anode material.

PEC electrodes are typically semiconducting metal oxides to form electron-hole pairs when struck by light. In the photoanodes such as hematite, the generated holes must diffuse to the iron oxide surface where they can oxidize water to oxygen. However, the electronic structure of iron oxide is such that the photogenerated holes tend to recombine and annihilate with the electrons before reaching the surface and performing the required chemical work on water splitting. Currently, researchers worldwide try to understand the peculiarities of iron oxide so as to invent strategies to improve this material.

The Advanced Light Source produces soft X-rays which are optimally suited to study the electronic structure of electrode materials and which can detect electron holes. But the holes needed for solar water splitting by iron oxide require an anodic electric bias plus the illumination. Moreover, the holes are transitional and quite elusive. Also, soft X-rays cannot easily peek into a PEC cell. The unique design of the in-situ cell at the ALS has overcome the burden [1-3]. Recently the experiment has been performed for studying, under in-situ and operando conditions, the hole generation in a specifically designed photoelectrochemical cell. The oxygen valence band signature was recorded while tuning the PEC relevant parameters, two different types of holes in the valence band near the Fermi energy are discovered [4].

References:

- [1] "X-ray Emission Spectroscopy of Hydrogen Bonding and Electronic Structure of Liquid Water", J.-H. Guo et al., *Phys. Rev. Lett.* **89**, 137402 (2002).
- [2] "Electronic Structure of Cobalt Nanocrystals Suspended in Liquid", H. Liu et al., *Nano Lett.* **7**, 1919 (2007).
- [3] "In situ soft X-ray absorption spectroscopy investigation of electrochemical corrosion of copper in aqueous NaHCO₃ solution", P. Jiang et al., *Electrochem. Comm.* **12**, 820 (2010).

[4] "Direct Observation of Two Electron Holes in a Hematite Photoanode during Photoelectrochemical Water Splitting", A. Braun et al., *J. Phys. Chem. C* **116**, 16870 (2012).

9:00am **IS+AS+SS+EN-TuM4 XANES and Ambient Pressure XPS (APXPS) Study: Investigations of the Local Structure and Final-State Effect in Partially Reduced SnO_x Nanoislands on Pt(111), S. Axnanda, Z. Liu, B. Mao**, Lawrence Berkeley National Laboratory

Heterogeneous catalysts consisting of small particles having a high concentration of structural defects and under-coordinated sites make up the majority of the catalytic processes in industrial chemistry. One important recent example of interest shows that the interface-confined coordinatively unsaturated ferrous (CUF) sites together with the metal supports (FeO_x/Pt(111)) are active for dioxygen activation which causes the ensemble to be highly efficient for CO oxidation at low temperature under typical operating conditions of a proton-exchange membrane fuel cell.[1-2] In this work, we report another spectroscopic evidence to further confirm an enhanced reactivity at the edges of small catalyst particles. The system of interest is partially oxidized SnO_x (Sn²⁺) nanoislands supported on Pt(111) for ethanol oxidation reaction (EOR), an electrode material in a direct alcohol fuel cell (DAFC). Our findings suggested that SnO_x/Pt(111) inverse catalysts have improved activity for EOR in acidic media as compared to a bare Pt(111) surface.[3] We also found that the most active surface had a small coverage of SnO_x (0.3- 0.4 ML). Water activation at low potentials is currently attributed to be the promoting effect of SnO_x nanoparticles, since this enhances the oxidation of chemisorbed CO formed on Pt sites during the EOR.[4] To better understand this increased activity, we performed study with the goal to indicate the actual state of Sn in SnO_x nanoislands before and after the SnO_x /Pt(111) is used in EOR showing the increased activity: purely oxide Sn or mixed Sn alloy and Sn oxide, using a combination of APXPS and XANES techniques. BE shift in the XPS core-line spectra of Sn and O, soft X-ray XANES spectra (Sn M_{4,5}-edge, O K-edge) will be collected and compared to the corresponding XPS spectra (Sn 3d, O 1s) to explain the actual state of Sn before and after the SnO_x/Pt(111) is used in the EOR.

1. Fu, Q., et al., Interface-Confined Ferrous Centers for Catalytic Oxidation. *Science*, 2010. 328: p. 1141.
2. Deng, X., et al., Reactivity Differences of Nanocrystals and Continuous Films of α -Fe₂O₃ on Au(111) Studied with In Situ X-ray Photoelectron Spectroscopy. *J. Phys. Chem. C*, 2010. 114: p. 22619.
3. Zhou, W.P., et al., Enhancement in Ethanol Electro-Oxidation by SnO_x Nanoislands Grown on Pt(111): Effect of Metal Oxide-Metal Interface Sites. *Journal of Physical Chemistry C*, 2011. 115: p. 16247.
4. Axnanda, S., W.P. Zhou, and M.G. White, CO Oxidation on Nanostructured SnO_x/Pt(111) surfaces: Unique Properties of Reduced SnO_x. *Phys. Chem. Chem. Phys.*, 2012. Submitted.

9:20am **IS+AS+SS+EN-TuM5 Epitaxial Strontium Substituted Lanthanum Cobalt Oxides Investigated using In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Near Operating Conditions Under Applied Potentials, E. Crumlin, E. Mutoro**, Massachusetts Institute of Tech., *Z. Liu*, Lawrence Berkeley National Lab, *M.D. Biegalski*, Oak Ridge National Lab, *W.T. Hong*, Massachusetts Institute of Tech., *H.M. Christen*, Oak Ridge National Lab, *H. Bluhm*, Lawrence Berkeley National Lab, *Y. Shao-Horn*, Massachusetts Institute of Tech.

