

# Monday Morning, October 31, 2011

## In Situ Spectroscopy and Microscopy Focus Topic

Room: 106 - Session IS+AS+SS-MoM

## In Situ Studies of Catalysis and Gas-Solid Reactions

Moderator: G. Rijnders, University of Twente, the Netherlands

### 8:20am IS+AS+SS-MoM1 In Situ X-ray Studies of Model and Real Catalysts: Bridging the Complexity Gap. A.I. Frenkel, Yeshiva University **INVITED**

In the last decade, there was a surge in advanced characterization methods to study catalytic materials at work. Most notable innovations in synchrotron-based techniques include the coupling of in situ/operando x-ray absorption and scattering methods to vibrational spectroscopies, empowered by improved time and energy resolutions. For example, in situ XAFS-XRD combination enables complementary studies of short and long range order in the same system, a great tool when multiple spatial dimensions evolve in a certain process, such as: modifications of both the catalyst and the support during catalytic reaction, the nucleation and growth of a nano-catalyst, oxidation/reduction of a bulk oxide. Combining in situ XAS or XRD with infrared or Raman spectroscopy is critical for understanding how the structural and electronic properties of a catalyst relate to its reactivity.

Although these are important new improvements in the way we currently study, and understand, processes in nanomaterials, they are done by methods that are not sensitive to local fluctuations in size, shape, structure of nanomaterials, that are present even in well-defined, model catalysts. Thus, in addition to the ensemble averaging that these and other commonly used methods provide, local information, such as one provided by electron microscopy, is needed. In this talk, I will focus on the new efforts in combining the local and average information by coupling the in situ x-ray absorption spectroscopy to in situ environmental transmission electron microscopy (E-TEM) for in situ investigations. Such experiments, done in two separate facilities (NSLS and CFN) at Brookhaven National Laboratory, revealed anomalous, mesoscopic phenomena in the electronic, structural and thermal properties of supported Pt nanoparticles. These systems have long been excellent model systems in catalysis research, yet, at a closer look, as our in situ measurements demonstrated, they turned out to be much more unstable and complex than previously perceived. These clusters exhibited unique physical properties, such as negative thermal expansion, increase in the Debye temperature, broad amorphous-to-crystalline transition zone, large surface strain, as well as charge exchange with support and adsorbates.

I will review recent works showing how such complex behaviors can be, in the case of Pt on  $\gamma$ -alumina and carbon supports, theoretically understood by separately studying the effects of their size, shape, support and adsorbates.

### 9:00am IS+AS+SS-MoM3 Communicating Nanostructures: Spillover Processes Studied on Ceria-supported Platinum Nanoparticles, M. Happel, Friedrich-Alexander-Univ., Germany, Y. Lykhach, T. Staudt, Friedrich-Alexander-Univ., Germany, N. Tsud, Charles Univ., Czech Republic, T. Skála, K.C. Prince, Sincrotrone Trieste, Italy, V. Matolin, Charles Univ., Czech Republic, A. Migani, Univ. de Barcelona, Spain, G.P. Petrova, Univ. of Sofia, Bulgaria, A. Bruix, F. Illas, K.M. Neyman, Univ. de Barcelona, Spain, G.N. Vayssilov, Univ. of Sofia, Bulgaria, J. Libuda, Friedrich-Alexander-Univ. Erlangen-Nuremberg, Germany

Ceria-based catalysts are technologically important for various applications, including automotive catalysis,  $\text{SO}_x$  scrubbers, and hydrocarbon transformation reactions. The complex surface chemistry and reaction kinetics in these systems are assumed to be strongly influenced by so-called metal-oxide (MO) interactions. We use a surface science-based model approach to obtain detailed insight into the origins of such effects at the microscopic level.

The model catalysts are based on ordered  $\text{CeO}_2(111)$  films on  $\text{Cu}(111)$ , on which noble metal nanoparticles (e.g. Pt) are grown by PVD under UHV conditions. The growth and geometric structure of the model catalysts are characterized by STM. Adsorption and reaction are followed by XPS, synchrotron radiation photoelectron spectroscopy (SR-PES), IRAS, and molecular beam (MB) methods, in combination with DFT calculations. Resonant PES (RPES) is used to monitor the changes in the cerium oxidation state with high sensitivity.

Two types of MO interaction are identified, electron transfer from the Pt nanoparticle to the support, and oxygen transfer (spillover) from ceria to Pt. Whereas electron transfer occurs on ceria supports irrespective of their

morphology, oxygen transfer shows a pronounced structure dependency, i.e. it requires the presence of nanostructured ceria aggregates in close contact with Pt.[1]

Not only oxygen spillover, which is a key step in oxidative-self cleaning of carbon-poisoned catalysts, but also spillover and reverse-spillover of hydrogen and hydrocarbon fragments can be followed in detail by RPES. A particularly complex behavior is expected for  $\text{SO}_x$ , for which strong MO effects and spillover have been suggested in previous studies on powder catalysts. On the Pt-free model support we identify different sulfur species forming upon  $\text{SO}_2$  exposure even at 150 K (sulfites, atomic sulfur, and potentially sulfates), formed via different adsorption, decomposition and disproportionation pathways. At higher temperature, these species transform into a bulk-like cerium oxysulfide. For interpretation of the sulfur-chemistry on Pt/ $\text{CeO}_2$ , reference experiments on Pt(111) were performed and numerous  $\text{SO}_x$  species were identified by IRAS and SR-PES. RPES for  $\text{SO}_2$  adsorption on Pt/ $\text{CeO}_2$  provides direct evidence for spillover of  $\text{SO}_x$  to the Pt nanoparticles above 300 K. Between 300 K and 600 K Pt acts as a "sulfur-collector", before at even higher temperatures sulfur is finally transformed into a cerium oxysulfide species.

[1] G. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G.P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K.C. Prince, V. Matolin, K.M. Neyman, J. Libuda, *Nat. Mater.* **2011**, *10*, 310.

### 9:20am IS+AS+SS-MoM4 HPXPS Study of the Oxidation of 10 nm PdAg Nanoparticles, S. Blomberg, J. Gustafson, N.M. Martin, M.E. Messing, K. Deppert, J.N. Andersen, Lund University, Sweden, L.E. Walle, A. Borg, Norwegian University of Science and Technology, Norway, H. Grönbeck, Chalmers University of Technology, Sweden, M.E. Grass, Z. Liu, Lawrence Berkeley National Laboratory, E. Lundgren, Lund University, Sweden

Due to the economic and environmental rewards, one goal in catalysis related research is to create cheaper catalysts. One way to realize this is to dilute the more expensive active catalyst material with a less costly one. This requires that the active material stays at the surface. This could be achieved by using a material which is less prone to interact with the reactant gases, such as a noble metal. In most catalysts, the active material is dispersed in a high area complex oxide support as nanoparticles. In order to maintain the high activity, it would be necessary to ensure that the active material is at the surface of the nanoparticle.

In the present contribution we report on our initial findings from attempts to produce PdAg alloy particles using an aerosol deposition technique [1]. The particles have a diameter of 10 nm distributed over a  $\text{SiO}_x$  wafer. The samples was characterized by high pressure XPS, SEM and TEM as was done previously for aerosol Pd particles [2,3]. By comparing to XPS data from a single crystal  $\text{Pd}_{75}\text{Ag}_{25}(100)$  and from The X-ray Energy Dispersive Spectroscopy (XEDS) analysis we show that the PdAg particles have a similar alloy composition.

The *in-situ* high pressure XPS data from the 10 nm PdAg particles demonstrates that the Pd segregates to the surface in an oxygen rich environment and that the core of the particles are rich in Ag. Although a thin PdOx shell is formed, bulk oxidation is inhibited. The limited oxide formation is promising for the full oxidation of methane, since recent investigations [4] suggest that the PdO is less active for methane oxidation than the metallic Pd.

[1] M. E. Messing, K. A. Dick, L. R. Wallenberg, K. Deppert, *Gold Bull.* **42** (2009) 20.

[2] M. E. Messing *et al.*, *J. Phys. Chem. C* **114** (2010) 9257.

[3] R. Westerström *et al.*, *Phys. Rev. B* **83**, (2011) 115440.

[4] A. Hellman *et al.*, submitted.

### 9:40am IS+AS+SS-MoM5 New Assignment for Ag(III) from In Situ XPS of Highly Oxidized Silver Films, T.C. Kaspar, T. Droubay, S.A. Chambers, Pacific Northwest National Laboratory, P.S. Bagus, University of North Texas

For decades, it has been a goal to elucidate the mechanisms behind the unique chemistry of both oxygen-exposed silver metal and silver oxides. Silver compounds in bulk, thin film, and nanoparticle form are widely investigated for applications including industrially-relevant catalysis, electrochemistry, transparent conducting oxides, and antimicrobial coatings. Determining the chemical state of both silver and oxygen is critical to developing a mechanistic understanding of the remarkable properties of these materials. *Ex situ* x-ray photoelectron spectroscopy (XPS) has been applied, starting in the 1970's, to determine the chemical state of Ag in various silver metal and silver oxide compounds. In contrast to most elements,  $\text{Ag}^{x+}$  ( $x>0$ ) cations exhibit a negative binding energy (BE) shift

relative to metallic Ag(0); thus, the lowest XPS core level binding energy observed for the Ag 3d peak, 367.3 eV, has been assigned to Ag(III) in AgO [Ag(I)Ag(III)O<sub>2</sub>]. However, the XPS analysis has been hindered by the ease with which silver oxides form carbonate species upon atmospheric exposure, as well as the instability of silver oxides in vacuum. In this work, silver oxide films have been formed under very oxidizing conditions, by molecular beam epitaxy (MBE) deposition of silver metal in the presence of activated oxygen. *In situ* XPS was then collected in an appended chamber. For the most highly oxidizing deposition conditions, a substantially lower BE, 366.8 eV, was found for the Ag 3d peak, with an associated satellite located at 368.2 eV. This oxide species proved unstable in vacuum over several days, but could be recovered by further exposure to activated oxygen. Based on the decomposition behavior of the Ag 3d and O 1s spectra, the low BE species was assigned as Ag(III), while the previous peak position for Ag(III) was re-assigned as Ag(I). These assignments are supported in part by electronic structure calculations predicting the photoemission spectra of Ag(III). The combination of highly oxidizing deposition conditions and *in situ* characterization allowed identification of the true Ag(III) XPS spectrum for the first time.[1]

[1] T.C. Kaspar, T. Droubay, S.A. Chambers, and P.S. Bagus. *J. Phys. Chem. C* **114** 21562 (2010).

10:00am **IS+AS+SS-MoM6 The Oxidation of Methane Over Pd**, A. Hellman, Chalmers Univ. of Tech., Sweden, A. Resta, European Synch. Rad. Fac., France, J. Gustafson, N.M. Martin, Lund Univ., Sweden, A. Trincherio, P.-A. Carlsson, Chalmers Univ. of Tech., Sweden, O. Balmes, European Synch. Rad. Fac., France, J.N. Andersen, Lund Univ., Sweden, R. Feici, European Synch. Rad. Fac., France, E. Lundgren, Lund Univ., Sweden, H. Grönbeck, Chalmers Univ. of Tech., Sweden

An important goal in surface science is to provide fundamental information on gas-surface interactions for the design of cheaper and more efficient catalysts. For this purpose, the required minimum knowledge is the composition of a catalyst for a certain reaction under realistic reaction conditions. Although this information seems trivial it is surprisingly difficult to obtain due to the complex structural nature of a real catalyst and the sometimes high temperatures and pressures under reaction conditions.

In the case of the complete oxidation of methane using Pd as the catalyst, pure Pd metal, Pd surface oxides and bulk PdO have all been reported to be most efficient to convert CH<sub>4</sub> into CO<sub>2</sub> and H<sub>2</sub>O [1-5]. This highlights the complexity of catalysis even for a relatively simple catalytic reaction.

In order to shed some light on the state of Pd during complete methane oxidation, we have performed in-situ Surface X-Ray Diffraction (SXRD) over a Pd(100) surface in a realistic reaction environment combined with DFT calculations. Our study demonstrates that significant roughening of the surface occur during the reaction, which increases the active surface area and thus affects the overall reactivity. Nevertheless, our study strongly suggests that the Pd metal is the most active phase for the full oxidation of methane.

[1] R. Burch, P. K. Loader, and F. J. Urbano, *Catalysis Today* **27** (1996) 243.

[2] R. F. Hicks, H. H. Qi, M. L. Young, and R. G. Lee, *J. Catal.* **122** (1990) 280.

[3] M. Lyubovsky and L. Pfefferle, *Catalysis Today* **47** (1999) 29.

[4] S. Oh, P. J. Mitchell, and R. Siewert, *J. Catal.* **123** (1991) 287.