Operating conditions for solid oxide fuel cell (SOFC) are typically at high temperatures (~500 – 1000 °C) and ambient pressures (~1 atm). We have to understand how the physical and chemical properties of SOFC materials, particularly the cathode which is responsible for a majority of the fuel cells area specific resistance, change under operating conditions. Such data can provide insights into the mechanism of the oxygen reduction reaction (ORR) which may lead to material development strategies to improve the cathode performance. However, these operating conditions are far away from conventional characterization techniques that are often applied at room temperature or even in ultrahigh vacuum (UHV). Our recent work using *in situ* ambient pressure X-ray photoelectron spectroscopy (APXPS) has shown that (001) oriented epitaxial films of La_{0.8}Sr_{0.2}CoO_{3- δ} (LSC₁₁₃) can exhibit Sr enrichment in the near-surface perovskite lattice structure ("lattice") as temperatures were raised from 220 °C to 520 °C in a *p*(O₂) of 1×10⁻³ atm. In contrast under the same conditions, a bulk pellet of LSC demonstrated no changes in Sr content within the "lattice" region. The Sr enrichment is believed to play a key role in the observed one order of magnitude enhancement in ORR activity (as measured by the surface exchange coefficient, *k*^s) of the (001) epitaxial films relative to bulk LSC₁₁₃. In this work, we continue the previous investigations of the chemical properties of (001) epitaxial LSC₁₁₃ as a function of temperature cycling

between 220 °C and 520 °C at a $p(\text{O}_2)$ of 1×10^{-3} atm. Additionally, the comparison of LSC₁₁₃, (La_{0.5}Sr_{0.5})₂CoO_{4±δ} (LSC₂₁₄), and LSC₂₁₄-decorated LSC₁₁₃ (LSC_{113/214}) at $p(\text{O}_2)$ of 1×10^{-3} atm as a function of temperature and under applied cathodic potentials will be presented in order to provide insights into the physical origin responsible for the observed ~3 orders of magnitude ORR activity enhancement of LSC_{113/214} relative to (001) epitaxial LSC₁₁₃.

9:40am **IS+AS+SS+EN-TuM6 Probing Nitrogen and Metal Speciation in Non-Platinum Electrocatalysts by Ambient Pressure X-ray Photoelectron Spectroscopies and DFT Calculations.** *K. Artyushkova, B. Halevi, A. Serov, The University of New Mexico, B. Kiefer, New Mexico State University, P. Atanassov, The University of New Mexico*

X-ray Photoelectron Spectroscopy (XPS) has been the main surface analysis method for determining the chemical environment and coordination of nitrogen and transition metal (TM) in the non-precious group metal oxygen reduction reaction (ORR) electrocatalysts. Even though there is an agreement that Me-N_x serve as one of the possible active sites in ORR, the distribution of Me-N₂ vs Me-N₄ centers and their specific role still remains unresolved. XPS which heavily relies on use of reference spectra in accurate identification of species cannot address this issue directly as no reference compounds with Me-N₂ moieties are available. The assignment of peaks and nitrogen coordination is not straightforward due to overlapping peaks that appear within a narrow energy window of 2.5-eV and the full width half maximum (fwhm) for individual species is on the order of 1.2-1.5-eV. Being able to calculate binding energy shifts based on molecular structure can be very important tool for assisting in this task. We will report on BE shifts that have been calculated at the DFT level and their comparison to experimentally obtained values for metal-less and metal-containing porphyrins. Information obtained from the DFT calculations will be used as input into curve-fitting XPS spectra for various model N-Me containing compounds as well as from electrocatalyst. We will compare chemical information derived from conventional XPS as well as in-situ ambient-pressure XPS using variable energy synchrotron source.

10:40am **IS+AS+SS+EN-TuM9 Resolving Growth of Palladium Nanocatalysts Using In Situ FT-IR, XAS and PDF under Practical Atomic Layer Deposition Conditions.** *Y. Lei, J. Lu, B. Liu, H. Zhao, J. Greeley, P. Chupas, J. Miller, J.W. Elam, Argonne National Laboratory*

Nanostructured Pd catalysts prepared by ALD have been demonstrated highly active for alkene hydrogenation, methanol decomposition reaction, and alcohol oxidation for fuel cells. Development of supported Pd nanoparticles with Controlled size/structure relies on the fundamental understanding of the two half reactions with high precision during Pd ALD. However, evolution of Pd surface species, as well as the subsequent nucleation and growth of palladium nanoparticles during Pd ALD is still not clear.

Mechanism of assembly of highly dispersed Pd nanoparticles on TiO₂ surfaces from palladium hexafluoroacetylacetonate (Pd(hfac)₂) were investigated by means of *in situ* Infrared (IR) spectroscopy, X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) under practical atomic layer deposition condition simultaneously. Density function theory simulation was applied to understanding the reaction mechanism. On chlorine-containing TiO₂ surface, Pd(hfac)₂ primarily adsorbed on TiO₂ surface as Pd(hfac)Cl₂* species, confirmed by both XAS and DFT calculations. *In-situ* FT-IR results reveal that deligation of Pd(hfac)Cl₂* species began at as low as 100 °C with the present of formalin. Further on, *in-situ* XAS results indicated that cleavage of Pd-O bond occurred first, followed by cleavage of Pd-Cl bond. Sequentially, Pd atoms started to gain mobility and agglomerate to small nanoparticles. The hfac ligands spilled to TiO₂ surface as site blockers for ALD. The surface poisons were eventually removed at 225 °C. Nano-size palladium-carbon phase was also found after long exposure of formalin. Atomic resolution aberration-corrected STEM image showed one nanometer size crystalline Pd particles were synthesized using ALD. The catalytic performance of these Pd nanocatalysts was further demonstrated in several applications.

In summary, dynamic growth of Pd nanocatalysts was obtained utilizing a combination of *in-situ* techniques.

11:00am **IS+AS+SS+EN-TuM10 Catalyst Characterization using In Situ XAS and XPS: From Nanoparticles Synthesis to Evolution of Structural/Electronic Properties under Reaction Conditions.** *A.M. Karim, Pacific Northwest National Laboratory* **INVITED**

Catalysts are used to facilitate the important industrial chemical processes, leading to products valued in the trillions of dollars annually just in the U.S and most catalysts used in large-scale processes are solids. To maximize the number of sites available for reaction, catalysts are typically comprised of metallic/metal oxide nanoparticles dispersed on high surface area supports.

The activity and selectivity of metallic nanoparticles strongly depend on their size, shape and composition [1-8]. In order to design more active and selective catalysts, it is essential to identify the catalytically active sites and understanding their geometric and electronic properties which requires: (1) synthesis of well-defined catalyst structures and (2) the ability to correlate individual reaction pathway(s) with the type of active site(s) available on the catalyst surface under reaction conditions.

This talk is going to cover our work on *in situ* characterization of nanoparticles from the synthesis stage to the evolution of their structural/electronic properties under reaction conditions using X-ray photoelectron and X-ray absorption spectroscopies. The catalyst systems that will be covered include:

Pd nanoparticles synthesis in solution: Understanding the nucleation and growth mechanisms.

Supported Pt, PtRe and PtNi nanoparticles under aqueous phase reaction condition: Correlating the structural and electronic properties with the catalytic activity and selectivity.