[5] J. G. McCarthy, *Catalysis Today* **26** (1995) 283.

11:00am **IS+AS+SS-MoM9 The New Ambient Pressure X-ray Photoelectron Spectroscopy Instrument at MAX-lab - An Instrument also for Ultrahigh Vacuum Studies**, J. Schnadt, J. Knudsen, A. Pietzsch, N. Johansson, A. Olsson, F. Hennies, Lund University, Sweden, N. Mårtensson, H. Siegbahn, Uppsala University, Sweden, J.N. Andersen, Lund University, Sweden

Ambient pressure x-ray photoelectron spectroscopy (APXPS) is a technique, which dates back to the 1970s and 1980s, but which only during the past ten years has developed a very significant impact, driven forward especially by groups at the Advanced Light Source and BESSY. APXPS makes possible x-ray photoelectron spectroscopy (XPS) measurements under realistic or close-to realistic conditions, while conventional XPS is limited to vacuum conditions of 10<sup>-6</sup> mbar or better. APXPS thus contributes to closing the "pressure gap" of surface science, which has inhibited the understanding of processes and chemical reactions, for which the chemical potential of the gas atmosphere plays a decisive role. It also renders possible experiments on samples with a large vapour pressure, such as liquids or solid samples with a high degassing rate. Today, there exist a

number of APXPS instruments around the world, including a small number of systems at synchrotrons. Common to these instruments is that they perform well at elevated pressures, but none of them is specifically designed to also allow studies under ultrahigh vacuum conditions. This complicates the connection to results from ultrahigh vacuum studies.

A new instrument for APXPS has just been installed at beamline I511 of the Swedish Synchrotron Radiation Facility MAX-lab. This instrument, which has been delivered by SPECS GmbH, Berlin, Germany, and which makes use of a PHOIBOS 150 NAP analyser, has been developed with the particular aim of building a strong link between ultrahigh vacuum and ambient pressure experiments and science. The instrument is capable of performing XPS measurements on the same sample in both types of environment. This is made possible by a unique design, which is based on the use of a retractable ambient pressure cell. For ambient pressure measurements at pressures of around 0.1 to 10 mbar the cell is docked to the electron energy analyser. Once the sample is loaded the cell is locked, and the only leak to the vacuum is through the nozzle of the analyser's lens system. Hence, even during ambient pressure measurements the vacuum remains intact in the analysis chamber. For UHV measurements the cell together with the nozzle is retracted into a separate chamber, and UHV XPS measurements can be performed normally. This entails also another attractive feature of the instrument, namely, that the high pressure cell easily can be replaced by dedicated cells for other sample environments.

In this contribution the design and concept of the APXPS instrument at MAX-lab will be discussed and first results shown. Also plans for an upgraded and dedicated new beamline at MAX-lab will be presented.

11:20am **IS+AS+SS-MoM10 In Situ XPS and STM Studies of Ge<sub>2</sub>H<sub>6</sub> Interactions with the Si(100) Surface**, S. McDonnell, J.F. Veyan, University of Texas at Dallas, J. Ballard, J.H.G. Owen, J.N. Randall, Zyvyx Labs, Y.J. Chabal, R.M. Wallace, University of Texas at Dallas

We present a study of the reactions between Ge<sub>2</sub>H<sub>6</sub> and Si(100) surfaces. Ge<sub>2</sub>H<sub>6</sub> is a potential precursor that could allow atomic layer epitaxy (ALE) on Ge(100) and Si(100) surface [1,2] which will be a vital component for atomically precise manufacturing (APM). We investigate the effects of various growth conditions such as substrate temperature, dosing pressure and post deposition annealing. We study the formation of seed layers for ALE along with the reactions on both the atomically clean and the hydrogen passivated surfaces, where we see evidence of Ge<sub>2</sub>H<sub>6</sub> reacting with the dangling bonds.

To facilitate these studies, we utilize a UHV deposition/characterization tool. Chemical analysis of the surfaces is achieved using *in-situ* x-ray and ultraviolet photoelectron spectroscopy. Differences in the chemical states of germanium present on the surface under the various growth conditions are identified. This analysis is supplemented by *in-situ* scanning tunneling microscopy, which allows us to monitor the growth of germanium on silicon and confirm 2D or 3D growth. Comparisons are made with similar experiments carried out in a different UHV chamber where the surface is characterized with Fourier transform infrared spectroscopy (FTIR) and shows evidence of the digermane reacting with the surface at 173K as Ge<sub>2</sub>H<sub>5</sub> rather than GeH<sub>3</sub>.

This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

[1] D.-S. Lin, K.-H. Huang, T.-W. Pi, and R.-T. Wu. *Phys. Rev. B*, **54** 16 (1996) 958

[2] K.-H. Huang, T.-S. Ku, and D.-S. Lin *Phys. Rev. B*, **56** 8 (1997) 4878

# Monday Afternoon, October 31, 2011

**In Situ Spectroscopy and Microscopy Focus Topic**  
**Room: 106 - Session IS+AS+SS-MoA**

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

**Moderator:** M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **IS+AS+SS-MoA1 A New Approach to Defect Evolution Studies – Combined In Situ Experiments and Electron Tomography.** *I.M. Robertson, J. Kacher, G. Liu*, University of Illinois at Urbana-Champaign **INVITED**

Electron micrographs are two-dimensional images capturing specific instances in the evolution of the microstructure and composition as well as the electronic and magnetic state. As these yields no insight as to how the state evolved, *a posteriori* knowledge is used to determine the most likely pathway. This challenge can be addressed by conducting experiments *in situ* in the transmission electron microscope, which allows direct observation and in some cases quantification of the reactions and interactions responsible for the evolved structure. The information, however, remains two-dimensional and with increasing use of this technique it is becoming apparent that lack of three-dimensional knowledge is hindering interpretation. Information in the beam direction can be recovered by applying electron tomography, but this is a relatively new technique to defect studies and despite its potential it remains a static snapshot. In this talk, I will illustrate how time-resolved deformation studies have improved our understanding of the behavior of dislocations and how this information has informed the development of new models. I will also demonstrate how three-dimensional images yield a better understanding of complex dislocation interactions and configurations. Finally, I will address the challenges faced in combining these two techniques such that three-dimensional snapshots of the evolving microstructure can be acquired periodically.

2:40pm **IS+AS+SS-MoA3 Real-time Oxide Growth Characterization using Atomic Force Microscopy.** *G. Rijnders*, University of Twente, the Netherlands **INVITED**

Complex oxides have attracted great interest since they exhibit a rich spectrum of physical properties such as ferromagnetism, antiferromagnetism, colossal magnetoresistance, ferroelectricity, dielectricity, and superconductivity. Novel heteroepitaxial devices based on these complex oxides, like spin-polarized ferromagnetic tunnel junctions, superconducting devices and piezoelectric devices, have great potential and are currently under investigation in many groups.

The nature of the above-mentioned physical properties in complex oxides is determined by very small characteristic length scales, comparable to the unit cell lattice parameters of complex oxide. Because of these small characteristic length scales, growth control on an atomic level as well as understanding of the different mechanisms affecting the growth mode is essential for the fabrication of epitaxial heterostructures.

Two independent processes, i.e., nucleation and growth of islands, play an important role during vapor-phase epitaxial growth on an atomically flat surface. Here, nucleation causes the formation of surface steps and subsequent growth causes the lateral movement of these steps. Both processes are determined by kinetics, since they take place far from thermodynamic equilibrium. These kinetic processes affect the final surface morphology and are, therefore, extensively studied. I will demonstrate the applicability of high-pressure RHEED as well as Scanning Force Microscopy (SFM) to monitor to the growth of complex oxides during Pulsed Laser Deposition (PLD). Because of recent developments, SFM is nowadays also used to study dynamic processes, such as thin film growth and surface reaction mechanisms.

We have realized a system, in which SFM can be performed during Pulsed Laser Deposition (PLD). Deposition and force microscopy are performed in one vacuum chamber and via a fast transfer (in the order of seconds) the surface of a sample can be scanned. In our system we take advantage of the *pulsed* deposition process, because microscopy measurements can be carried out between the pulses. This provides real-time morphology information on the microscopic scale during growth. The transfer mechanism allows switching between microscopy and deposition with a re-position accuracy of  $\pm 500$  nm which gives new opportunities to study growth processes. Furthermore, it can provide information if RHEED is not possible, for example during amorphous and polycrystalline growth.

In this contribution, I will highlight recent advances in oxide thin film growth as well as the latest equipment developments.

3:40pm **IS+AS+SS-MoA6 An Auger Electron Analyzer System for In Situ MBE Growth Monitoring.** *W.L. Calley*, Georgia Institute of Technology, *P.G. Staib*, Staib Instruments, *J.E. Lowder, J.D. Greenlee, M.W. Moseley, W.E. Henderson, W.A. Doolittle*, Georgia Institute of Technology

Auger Electron Spectroscopy (AES) analysis is a surface sensitive technique for thin film analysis, able to detect nearly all elements [1]. Not only can AES help determine the species present at the surface, but AES can also yield information about the chemical bonding [1]. However, this analysis tool has historically been an *ex situ* technique with a few noted exceptions [2]. Herein we demonstrate the capabilities and usefulness of an Auger probe, the Staib *In situ* Auger Probe (SIAP) that has a sufficient working distance (tested up 82 mm) so as to not shadow beam fluxes allowing use during growth. The probe leverages an existing RHEED gun as an e-beam source for Auger electron excitation.

The configuration and operation of the SIAP has been described in detail [3]. The tool is installed on an MBE system configured for Terfenol growth, a miscible alloy of TbFe<sub>2</sub> and DyFe<sub>2</sub>. Initial growths performed without Auger monitoring exhibited substantial oxidation even after Ar etched to remove surface contamination, figure 1. The SIAP was then employed to determine the sources of oxygen contamination.

Three sources of O were identified. The growth chamber had a high enough partial pressure of oxygen to oxidize the highly reactive rare earth elements. After 30 hours in the chamber, uncapped Tb showed a substantial increase in the ratio of O to Tb, figure 2. The Tb source material also delivered O and the rate of O delivery increased with cell temperature, figure 3. A final oxygen source was identified to be the Tb/SiO<sub>2</sub> interface as shown in the SIMS data in figure 4. Figure 5 shows the Si wafer with C and O present at the surface. After growth is initiated the C is not detected after 40 Å of deposition, however, the O can be detected until 200 Å are deposited, indicating intermixing with the SiO<sub>2</sub> interface.

Further tests were conducted starting with a layer of Dy and depositing part of a monolayer of Tb in 2% increments. Figure 6 shows a clear distinction between bare Dy and 2, 4, 6, 8, and 10% monolayer coverage of Tb on a Dy layer, demonstrating the SIAP's sensitivity is at least 2% of a monolayer for these heavy elements.

The SIAP is complementary to existing RHEED systems. While RHEED gives information about the crystal structure of the growing film, the SIAP provides chemical information. This is especially useful when working with films without line compositions. The SIAP coupled with a future closed loop control system may enhance growth of films with multiple oxidation states or other similar phase/chemical transitions. Finally this technique could give information about transitions between layers in multilayered films grown via MBE.

4:00pm **IS+AS+SS-MoA7 Quantum Size Effect Driven Structure Modifications of Bi-films on Ni(111).** *T.R.J. Bollmann, R. van Gastel, H. Zandvliet, B. Poelsema*, University of Twente, The Netherlands

We have investigated the initial growth of Bi/Ni(111) using Low Energy Electron Microscopy (LEEM) and Selected Area Low Energy Electron Diffraction ( $\mu$ LEED). Bismuth represents an interesting material since 1) it has a tendency for allotropism, 2) it forms several ordered alloys with Ni and 3) with Bi being a neighbor of Pb in the periodic system, one may find evidence for quantum size effects in ultrathin Bi layers. Indeed we obtain ample evidence for Bi/Ni(111) as being a very rich system, even at a fixed substrate temperature of 474 K.

We find first that the deposition of Bi leads to the formation of a surface alloy with a  $(\sqrt{3}\times\sqrt{3})\text{-R}30^\circ$  structure at a Bi-coverage of 1/3. Continued Bi deposition leads to the formation of an incommensurate wetting layer with a continuously decreasing lattice parameter, finally ending in a  $(7\times 7)$  structure. From the variation of the step position at the buried interface, nicely accessible with LEEM, we conclude that the dealloying of the  $\sqrt{3}$  phase is incomplete and that the  $(7\times 7)$  wetting layer in fact involves two layers with a small, but finite Bi content in the second layer. Upon further Bi deposition elongated, 3-4 layers high nanowires emerge, with a  $p(5\times 2)$  structure and a width of about 80 nm, oriented along  $\langle 110 \rangle$  and  $\langle 100 \rangle$ -azimuths. Further deposition of Bi leads to different (sometimes coexisting) structures:  $(3\times 3)$ -patches with a thickness of three atomic layers and patches with a matrix structure ( $m_{11}=3, m_{12}=1, m_{21}=1, m_{22}=2$ ) and a thickness of five atomic layers. This accurate height assignment is uniquely enabled by the analysis of LEEM-IV data.