References:

- [1] Boudart, M. *Adv. Catal.* 1969, 20, 153.
- [2] Boudart, M. *Journal of Molecular Catalysis* 1985, 30, 27.
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- [6] Alayoglu, S.; Nilekar, A. U.; Mavrikakis, M.; Eichhorn, B. *Nature Materials* 2008, 7, 333.
- [7] Sinfelt, J. H. *Journal of Catalysis* 1973, 29, 308.
- [8] Sinfelt, J. H. *Accounts of Chemical Research* 1977, 10, 15.

11:40am **IS+AS+SS+EN-TuM12 In Situ Study of the Oxidation of CO over Ir(111).** *J. Knudsen, Lund University, Sweden, Y. Monya, Keio University, Japan, J. Schnadt, M.A. Arman, E. Grånäs, Lund University, Sweden, H. Kondoh, Keio University, Japan, J.N. Andersen, Lund University, Sweden*

The platinum group metals are known to be excellent catalysts for the oxidation of carbon monoxide, and the reaction mechanisms over the surfaces of these metals have been studied for a long time. Nevertheless, only during recent years a new picture has emerged which suggests that the catalytically active phase often is formed first under reaction conditions – which implies realistic pressures rather than ultrahigh vacuum (UHV) – and that it is different from the adsorption structures known from UHV experiments. In the case of the Pt(111) surface a very oxygen-rich chemisorbed phase has been suggested as the catalytically active phase [1], whereas a surface oxide have been suggested for the Ru(0001) surface [2]. Thus, for each different surface different phases and mechanisms might be at play, and, moreover, the phase might depend quite strongly on the conditions (pressure and temperature) used.

With this in mind we have studied the CO oxidation reaction over the Ir(111) surface and the related adsorption systems of CO and oxygen on Ir(111) using a combination of *in situ* Ambient pressure x-ray photoelectron spectroscopy (APXPS) – carried out at the new APXPS instrument at the Swedish synchrotron radiation facility MAX IV Laboratory – and *ex situ* Scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) measurements performed in UHV.

A recent surface x-ray diffraction study reports different oxygen phases for the Ir(111) surface at oxygen pressures from 10⁻⁶ to 100 mbar – chemisorbed oxygen, a trilayer, a multilayer oxide, and a bulklike oxide [3]. Concentrating on pressures at around 1 mbar, we find a variety of oxygen-rich structures. The corresponding CO adsorption phase formed at 1 mbar CO pressure is an assembly of separated CO₁₆ clusters with the CO molecules sitting in on-top sites [4].

The reactivity at 1 mbar total pressure (O₂:CO ratio 9:1) and at different temperatures was studied by APXPS and simultaneous monitoring of the gas composition. We find that the phase with the highest activity for the oxidation of CO is a surface phase which contains both CO and oxygen. By comparing with the measured adsorption structures of oxygen we find that the oxygen structure is quite similar to the p(2x1)-O structure formed on Ir(111) under UHV conditions. This contrasts with what is found for other platinum group metals such as the Pt(111) surface [2], for which CO oxidation is favoured over oxygen rich phases.

- [1] A. L. Gerrard, J. F. Weaver, *J. Chem. Phys.* **123** (2005) 224703.
- [2] H. Over et al., *Science* **287** (2000) 1474.
- [3] Y. B. He et al., *J. Phys. Chem.* **112** (2008) 11946.
- [4] L.-M. Yang, S.-L. Yau, *J. Phys. Chem. B.* **104** (2000) 1769.

Tuesday Afternoon, October 30, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+BI+ET+GR+NS-TuA

In Situ Studies of Organic and Soft Materials and In Situ Microscopy

Moderator: K. Artyushkova, The University of New Mexico, J.A. Eastman, Argonne National Laboratory

2:00pm **IS+AS+BI+ET+GR+NS-TuA1 Micronutrient Detection and Quantification from Data Obtained from Plasma Pencil Atmospheric Mass Spectrometry, M.J. Stein, E. Lo, C. Waterton, D.G. Castner, B.D. Ratner, University of Washington**

The analysis of micronutrient quantities is one component in the strategy to reduce the global burden of malnutrition-related disease. Accessibility of the proper equipment and equipment complexity impede nutrient testing in the areas that might benefit most from these studies. In this work, we present an analysis of micronutrients in a physiological range from blood plasma using plasma pencil atmospheric mass spectrometry (PPAMS), a method for sampling a sample's surface at ambient temperature and pressure conditions. The effectiveness of our PPAMS system is demonstrated using characteristic and tandem mass spectra on raw nutrient controls. Key micronutrient peaks and fragmentation patterns are observed. Next, we analyze a sample matrix of micronutrients in porcine plasma in which the nutrient concentrations are varied. Principal component analysis (PCA) is then employed on the spectra. The resulting PCA scores showed that these nutrients are separable at different nutrient concentrations to 95% confidence. The loadings peaks are shown to contain several of the key peaks observed in the raw nutrient powders as principal separators. The PPAMS technique is compared to several traditional techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrospray ionization mass spectrometry (ESI-MS). Separation of the nutrients at concentrations relevant for human blood-based nutrient detection is possible in both ESI-MS and PPAMS. However, ToF-SIMS is found to require 5x to 1000x higher concentrations than PPAMS for folate, vitamin A, and iodine in order to achieve similar separation of the micronutrients. In addition to the qualitative information obtained from the PCA results, quantitative predictive values are obtained by the application of a Bayesian wavelet-based functional mixed model. Since the mass spectra are modeled as functions in this model, peak detection methods are not required and the final results utilized the full spectral response. The final predicted values are compared to the known concentration values and the mean standard error of prediction (MSEP) is calculated. The accuracy of the predictive model was found to be dependent on the ionization potential of the individual nutrients. Metallic-nutrients were hypothesized to be more sensitive to outside cationization effects than their larger organic counterparts. In addition to quantitation, the physical properties of the ionization process were explored. Using XPS and ellipsometry in conjunction with carefully timed exposures and concurrent fragment PCA, it is determined that the PPAMS ionization is a softer form of ionization than most vacuum-based techniques.