The results are fully consistent with quantum size effect driven thin film morphology: the different film structures and their thicknesses nicely fit with integer numbers of nodes in their specific Fermi wave function, even for the seven layers thick (7x7) structure obtained at a lower temperature of 422 K. Tensor LEED calculations of the interlayer spacing of the different structures concur with this assignment.

The influence of the structure and morphology on electronic properties of various materials is well known. The interaction between electronic and crystal structure should be reciprocal. The Bi/Ni(111) system provides a nice and we think first illustration: electronic properties, in particular quantum size effects, actually drive the structure of the thin bismuth films.

4:20pm **IS+AS+SS-MoA8 Growth and Structure of Sm on an Ultrathin Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) Film: A Comprehensive Study, J.F. Zhu, Q. Xu, S. Hu, X. Feng, D. Chen, University of Science and Technology of China**

The growth and electronic structure of vapor-deposited Sm onto a well-ordered Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) ultrathin film under ultrahigh vacuum (UHV) conditions at room-temperature has been studied comprehensively using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), scanning tunneling microscopy (STM) and low electron energy diffraction (LEED). Our results indicate that at room temperature Sm grows in a layer-by-layer fashion for the first two layers, followed by three-dimensional (3D) growth. The interaction of Sm with Al<sub>2</sub>O<sub>3</sub> thin films is so strong that deposited Sm is immediately oxidized at beginning. Both the oxidation states of Sm<sup>2+</sup> and Sm<sup>3+</sup> are found at low coverages (<1 ML) with the situation that the concentration of Sm<sup>2+</sup> dominates below 0.2 ML and subsequently that of Sm<sup>3+</sup> dominates. With increasing Sm coverage, the metallic state of Sm gradually appears. Annealing the film of 0.2 ML Sm/Al<sub>2</sub>O<sub>3</sub> at T < 500 K results in further oxidation of the Sm species where all the Sm<sup>2+</sup> species converts to Sm<sup>3+</sup>. Further annealing at higher temperatures leads to loss of Sm from the surface via subsurface diffusion.

4:40pm **IS+AS+SS-MoA9 In Situ Study of the Reaction Mechanism Kinetics of Pt ALD from (<sup>Me</sup>Cp)PtMe<sub>3</sub> and O<sub>2</sub>, I.J.M. Erkens, A.J.M. Mackus, H.C.M. Knoops, F. Roozeboom, W.M.M. Kessels, Eindhoven University of Technology, Netherlands**

Atomic layer deposition (ALD) of noble metals and noble metal oxides on high-aspect-ratio 3D nanostructures has a wide variety of potential applications in sensing and catalysis. Despite several studies,<sup>1-3</sup> much is still unknown about the reaction mechanism of Pt ALD using (<sup>Me</sup>Cp)PtMe<sub>3</sub> and O<sub>2</sub>, which can be considered a model system for noble metal ALD processes. Questions remain regarding the surface species and reactions, and the temperature dependence of the growth per cycle (GPC). In this contribution we expand the understanding of the Pt ALD mechanism by combining quadrupole mass spectrometry (QMS) and spectroscopic ellipsometry (SE). Using these in-situ techniques to study the process as a function of temperature between 100 and 300°C, we have gained a unique perspective, which has led to several new insights. The time-resolved QMS data for CH<sub>4</sub> and CO<sub>2</sub> show that combustion and other ligand reactions at the surface occur in sequence, while competing for the available carbon atoms. Quantification of the data showed that approximately 80% of the C atoms are combusted during the O<sub>2</sub> pulse. By performing the QMS measurements in a temperature series, valuable information was obtained on the rate of combustion of the hydrocarbon ligands at the Pt surface during the O<sub>2</sub> pulse. Using a combination of QMS and SE data, we were able to formulate a mechanism explaining growth inhibition at low temperatures. This mechanism manifests itself through three temperature dependent growth regimes: no growth below 100°C; limited growth between 100 and 250°C; and full growth between 250 and 300°C. Using results from surface science literature a likely explanation for these regimes was given. This involves the cyclopentadienyl ligands at the Pt surface forming reactive intermediates or being thermally decomposed. The mechanism was corroborated by QMS and SE data on post-plasma treatment cycles, by which catalytic activity was temporarily restored. We were therefore able to link the temperature dependence of the GPC to combustion kinetics. A detailed description of our methods and results will be given in our contribution.

1. Aaltonen *et al.*, *Electrochem. Solid-State Lett.* **6**, C130 (2003).
2. Kessels *et al.*, *Appl. Phys. Lett.* **95**, 013114 (2009).
3. Setthapun *et al.*, *J. Phys. Chem. C* **114**, 9758 (2010).

5:00pm **IS+AS+SS-MoA10 In Situ Surface Analytical Characterization of Electronic Devices: Thin Film Solar Cells and Lithium Ion Batteries as Examples, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany**

Electronic devices have revolutionized everyday life in industrial countries over the last decades. Especially devices for energy conversion and storage like thin film solar cells and lithium ion batteries are of importance for the future. Recently two main tasks for research and development are dominant: miniaturization for sophisticated applications targeting at the nanoscale, and designing low cost large scale devices. In both fields the device performance is strongly determined by materials quality, composition, combination and last but not least by processes at materials interfaces. Nanostructures, minimization of material consumption and the need to improve device efficiencies consequently leads to the widespread focussing on thin film preparation. For thin film devices surface and interface analysis like photoelectron spectroscopy and surface (spectro-)microscopies are an important tools for material and device characterization. Classical well defined model experiments already reveal important insights using highly integrated vacuum systems for analysis and preparation. But analysis of materials and devices under near ambient conditions and even in situ during operation is an inevitable future development to improve the significance of data for development and quality management. In this respect the application of techniques like Near Ambient Pressure XPS, XPS from liquids and solid liquid interfaces, hard x-ray PES (HAXPS), Near Ambient Pressure SPM on solar cell and lithium ion battery materials is the challenging tasks for manufacturing companies of surface analytical equipment.