2:20pm **IS+AS+BI+ET+GR+NS-TuA2 In Situ Real Time Examination of the Thin Film Growth of Pentacene on Polymeric Dielectrics Using X-Ray Synchrotron Radiation: Unexpected Changes in the Evolution of Surface Morphology with Substrate, T.V. Desai, A.R. Woll, J.R. Engstrom, Cornell University**

We have examined the thin film growth of pentacene on SiO₂ and on three different polymeric dielectrics using *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy (AFM). The polymeric dielectrics investigated spanned the range from a low surface energy hydrophobic surface (polystyrene, PS), to a medium surface energy hydrophobic surface (polymethylmethacrylate, PMMA), to a high surface energy hydrophilic surface [poly(ethylene imine), PEI]. We have also compared these results to pentacene growth on clean SiO₂. On all surfaces, pentacene forms a polycrystalline thin film, whose structure is that of the previously identified "thin film" phase. From *in situ* real-time x-ray scattering, we find that pentacene exhibits layer-by-layer (LbL) growth on all surfaces investigated, but the extent of LbL growth is a strong function of the underlying substrate. This result is unexpected as the transition to more 3D-like growth occurs for thicknesses where the underlying substrate is effectively almost entirely covered by the growing pentacene thin film. Layer-by-layer growth is significantly more prolonged on PEI (up to ~6 MLs), followed by SiO₂ and PMMA (up to ~4 MLs) and finally PS (up to ~3 MLs). This trend is also seen in the variation of both the roughness and the in-plane feature sizes of ~10 ML thick films, where the films are the smoothest, and the

feature sizes are the largest for growth on PEI, whereas on PS, the films are roughest, and the feature sizes are the smallest. Concerning possible reasons for this behavior, we can exclude the effects of the structure of the crystalline thin film (they were the same in all cases), and the roughness of the polymeric dielectric (rms roughness differed by < 0.1 nm) as major contributing factors. Surface energy of the polymeric thin films, however, provided the best explanation for the observed behavior, suggesting that thermodynamic driving forces play an important role in the evolution of thin film structure. In terms of molecular scale phenomena, interlayer transport and step-edge crossing events may be influenced by the mobility of the near-surface polymeric layers in the underlying substrate, which can be quite different for the ultrathin PEI layers vs. the much thicker PMMA and PS thin films.

2:40pm **IS+AS+BI+ET+GR+NS-TuA3 In Situ, Real-Time Diagnostics of Colon Cancer and Inflammatory Bowel Diseases by Direct Combination of Endoscopy and Rapid Evaporative Ionization Mass Spectrometry, Z. Takats, Imperial College, UK, L.A. Sasi-Szabo, University of Debrecen, Hungary, J. Kinross, Imperial College, UK, J. Balog, Medimass Ltd., L. Muirhead, K.C. Schafer, C. Guallar-Hoyas, Imperial College, UK**

INVITED

Rapid identification of biological tissues is a long-standing problem on various fields of interventional medicine, with special regard to cancer diagnostics and cancer surgery. While histological techniques provide the ultimate solution for the cellular-level identification of cancer cells, the approach is extremely complex and time consuming. Nevertheless, accelerated version of histopathology (so-called 'frozen section' method) is widely used for the intraoperative characterization of tissue samples removed from the surgical area. Since frozen section histology is less reliable than the traditional approaches, and the accelerated procedure still takes approx. 30 minutes for a single sample, there has been ongoing research for the development of more accurate and faster methods.

Molecular spectroscopy techniques including IR, Raman, solid state NMR and mass spectrometry have been used for the characterization of intact biological tissues and showed enormous potential for the differentiation of tissues with various histologies, including multiple different types of cancer.

Rapid Evaporative Ionization Mass Spectrometry is based on the observation that electrosurgical dissection of vital tissues involves the ionization of various tissue constituents, with special emphasis on membrane lipids. Electrosurgical methods employ electric current for the rapid heating and evaporation of tissue material and they are widely used both for dissection and coagulation on practically all fields of surgery. Hence, the direct combination of electrosurgery with mass spectrometry provides a tissue identification methodology, where the tissue manipulation part is already widely used by surgeons and fully approved from regulatory point of view. Electrosurgical methods are also employed on the field of endoscopy, both for coagulation and dissection. Combination of endoscopy with *in-situ* mass spectrometric tissue identification resulted in a diagnostic device which can potentially identify lesions in body cavities *in-situ*, in real-time.

Electrosurgical electrode assembly and ion transfer device were embedded into working channel of commercially available colonoscope. The device was coupled with a linear ion trap mass spectrometer, and the system was utilized during diagnostic colonoscopic interventions. Adenomae, adenocarcinomae and mucosal areas affected by inflammatory bowel diseases were successfully identified, in complete agreement with histopathological examination.

4:00pm **IS+AS+BI+ET+GR+NS-TuA7 Nanocrystal Phase Transformations in ZBLAN Glass Ceramics, J.A. Johnson, University of Tennessee Space Institute, C. Alvarez, Northwestern University, Y. Lui, Argonne National Laboratory, C.E. Johnson, University of Tennessee Space Institute, A. Petford-Long, Argonne National Laboratory**

In-situ and *ex-situ* TEM investigations of fluorochlorozirconate (FCZ) glass have led to the discovery of previously unreported BaF₂ in the face-centered-cubic (FCC) and orthorhombic phases. These FCZ glasses are a class of material based on ZBLAN glasses, which are being developed for uses in advance mammography systems. The FCZs of interest have been doped with Eu (II) for use as either a scintillator or a storage phosphor material but need to be partially crystalline to show good optical properties. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu²⁺ present in the BaCl₂ nanocrystals. The crystals formed are known from XRD experiments to be hexagonal and orthorhombic BaCl₂ depending on the annealing temperature, 265 and 295°C respectively. *In-situ* and *ex-situ* TEM heating experiments were used to study the nucleation and growth process

of the nanocrystals at the EMC. The nanocrystals nucleate and grow through-out the glass matrix when annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The traditional BaCl₂ orthogonal phase in addition to the unreported FCC and orthogonal BaF₂ phase have been found in multiple ZBLAN compositions in which the content of Cl and F has been varied. This indicates that annealing FCZ glasses produces polymorphic crystals of both BaCl₂ and BaF₂, which vary in size from 10 nm to 100 nm.

Mössbauer Spectroscopy has also given indisputable evidence that the divalent Europium enters the nanocrystals.

4:20pm IS+AS+BI+ET+GR+NS-TuA8 In Situ Microscopy of Organic Film Growth: Zn-Phthalocyanine on Ag(100), A. Al-Mahboob, J.T. Sadowski, Brookhaven National Laboratory

Metal phthalocyanines are attracting significant attention, owing to their potential for applications in chemical sensors, solar cells and organic magnets. As the electronic properties of molecular films are related to their crystallinity and molecular packing, the optimization of film quality is important for improving the performance of organic devices.