# Tuesday Morning, November 1, 2011

## In Situ Spectroscopy and Microscopy Focus Topic

Room: 106 - Session IS+AS+SS-TuM

## In Situ Studies of Organic and Soft Materials and Liquid-Solid Interfaces

Moderator: A.I. Frenkel, Yeshiva University

8:00am **IS+AS+SS-TuM1 Solid-Vacuum, Solid-Gas, and Solid-Liquid Interfaces: Structure and Dynamics under Environmentally Relevant Conditions**, *M. Salmeron, C. Escudero*, Lawrence Berkeley National Laboratory **INVITED**

Surfaces play a fundamental role in many of today's frontier topics, such as clean and renewable energies, efficient and highly selective chemical processes (green catalysis), high capacity rechargeable batteries and fuel cells, and also environmental problems. To advance our For this it is imperative to develop new fundamental approaches to the study of the interface of solid materials with gases, liquids and solids, because it is in these environments that crucial processes occur that need to be understood to enable game-changing discoveries.

One way to control the structure of interfaces and their properties is through the design of materials of nanoscale dimensions, with specific shape, size and composition. It is equally imperative to develop and use techniques for in situ atomic level structural and spectroscopic characterization of the interfaces. New advances in instrumentation are fulfilling this need. I will illustrate this with examples from research carried out in my laboratory, which include scanning tunneling microscopy (STM), photoelectron and x-ray absorption spectroscopies (PES) under ambient conditions, for studies of catalyst models, thin films, single crystals and nanoparticles, for applications in catalysis and electrochemistry. The results obtained so far demonstrate that the information obtained with these new techniques is unique and could not have been obtained or extrapolated from other more traditional surface sensitive techniques.

8:40am **IS+AS+SS-TuM3 Imaging Tagged Proteins in Whole Eukaryotic Cells in Liquid with Scanning Transmission Electron Microscopy**, *N. De Jonge, D.B. Peckys*, Vanderbilt University School of Medicine **INVITED**

We have recently introduced a novel electron microscopy technique for the imaging of whole cells in aqueous media using scanning transmission electron microscopy (STEM) [1, 2]. Eukaryotic cells in liquid were placed in a microfluidic chamber with a thickness of 5 - 10  $\mu\text{m}$  contained between two ultra-thin electron-transparent windows. On account of the atomic number (Z) contrast of the STEM, nanoparticles of a high-Z material (e.g., gold) were detected within the background signal produced by a micrometers-thick layer of a low-Z liquid (e.g. water, or cellular material). Nanoparticles specifically attached to proteins can be used to study protein distributions in whole cells in liquid, similar as proteins tagged with fluorescent labels can be used to study protein distributions in cells with fluorescence microscopy.

COS7 fibroblast cells were labeled with gold nanoparticles conjugated with epidermal growth factor (EGF). Intact fixed cells in liquid were imaged with STEM with a spatial resolution of 4 nm and a pixel dwell time of 20 microseconds [1]. In test experiments we demonstrated a maximal spatial resolution of 1.5 nm on gold nanoparticles placed above a water layer of a thickness of 3 micrometer, consistent with theoretical predictions, and with Monte Carlo simulations of the STEM imaging [3]. The use of quantum dots (QDs), which are fluorescent nanoparticles, allowed STEM images to be correlated with fluorescence images [4]. Eukaryotic cells were grown directly on microchips for the microfluidic chamber, fixed, and imaged with fluorescence microscopy. The intact cells were then imaged in liquid with STEM. The STEM images showed individual QDs, and their locations were correlated with the cellular regions, as imaged with fluorescence microscopy. We have also demonstrated the imaging of nanoparticle uptake in live cells [5], and the ultrastructure of pristine yeast cells was studied [6]. Liquid STEM presents an innovative approach for the imaging of whole cells, with significantly improved spatial resolution and imaging speed over existing methods.

URL: <http://www.mc.vanderbilt.edu/labs/dejongelab/>

### References

- [1] de Jonge, N., Peckys, D.B., Kremers, G.J. & Piston, D.W., Proc. Natl. Acad. Sci. 106, 2159-2164, 2009.
- [2] Peckys, D.B., Veith, G.M., Joy, D.C. & de Jonge, N., PLoS One 4, e8214-1-7, 2009.

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- [5] Peckys, D.B. & N. de Jonge, Nano Lett. 11, 1733-1738, 2011.

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9:20am **IS+AS+SS-TuM5 Imaging Live Cells in Liquid with Scanning Transmission Electron Microscopy**, *D.B. Peckys, N. De Jonge*, Vanderbilt University School of Medicine

We have applied a novel electron microscopy technique, referred to as liquid scanning transmission electron microscopy (liquid STEM) [1, 2] for the imaging of live eukaryotic cells. In two separate experiments, we studied a) nano particle (NP) uptake in COS-7 cells [3], a green monkey kidney fibroblast cell line, and, b) the ultrastructure of *Schizosaccharomyces pombe* cells [4], also known as fission yeast. The cells were confirmed to be alive at the onset of the liquid STEM imaging using specific fluorescent, live indicating dyes and correlative fluorescence microscopy. For the STEM imaging in liquid the cells were placed (in liquid) in a microfluidic chamber. The chamber had two ultra-thin electron-transparent windows allowing the passage of electrons and photons. The dimensions of the COS-7 cells required a thicker liquid filled space in the microfluidic chamber compared to the experiments with the fission yeast cells, and contrast was mainly obtained on the gold NP's. However, the thinner *S. pombe* cells allowed a thinner liquid layer, and images were recorded of the cellular ultrastructure.

Despite the fact, that the cells were not anymore alive after the STEM imaging, we consider the first STEM images taken from a cell or a specific cellular region, to represent the unperturbed and therefore physiological state. We derived this assumption after evaluation of the STEM images for signs of radiation damage at the achieved resolution. Our STEM results were found to be consistent with known data about intracellular NP trafficking and storage in mammalian cells and data about the dimensions and distribution of organelles in fission yeast.

In conclusion, we have demonstrated the feasibility of STEM imaging live eukaryotic cells. The advantages of this approach are a) a several-fold higher resolution than live cell imaging with conventional light microscopy, b) a much faster (hours versus days) sample preparation than needed for conventional transmission electron microscopy (TEM) imaging of cells, c) absence of artifact introduction associated with conventional TEM sample preparation, and d) no need for introducing any kind of labels in order to achieve a similar range of resolution as possible with the new nanoscopic imaging techniques.