In this work, we studied the dynamics of nucleation and structural evolution of zinc-phthalocyanine (ZnPc) films on Ag(100) surface, employing real-time low-energy electron microscope (LEEM) complemented by DFT calculations. We have observed two different modes of ZnPc nucleation, depending on the growth temperature. At lower temperatures ZnPc nucleates in a double domain structure, with bulk-like square lattice similar to one reported by Dou et al. [2]. LEED patterns recorded in LEEM experiment show that ZnPc monolayer (ML) grows epitaxially, having a square lattice with $(4/3)\sqrt{13} \times (4/3)\sqrt{13} R33.69^\circ$ unit cell (denoted R33.69) with respect to the substrate lattice. At temperatures of 170°C or above, nucleation of less dense epitaxial ZnPc, having single domain orientation, was observed, with square lattice parameters exactly 5 times larger (5x5) than the Ag(100) substrate.

Utilizing LEEM to observe the ZnPc nucleation at varying substrate temperatures – from room temperature (RT) to 225°C – we have observed that the nominal ZnPc coverage required for the onset of nucleation has strong temperature dependence. The nucleation commences at about 0.2 ML at RT, while 0.7 ML is required at 190°C. At the same time the completion of 1st layer occurs at constant nominal coverage of ZnPc, independent of substrate temperature. Based on that observation, the delay in onset of nucleation could be understood as a result of increased equilibrium concentration of diffusing ZnPc molecules at higher temperatures. This is in contrast to a delay in nucleation and giant island growth observed during vacuum deposition of anisotropic molecules like pentacene (Pn), in which case the energy barrier for the reorientation of the molecule from diffusing state into its crystalline orientation plays a critical role [3]. Real-time tracking of the evolution of ZnPc island area at varying deposition conditions combined with DFT analysis revealed that the 5x5 structure has both, a detachment barrier with respect to attachment, and a pre-factor (or attempt frequency), lower than those for bulk-like structures, allowing for controlling of the resulting ZnPc structure.

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[2] W. Dou et. al, J. Chem. Phys. **133**, 144704 (2010).

[3] Al-Mahboob et al, Phys. Rev. **B 82**, 235421 (2010).

4:40pm IS+AS+BI+ET+GR+NS-TuA9 In Situ Sub-Micrometer Scale Chemical Imaging with Scanning Transmission X-ray Microscopy, S.T. Kelly, P. Nigge, Lawrence Berkeley National Laboratory, A. Laskin, B. Wang, Pacific Northwest National Laboratory, A. Tivanski, S. Ghorai, University of Iowa, T. Tyliczszak, M.K. Gilles, Lawrence Berkeley National Laboratory

Spatially resolved chemical information on length scales shorter than 50 nm has become crucial in many areas of science and engineering -- from analyzing the chemistry of geological and environmental samples to quantifying the detailed chemical structure of novel materials engineered on the nanoscale. Scanning transmission x-ray microscopy (STXM) allows collection of specific chemical speciation data on these length scales through the acquisition and analysis of near-edge x-ray absorption fine structure (NEXAFS) spectra at each image pixel. However, the full usefulness of the STXM instrument may ultimately be realized in the in situ analysis of chemical transformations by controlling the local sample environment.

In situ STXM/NEXAFS measurements have been made in several ways thus far, ranging from simple to very complex. Introducing gases directly into the microscope chamber is effective, yet the presence of the gas along the entire optical path of the x-rays reduces signal at the detector. Furthermore, gas choice with this configuration is limited to those compatible with the microscope components. Separate in situ reactor cells circumvent these limitations by confining the gaseous environment to a

small region immediately around the sample. Several groups have used reactor cells to this end, with reactors ranging widely in complexity -- from simple cells with limited capability to complex systems which require substantial instrument reconfiguration.

Ideally, an in situ reactor for STXM should be capable, flexible, easy to install and configure, and easily fabricated. We have developed a gas phase STXM reactor cell to meet many of these requirements. The reactor mounts directly to the standard STXM sample mount (making installation relatively simple) and contains an integrated sensor to actively measure relative humidity inside the cell for experiments using water vapor. We present here recent results using the reactor cell to examine two different systems. In the first system, we observed the hygroscopic properties of mixed organic/inorganic aerosol particles at increasing levels of relative humidity. In the second system, we monitored carbon dioxide sorption in metal organic framework materials. The advantages afforded by this reactor (and future improvements to it) will enable new scientific discoveries across a wide range of fields.

5:40pm IS+AS+BI+ET+GR+NS-TuA12 In Situ SEM and ToF-SIMS Imaging of Liquids for Biological Applications, L. Yang, X.-Y. Yu, Z. Zhu, S. Thevuthasan, Pacific Northwest National Laboratory, J. Cowin, Cowin In-Situ Science, L. L. C.

A vacuum compatible microfluidic interface was developed to enable surface analysis of liquids. The unique feature of the liquid flow cell is that the detection window is open to the vacuum allowing direct probing of the liquid surface. The flow cell is composed of a silicon nitride membrane and polydimethylsiloxane; and it is fully compatible with vacuum operations for surface analysis. The aperture can be drilled through the 100 nm silicon nitride membrane by using the focused ion beam/scanning electron microscope (FIB/SEM). Alternatively the primary Bi⁺ ions in ToF-SIMS can be used to fabricate the aperture window in real-time. New results using this vacuum interface and recent development will be presented in this paper. Several aqueous solutions containing conjugated IgG gold nanoparticles and representative biological solutions were studied *in situ* using scanning electron microscope (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Characteristic signals of the conjugated gold nanoparticles were successfully observed through the aperture by both energy-dispersive X-ray spectroscopy (EDX) in SEM and ToF-SIMS. Comparisons were also made among wet and dry samples and liquid sample in the flow cell using SEM/EDX. Stronger gold signal can be observed in our novel portable device by SEM/EDX compared with the wet or dry samples, respectively. Our results indicate that analyses of the nanoparticle conjugated antibodies are better made in their native liquid environment. Our unique microfluidic flow cell permits *in situ* liquid observations. In addition, a variety of aqueous solutions relevant to biological systems were analyzed. Our results indicate that chemical imaging by SEM and ToF-SIMS is applicable in analyzing more complicated aqueous solutions when coupled with our novel portable microfluidic platform.