### References

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9:40am **IS+AS+SS-TuM6 Microscopic Imaging of Biological Samples using Coherent Soft X-rays from Free-Electron Laser and Synchrotron Sources**, *T. Gorniak, T. Senkbeil, M. Beckers, C. Christophis*, University of Heidelberg, Germany, *K. Giewekemeyer*, University of Göttingen, Germany, *M. Grunze*, University of Heidelberg, Germany, *T. Salditt*, University of Göttingen, Germany, *A. Rosenhahn*, University of Heidelberg, Germany

Coherent 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 contrast of organic matter with respect to the aqueous background. Especially free-electron lasers can provide highly intense and coherent pulses, which allow single pulse imaging to overcome resolution limits set by radiation damage. We present the first holographic microscopy images of dehydrated biological material acquired in the water window with higher harmonic radiation provided by the free-electron laser FLASH. In order to increase the photon flux we used high efficiency zone plates instead of pinholes to create the divergent light cone for holography. The results pave the way to the vision of holographic imaging of hydrated biological samples with single FEL pulses. We supplement single pulse imaging experiments byptychographic imaging with synchrotron radiation at BESSY II. This method uses coherent diffraction imaging at different

sample positions while maintaining a fixed spatial overlap between the fields of view. By introducing this spatial redundancy to the data an additional constraint for the iterative reconstruction algorithm is achieved. This enhances the convergence of phase retrieval drastically. The spatial resolution of below 50 nm and the imaging properties were characterized using lithographic and biological test samples. We also show results on resonant imaging with chemical contrast caused by both, absorption and phase shifts, in the vicinity of core level absorption edges.

10:40am **IS+AS+SS-TuM9 Surface Chemistry of Amino Acids at Near Ambient Pressure of Water Vapor**, *A. Shavorskiy*, Lawrence Berkeley National Laboratory, *T. Eralp*, The University of Reading, UK, *F. Aksoy*, Nigde University, Turkey, *M.E. Grass*, *Z. Liu*, *H. Bluhm*, Lawrence Berkeley National Laboratory, *G. Held*, The University of Reading, UK

The co-adsorption of water with organic molecules under near-ambient pressure and temperature conditions opens up new reaction pathways on model catalyst surfaces that are not accessible in conventional ultra-high vacuum surface-science experiments. The surface chemistry of glycine and alanine at the water-exposed Cu{110} and Pt{111} interface was studied both in situ and in UHV using ambient-pressure photoemission and X-ray absorption spectroscopy techniques [1,2]. At water pressures above 10<sup>-5</sup> Torr a significant pressure-dependent decrease in the temperature for dissociative desorption was observed for both amino acids on Cu{110}[3]. On Pt{111}, on the other hand, desorption temperature does not depend significantly on the presence of water vapor. The most likely reaction mechanism of decomposition involves dehydrogenation induced by O and/or OH surface species resulting from the dissociative adsorption of water on Cu{110}, but not on Pt{111}.

The linear relationship between the inverse decomposition temperature on Cu{110} and the logarithm of water pressure enables determination of the activation energy for the surface reaction, between 213 and 232 kJ/mol, and a prediction of the decomposition temperature at the solid-liquid interface by extrapolating towards the equilibrium vapour pressure. Such experiments near the equilibrium vapour pressure provide important information about elementary surface processes at the solid-liquid interface, which can neither be retrieved under ultra-high vacuum conditions nor from interfaces immersed in a solution.

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[2] G. Jones, L. B. Jones, F. Thibault-Starzyk, E.A. Seddon, R. Raval, S. Jenkins, G. Held, *Surf. Sci.* 600 (2006) 1924.

[3] A. Shavorskiy, F. Aksoy, M.E. Grass, Z. Liu, H. Bluhm, G. Held, *J. Am. Chem. Soc.* 133 (2011) 17

11:00am **IS+AS+SS-TuM10 STM Tip Catalyzed Adsorption of Thiol Molecules and Functional Group-Selective Adsorption of Bi-Functional Molecule Using This Catalysis**, *Y.H. Min*, *S. Kim*, *S.J. Jung*, *Y.-S. Youn*, Korea Advanced Institute of Science and Technology, Republic of Korea, *D.H. Kim*, Daegu University, Republic of Korea, *E.H. Park*, Korea Advanced Institute of Science and Technology, Republic of Korea

In this study, in contrast with cases in which Scanning Tunneling Microscopy (STM) tip-induced reactions were instigated by the tunneling electrons, the local electric field, or the mechanical force between a tip and a surface, we found that the tungsten oxide (WO<sub>3</sub>) covered tungsten (W) tip of a STM acted as a chemical catalyst for the S-H dissociative adsorption of phenylthiol and 1-octanethiol onto a Ge(100) surface. By varying the distance between the tip and the surface, the degree of the tip-catalyzed adsorption could be controlled. We have found that the thiol head-group is the critical functional group for this catalysis and the catalytic material is the WO<sub>3</sub> layer of the tip. After removing the WO<sub>3</sub> layer by field emission treatment, the catalytic activity of the tip has been lost.

3-mercapto isobutyric acid is bi-functional molecule which has two functional groups, carboxylic acid group and thiol group, at each end. 3-Mercapto Isobutyric Acid adsorbs at Ge(100) surface only through carboxylic acid group at room temperature and this adsorption was enhanced by the tunneling electrons between a STM tip and the surface. Using this enhancement, it is possible to make thiol group-terminated surface where we desire. On the other hand, surprisingly, the WO<sub>3</sub> covered W tip of STM was found to act as a chemical catalyst to catalyze the adsorption of 3-mercapto isobutyric acid through thiol group at Ge(100) surface. Using this catalysis, it is possible to make carboxylic acid group-terminated surface where we want. This functional group-selective adsorption of bi-functional molecule using the catalysis may be used in positive lithographic methods to produce semiconductor substrate which is terminated by desired functional groups.

Min, Y. H.; Jung, S. J.; Youn, Y. -S.; Kim, D. H.; Kim, S. *J. Am. Chem. Soc.* 2010, 132, 9014.