Tuesday Afternoon Poster Sessions

In Situ Microscopy and Spectroscopy Focus Topic

Room: Central Hall - Session IS-TuP

In Situ Microscopy and Spectroscopy Poster Session

IS-TuP2 *In Situ* Infrared Spectroscopic Studies of the Stability of Nanoporous Materials in Water Vapor for Gas Adsorption and Separation. K. Tan, N. Nijem, The University of Texas at Dallas, P. Canepa, Wake Forest University, Q. Gong, J. Li, Rutgers University, T. Thonhauser, Wake Forest University, Y.J. Chabal, The University of Texas at Dallas

The stability of nanoporous metal organic frameworks (MOFs) materials in water vapor is a critical issue that must be taken into account for its potential industrial applications such as energy carrier gases (H_2 , CH_4) storage, greenhouse gas CO_2 capture. Many previously reported MOFs structures decompose upon exposure to air, which results in a reduced gas uptake and limits their large scale application. In this context, the study of the interaction and possible reaction of water with MOFs is extremely important to obtain insight into the mechanism of MOFs dissociation in humid environments. In our study, the hydration process of prototypical MOFs $M(bdc)(ted)_{0.5}$ [$M=Cu, Zn, Ni, Co$; $bdc=1,4$ -benzenedicarboxylic acid; $ted=$ triethylenediamine] by water vapor was monitored by *in situ* infrared spectroscopy as a function of pressure and temperature. Infrared spectroscopic results from $M(bdc)(ted)_{0.5}$ compounds indicate that the condensation of water vapors into the framework is necessary to initiate the dissociation reaction of the metal-ligand bond; the stability or modification of $M(bdc)(ted)_{0.5}$ -compound structure upon exposure to water vapor critically depends on the central metal ions. Combining with results taken by *ex situ* Raman spectroscopy and X ray diffraction, we conclude that the hydrolysis reaction of water molecules with Cu-O-C group induces the $Cu(bdc)(ted)_{0.5}$ structure decomposition; for $Zn(bdc)(ted)_{0.5}$, $Co(bdc)(ted)_{0.5}$, the water molecules replace ted pillars and bond to the apical sites of the paddle wheel building units of $Zn_2(COO)_4$ and $Co_2(COO)_4$ by oxygen atoms; $Ni(bdc)(ted)_{0.5}$ is less susceptible to reaction with water vapors than the other three compounds under the same conditions. These experimental conclusions are well supported by first principles theoretical van der Waals density functional (vdW-DF) calculations of overall reaction enthalpies. This work constitutes the first systematic investigation of the decomposition mechanism of isostructural MOFs with different central metal ions in the presence of moisture. The findings within this work make it possible to determine the operating conditions of this class of MOFs with paddle wheel secondary building units and provide guidance for developing more robust units.

IS-TuP3 Determination of the Mechanisms of Photooxidation of CdSe/ZnS Quantum Dots/Shells. L.J. Powell, S. Saurabh, M. Bruchez, Carnegie Mellon University, L.F. Allard, Oak Ridge National Laboratory, L. Qu, M. Bootman, Crystalplex Inc., R.F. Davis, Carnegie Mellon University

Realization of the potential of Quantum Dots (QDs) for biological, energy-efficient lighting and energy harvesting applications requires that their long-term photostability be improved, especially with regards to protection from photooxidation. The overarching objective of this project is the determination of the chemical and physical mechanisms of photooxidation of CdSe QDs. Pittsburgh-based Crystalplex, Inc. is providing 5 nm CdSe QDs for this research. Three integrated *in situ* characterization techniques are being used to observe changes in QD morphology, optical behavior, and surface chemistry during photooxidation conditions. We are conducting novel microstructural *in situ* experiments in an aberration-corrected STEM/TEM using a Protochips environmental chamber. Changes in the morphology of single QDs are observed in real-time under O_2 and N_2 atmospheres up to 1 atm while maintaining atomic resolution. Multiple series of digital micrographs and EDX data are shown. Single-molecule fluorescence microscopy experiments are allowing us to observe real-time changes in the photoluminescence (PL) behavior of single QDs. The QDs are exposed to 1 atm of either pure O_2 or an inert gas in an environmental chamber and excited with a 490 nm light source during measurements. Changes in blinking rates and PL intensities are analyzed with respect to the periods of exposure to O_2 and light. A series of images and associated statistical analysis are discussed in this poster. *In situ* XPS at CMU is being used to identify the chemical and bonding states of the reacting species. Analysis of the acquired spectra is also presented. These complementary *in situ* experiments allow us to assemble a description of the step-by-step photooxidation mechanism.

IS-TuP4 Coherent X-ray Imaging. T. Senkbeil, T. Gorniak, A. Buck, Karlsruhe Institute of Technology, Germany, K. Giewekemeyer, T. Salditt, University of Goettingen, Germany, A. Rosenhahn, Karlsruhe Institute of Technology, Germany

X-ray microscopy of hydrated biological samples – especially in the so-called water window of 284-540 eV – is of tremendous interest for life sciences due to the high intrinsic contrast of organic matter with respect to the aqueous background and the higher penetration depth compared to transmission electron microscopy. We present X-ray microscopy of cryogenic samples using the coherence-based imaging technique called ptychography.

Ptychography combines previous coherent X-ray diffraction imaging (CXDI) approaches with a scanning scheme, thus providing the ability to image bigger samples, like whole cells or bacteria. We have performed soft X-ray ptychography experiments using our dedicated vacuum chamber HORST at different soft X-ray beamlines at the synchrotron source BESSY II in Berlin, demonstrating chemical contrast and resolutions down to 50 nm in test samples. After upgrading our vacuum chamber with a cryo-sample stage, we now present first results of soft x-ray ptychography of cryogenic samples. Cryo-fixation preserves the natural hydrated state of biological specimens and eliminates the need for any further preparation step, which might possibly alter the ultra-structure. By keeping the sample at temperatures around 120 K at all times, recrystallization of the amorphous water is avoided and the effects of radiation damage during the scans are minimized.

Wednesday Morning, October 31, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+OX+ET-WeM

In Situ Characterization of Solids: Film Growth, Defects, and Interfaces

Moderator: P.W. Sutter, Brookhaven National Laboratory

8:00am **IS+AS+OX+ET-WeM1 Revealing Gas-Surface Radical Reaction Mechanisms of Self-Assembled Monolayers by Scanning Tunneling Microscopy**, *D.Y. Lee, M.M. Jobbins, S.A. Kandel*, University of Notre Dame

Scanning Tunneling Microscopy (STM) in ultra-high-vacuum is used *in situ* to investigate the surface changes of the octanethiolate self-assembled monolayer (SAM) on Au(111) upon reaction with atomic hydrogen and with atomic chlorine. For both reactions, the surface structure heavily influences the rate of monolayer degradation, but the effect of surface defects on reactivity is completely opposite when comparing the two systems. Monolayer reactivity increases with increasing hydrogen-atom exposure while decreases with further reaction with atomic chlorine. The monolayer-versus-exposure data are examined by kinetic Monte Carlo simulations and reveal that, for H-atom exposure, molecules located near surface defect sites are potentially over 500 times more reactive than close-packed areas. For Cl-atom interactions, however, the opposite occurs: close-packed regions are at least 100 times more reactive than defect sites. These observations result directly from the alkyl hydrogen abstraction and sulfur-gold bond cleavage mechanisms of SAM upon gas-phase radical bombardment.

8:20am **IS+AS+OX+ET-WeM2 In Situ Imaging of the Nucleation and Growth of Epitaxial Anatase TiO₂(001) Films on SrTiO₃(001)**, *Y.G. Du, D.J. Kim, T.C. Kaspar*, Pacific Northwest National Laboratory, *S.E. Chamberlin*, University of Wisconsin Milwaukee, *I. Lyubintsev, S.A. Chambers*, Pacific Northwest National Laboratory

TiO₂ has attracted much attention because of its potential utility in hydrogen production via water splitting, environmental remediation, and dye-sensitized solar cell fabrication. Heteroepitaxial growth of anatase is a powerful and unique way to fabricate model surfaces of the less stable anatase polymorph for fundamental surface science studies. In this work, the growth of TiO₂ anatase films on Nb doped SrTiO₃(001) by molecular beam epitaxy has been studied *in-situ* by scanning tunneling microscopy. We show that the initial growth follows the Stranski-Krastanov mode, where islands form on top of a wetting layer consisting of two monolayers (ML) of TiO₂. Well-defined (4x1) and (1x4) terraces are observed for film thicknesses in excess of 3 nm. At larger film thicknesses, large oriented crystallites form as a result of the coalescence of smaller islands. Within a given crystallite, either (4x1) or (1x4) reconstructed terraces account for majority of the surface. The anatase grows in units of bilayers, resulting in a step height of 2 ML. This result explains the fact that the measured period of the RHEED specular-beam intensity oscillations corresponds to the time required for deposition of 2 ML. Ar ion sputtering and UHV annealing results in a transformation to coexisting (4x1) and (1x4) reconstructed terraces on individual crystallites, as commonly observed by *ex-situ* STM studies. In addition, we show that the nucleation and growth of anatase films are influenced by Nb doping in the SrTiO₃ substrates by comparing with similar growth occurring on pure SrTiO₃ substrates.

8:40am **IS+AS+OX+ET-WeM3 In Situ Synchrotron X-Ray Studies of Epitaxial Oxide Thin Film Synthesis Behavior**, *J.A. Eastman, M.J. Highland, P.H. Fuoss*, Argonne National Laboratory, *T.M. McCleskey*, Los Alamos National Laboratory, *D.D. Fong, C.M. Folkman, S.K. Keun, E. Perret, P.M. Baldo*, Argonne National Laboratory, *E. Bauer, Q. Jia*, Los Alamos National Laboratory

INVITED

Intense interest is focused on the growth science of epitaxial oxide thin films because of continuing discoveries of new interesting and important properties. The key to achieving desired maximum functionality of oxide heterostructures is the ability to synthesize high-quality films with full control of factors such as composition, crystallographic orientation, surface termination, and strain state. Many of the most promising thin film synthesis techniques involve non-vacuum, high-temperature environmental conditions that are difficult or impossible to probe using standard spectroscopic or structural probes. However, the use of high-energy x-rays available at synchrotron sources such as the Advanced Photon Source (APS) provides an opportunity to obtain real-time atomic-level structural and chemical information during synthesis. This talk will describe results from recent studies at APS Sector 12ID-D using an *in-situ* x-ray approach

to understand and control the synthesis behavior of complex oxide epitaxial thin films prepared by two very different techniques: sputter deposition or polymer assisted deposition (PAD).

We recently built a new RF magnetron sputter deposition system at the APS, which brings to bear state-of-the-art real-time *in-situ* x-ray scattering and spectroscopy techniques to provide insight into the growth behavior of epitaxial oxide thin film heterostructures. Initial studies of the growth behavior of epitaxial films such as (001) LaGaO₃, SrZrO₄, and LaGaO₃/SrZrO₃ multilayer heterostructures during off-axis sputtering will be described, focusing on the effects of epitaxial strain and electrical compensation (e.g., surface polarity) on growth behavior.

PAD is a solution technique capable of synthesizing dense epitaxial thin films. Past work at Los Alamos has demonstrated that PAD can be used to prepare aligned epitaxial films of many different materials. We recently performed initial *in-situ* synchrotron x-ray experiments aimed at obtaining a fundamental understanding of the nucleation and growth processes associated with epitaxial film formation. Studies of the synthesis behavior of (001) BaTiO₃ epitaxial films will be described in this talk, focusing on the effects of thermal history and choice of substrate material on crystallization behavior and the development of epitaxy.

Argonne researchers were supported by the U. S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Los Alamos researchers were supported by the DOE through the LANL/LDRD Program. Use of the APS was supported by BES, under Contract DE-AC02-06CH11357 between UChicago Argonne LLC and the Department of Energy.

9:40am **IS+AS+OX+ET-WeM6 Understanding the Dynamic Electronic Properties of Electrode Materials by In Situ X-ray Absorption Spectroscopy**, *M. Bagge-Hansen, J.R.I. Lee, A. Wittstock, M.D. Merrill, M.A. Worsley, T. Ogitsu, B.C. Wood, T. Baumann, M. Stadermann, M. Biener, J. Biener, T. van Buuren*, Lawrence Livermore National Laboratory

In situ characterization of the evolution in electronic structure of electrode materials during repeated charge-discharge cycling is fundamentally important for more fully understanding the processes of charge storage and degradation, which, in turn, is essential for the development of new electrical energy storage (EES) materials with tailored properties and improved performance. X-ray spectroscopies provide ideal tools with which to obtain enhanced insight into the origins of electrode behavior in EES systems due to their capabilities for direct, element specific, characterization of the electronic densities of states. To date, *in situ* studies of EES materials have primarily focused on hard x-ray experiments due to the challenges associated with UHV compatibility and high photon attenuation of cells for soft x-ray measurements. Nonetheless, the use of soft x-ray spectroscopies to EES systems is vital since they provide complementary information that cannot be obtained via hard x-ray studies. We report the development of a cell for *in situ* soft x-ray emission spectroscopy and x-ray absorption spectroscopy studies of EES materials and will discuss experiments focused upon the x-ray spectroscopy characterization of a series of novel electrode materials. Prepared by LLNL under Contract DE-AC52-07NA27344.