11:20am **IS+AS+SS-TuM11 CO<sub>2</sub> Capture in Aqueous Monoethanolamine Solutions: Role of the Solution Interface Investigated with X-ray Photoelectron Spectroscopy**, *T. Lewis*, University of California, Irvine, *B. Winter*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, *M. Faebel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

Aqueous monoethanolamine (MEA) solutions are commonly used to capture CO<sub>2</sub> emitted into the atmosphere from industrial processes. It is likely that interactions between MEA and CO<sub>2</sub> at the aqueous solution surface are important to this process, yet surprisingly very few studies have explicitly addressed the role of the solution-gas interface. In the present study, interfacial chemistry of CO<sub>2</sub> capture is studied by surface sensitive photoelectron spectroscopy measurements from a liquid microjet of CO<sub>2</sub>-reacted MEA solutions with carbon loadings of 0.1 to 0.9 mol/mol. These experiments determine the spatial distribution of MEA and reaction products into the solution as a function of CO<sub>2</sub> loading. Results show that neutral MEA exhibits a propensity for the solution surface, whereas protonated MEA and reaction products prefer bulk solvation, suggesting enhanced reactivity at the solution interface, especially at high CO<sub>2</sub> loading. These observations indicate that a detailed understanding of the chemistry of CO<sub>2</sub> at the liquid/vapor interface and interface to bulk transport of the products will be important in understanding CO<sub>2</sub> capture.

11:40am **IS+AS+SS-TuM12 Fundamental Aspects of Organic Heterostructure Formation Examined using Supersonic Molecular Techniques and In Situ Real Time X-ray Synchrotron Radiation**, *E.R. Kish*, *T.V. Desai*, *A.R. Woll*, *J.R. Engstrom*, Cornell University

Over the past several years significant advances have been made concerning our understanding of the growth of crystalline small molecule organic thin films consisting of a single component. An important challenge in organic electronics, photonics and photovoltaics is to develop and improve methods to integrate both *p*-type and *n*-type small molecule organic semiconductors into the same device microstructure. Thus, developing an understanding of the molecular scale events that lead to heterojunction formation is essential in these systems consisting of multiple components. Here we report on our examinations of the nucleation, growth, and dynamics of adsorption of a *n*-type organic semiconductor, *N,N*-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C<sub>13</sub>), on SiO<sub>2</sub> surfaces modified by self-assembled monolayers (SAMs) and on a pre-deposited monolayer of pentacene (a *p*-type semiconductor) using supersonic molecular beam techniques, *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy. From real-time x-ray scattering we find that PTCDI-C<sub>13</sub> exhibits prolonged layer-by-layer growth for approximately the first 10 monolayers (MLs) of deposition on all three SAMs examined. Concerning the kinetics of growth we find that the adsorption probability of PTCDI-C<sub>13</sub> on itself is similar to that observed on two SAMs that possess aromatic endgroups, but it differs significantly to that observed on a relatively short, methyl-terminated SAM. These differences could reflect mechanisms such as direct molecular insertion of PTCDI-C<sub>13</sub> into either the existing PTCDI-C<sub>13</sub> film, or the longer chain SAMs with aromatic endgroups. Concerning growth in the submonolayer regime, we find that nucleation is homogeneous, and that the absolute density of islands depends on the nature of the surface, while the relative change of the island density with increasing growth rate is essentially independent of the underlying SAM. From the latter we find that a critical island size of a single molecule of PTCDI-C<sub>13</sub> can describe all the data. Finally, we will discuss our most recent results concerning the growth of heterostructures composed of a few to several monolayer stacks of PTCDI-C<sub>13</sub> and pentacene. In this work we find that PTCDI-C<sub>13</sub> grows in a smooth layer-by-layer fashion on pentacene, but the opposite is not true—pentacene grows in a purely 3D mode when deposited on PTCDI-C<sub>13</sub>. We will discuss the implications of this observation concerning the growth of organic heterostructures for applications in electronics, photonics and photovoltaics.

# Tuesday Afternoon Poster Sessions

## In Situ Spectroscopy and Microscopy Focus Topic

Room: East Exhibit Hall - Session IS-TuP

### In Situ Spectroscopy and Microscopy Focus Topic Poster Session

**IS-TuP1 In Situ Infrared Spectroscopy of Oxidation Process of Amorphous Carbon Film, Depending on Substrate Temperatures.** *M. Shinohara, Y. Takaki, K. Hara, Y. Takami, Y. Matsuda, H. Fujiyama*, Nagasaki University, Japan

There has been much interest in amorphous carbon films because they have a lot of useful properties: mechanical hardness, chemical inertness, and changeable electrical properties. The films can be deposited at low temperatures by using plasma process. The films have been used as coating materials for mechanical apparatus. The property of the film surface can be change with the addition of the other atoms on the surface. The addition of oxygen atoms to the surface leads the surface hydrophilic. The hydrophilic property on the surface has advantages to the further surface treatment. Therefore, it is important to understand the oxidation process of amorphous films. One of the effective oxidation methods is oxygen plasma exposure. We investigated the plasma oxidation process with in-situ infrared spectroscopy in multiple internal reflection geometry (MIR-IRAS). In this presentation, we focus on the dependence of oxidation process on the substrate temperatures. Infrared spectroscopic studies indicated that the oxygen plasma exposure induced the generation of OH components in the film. It means that carboxyl group would be formed by the exposure. With the increases of the substrate temperatures, the formation of OH components in the film was suppressed; moreover, the hydrophilic property was decreased with the substrate temperatures. On the other hand, the etching rate due to the oxygen plasma exposure was increased with the substrate temperatures. It is suggested that the etching rate is increased with substrate temperature, compared with the preservation of the OH components in the film.

**IS-TuP3 In Situ TEM Studies of Nanoparticle Growth in a Fluorozirconate (ZBLAN) Glass Matrix.** *J. Johnson*, University of Tennessee Space Institute

ZBLAN glass-ceramic materials are being developed as x-ray imaging plates. The materials are doped with europium and chlorine and can be heat treated in such a way that they form a novel nanocomposite material containing barium chloride nanocrystals, with the ability to convert x-rays into stable electron-hole pairs. The image can be read out afterwards with a scanning laser beam in a photostimulated luminescence process.

The ZBLAN glass only acts as an imaging plate upon annealing. As the annealing temperature and annealing time are increased, so a higher degree of nucleation of BaCl<sub>2</sub> crystallites inside the glass matrix is observed. As a result, more crystallites are available to incorporate Eu<sup>2+</sup> and hence increase the fluorescence intensity. However, a higher annealing temperature and a longer annealing time also lead to a larger degree of crystal growth, resulting in bigger nanoparticles. This leads to a decrease in spatial resolution of a ceramic-glass storage phosphor. The optimal annealing condition thus needs to compromise between the fluorescence intensity and the spatial resolution.

Here we present *in situ* TEM studies of ZBLAN glasses, being carried out to further understand the growth of nanoparticles inside a glass matrix under various heating conditions.

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