10:40am **IS+AS+OX+ET-WeM9 In Situ Studies of Al₂O₃ ALD Growth and Self-cleaning on III-V Surfaces by STM and XPS**, *L.N.J. Rodriguez, A. De Clercq*, IMEC, Belgium, *M. Tallarida*, BTU Cottbus, Germany, *D. Cuyppers*, IMEC, Belgium, *J.P. Locquet*, KU Leuven, Belgium, *S. Van Elshocht, C. Adelman, M. Caymax*, IMEC, Belgium

A custom built ALD UHV-compatible reactor has been used to study the growth of TMA on InP and InAlAs by STM in conjunction with additional studies performed in a reactor attached to a synchrotron XPS. The effects of selected *ex-situ* cleans has been measured along with the subsequent cycles of ALD growth from TMA and water. The STM data shows morphological differences between the *ex-situ* cleans on InP, with sulphuric acid cleans yielding plateaus but ammonium sulphide cleans yielding rough surfaces. *In-situ* measurements of these surfaces after TMA dosing shows the growth of islands which converge to film closure after ten cycles of ALD growth. *In-situ* measurements of the I-V curves by STS allowed the creation of bandgap maps of the III-V interfaces after TMA dosing. These bandgap maps showed a non-uniform distribution with regions of either higher or lower bandgap. The mean bandgap was seen to decrease with increasing numbers of ALD cycles. *In-situ* XPS data on similar systems showed a reduction in surface oxides for InAlAs but not for InP. The reduction of arsenic oxides with a creation of metallic arsenic, along partial reduction of indium oxides and a conversion of aluminium sub-oxides to aluminium oxide was seen in the former case. In the latter case, a formal oxidation of

the phosphorus was seen with increased TMA dosing instead of a self-cleaning effect.

11:00am **IS+AS+OX+ET-WeM10 *In Situ* Transport Measurement of Kinetically Controlled Bi Atomic Layers**, *Y. Fujikawa, E. Saitoh*, Tohoku University, Japan

Thin film growth of Bi and related compounds has been attracted much attention because of their exotic properties originating in the large spin-orbit interaction of Bi. Growth of its simple substance is known to result in the formation of a thin-film phase in the initial stage, which is taken over by the bulk growth when the coverage exceeds several monolayers (ML). [1] With typical growth conditions, this transition takes place before the completion of the thin-film layer, which tends to agglomerate to form 4-ML thick islands, making it difficult to measure the intrinsic property of the thin-film phase. In this work, Bi growth on Si(111)-7x7 has been performed in a multi-probe VT-STM system, which provides wide-ranging opportunity of kinetic control and *in-situ* transport measurement during the thin film growth. By tuning the kinetic condition of the growth, it becomes possible to grow the thin-film phase uniformly covering the substrate. Its conductivity, monotonically increasing with the increase of the temperature, would suggest the variable-range hopping conduction rather than the carrier excitation of semiconductors. *In-situ* transport measurement has been performed during the layer-by-layer growth of the Bi thin-film phase, distinguishing the conductivity of each growth unit. It fluctuates with periods of 2 and 4 ML, which may reflect the atomic structure of the thin-film phase.

[1] Nagao *et al.*, Phys. Rev. Lett. **93**, 105501 (2004).

11:20am **IS+AS+OX+ET-WeM11 CAMECA IMS Series Advanced Ion Microscopy: High Throughput, Repeatability & Automation**, *P. Peres, F. Desse, F. Hllion, M. Schuhmacher*, Cameca, S.a., France, *A.N. Davis*, CAMECA Instruments, Inc.

The advantage of CAMECA IMS Series high performance secondary ion mass spectrometers are well established: extreme sensitivity, high mass resolution, and high dynamic range, providing low detection limits while keeping high analysis throughput. This instrument delivers high analytical performance for a wide range of applications: Si based devices, III-V and II-VI devices, both bulk materials and thin-film technology, as well as for different material science applications.

In order to meet the growing demand in terms of reproducibility and throughput performance as well as ease of use, CAMECA has developed a new IMS series, 7F-Auto.

The primary column has been redesigned in order to provide an easier and faster primary beam tuning. For high efficiency operation, automated routines for tuning the instrument are added for both primary and secondary columns, nominally: aperture adjustment, secondary ion beam centering, detector adjustment, among others. These routines not only increase the ease of use, but also enhance the reproducibility of the instruments by minimizing operator-related biases.

A motorized storage chamber has also been developed allowing to keep, under UHV environment, up to six sample holders. The holder exchange between the storage chamber and analysis chamber is fully motorized and computer controlled, allowing a set of analyses to be performed in automated, unattended mode on multiple sample holders. This significantly improves the throughput of the tool, since up to 24 samples (assuming 4 samples per holder) can be analysed in chained mode, possibly overnight. These developments will be presented and discussed in detail.

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Takats, Z.: IS+AS+BI+ET+GR+NS-TuA3, 4
Tallarida, M.: IS+AS+OX+ET-WeM9, 7
Tan, K.: IS-TuP2, 6
Thevuthasan, S.: IS+AS+BI+ET+GR+NS-TuA12, 5
Thonhauser, T.: IS-TuP2, 6
Tivanski, A.: IS+AS+BI+ET+GR+NS-TuA9, 5
Tyliszczak, T.: IS+AS+BI+ET+GR+NS-TuA9, 5

— V —

van Buuren, T.: IS+AS+OX+ET-WeM6, 7
Van Elshocht, S.: IS+AS+OX+ET-WeM9, 7

— W —

Wang, B.: IS+AS+BI+ET+GR+NS-TuA9, 5
Waterton, C.: IS+AS+BI+ET+GR+NS-TuA1, 4
Wittstock, A.: IS+AS+OX+ET-WeM6, 7
Woll, A.R.: IS+AS+BI+ET+GR+NS-TuA2, 4
Wood, B.C.: IS+AS+OX+ET-WeM6, 7
Worsley, M.A.: IS+AS+OX+ET-WeM6, 7

— Y —

Yang, L.: IS+AS+BI+ET+GR+NS-TuA12, 5
Yu, X.-Y.: IS+AS+BI+ET+GR+NS-TuA12, 5

— Z —

Zhang, L.: IS+AS+SS+EN-TuM3, 1
Zhao, H.: IS+AS+SS+EN-TuM9, 2
Zhu, J.F.: IS+AS+SS+EN-TuM3, 1
Zhu, Z.: IS+AS+BI+ET+GR+NS-TuA12, 5