

# Thursday Morning, November 3, 2011

## Actinides and Rare Earths Focus Topic

Room: 207 - Session AC+SS-ThM

### The Surface Science of Actinides and Rare Earths

Moderator: R. Schulze, Los Alamos National Laboratory

8:00am AC+SS-ThM1 **The XPS of Heavy Metal Oxides: New Insights Into Chemistry**, P.S. Bagus, University of North Texas, E.S. Iltis, Pacific Northwest National Laboratory, C.J. Nelin, Consultant **INVITED**

The XPS of Rare Earth and Actinide oxides are commonly used to obtain information about the oxidation state of the metal by taking various features of the spectra as fingerprints of the metal oxidation state. However, it is possible to obtain detailed information about the nature of the chemical interactions from these features by using the predictions of rigorous theoretical analyses. One of our important concerns is to make direct assessments of the covalent character of the metal-ligand interaction; i.e., the mixing of O(2p) with partly occupied, or unoccupied, metal levels to form bonding and anti-bonding orbitals. We relate this covalent character to the XPS features. In particular, we investigate the connection between the covalent character of the interaction and the satellite intensity. We also investigate the characterization of the satellites and discuss their assignment as shake satellites, an assignment that is naturally connected with the extent of the covalent mixing of the metal and oxygen levels. Furthermore, we examine how vibrational excitations can lead to broadening of the XPS features and suggest that the observed broadening of XPS peaks may contain, hitherto not utilized, information about the chemical interactions in an oxide. Our focus will be on the XPS of two Rare Earth oxides, CeO<sub>2</sub> and LaAlO<sub>3</sub>, and two actinide oxides, UO<sub>2</sub> and UO<sub>3</sub>; these systems have different electronic character that permit the mechanisms discussed above to be explored and compared. Our theoretical analyses are based on relativistic molecular orbital wavefunctions, WF's, for both initial states, before ionization, and final states, after ionization. The WF's are for materials models that contain explicit cations and anions embedded in a point charge field. With the variationally optimized orbitals for these WF, covalent mixing is naturally taken into account. The cluster WF's include one-body and many-body effects and do not use parameters that are adjusted to make calculated relative energies and intensities fit to experiment.

8:40am AC+SS-ThM3 **New Insights into the Oxidation/Corrosion of Plutonium**, D.L. Pugmire, H.G. Garcia Flores, D.P. Moore, A.L. Broach, Los Alamos National Laboratory, P. Roussel, Atomic Weapons Establishment, UK **INVITED**

An understanding of the oxidation and corrosion processes of plutonium metal at room temperature is important to the safe, effective use and storage of this reactive metal. The oxidation rate for the  $\delta$ -phase stabilized, plutonium/gallium alloy (a commonly employed alloy) can be significantly affected by a number of parameters including the gallium content and the composition of the oxidizing atmosphere (O<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O, H<sub>2</sub>O). The nature of plutonium oxidation has typically been thought of as the growth of a dioxide (PuO<sub>2</sub>) overlayer on the metal to a thickness at which the film begins to spallate ( $\mu$ 's). Based on thermodynamic arguments, it has been pointed out that a relatively thin layer of the sesquioxide (Pu<sub>2</sub>O<sub>3</sub>) should exist at the dioxide/metal interface for thick oxide films.

Historically, the oxidation/corrosion of plutonium has been studied by oxygen uptake of samples at elevated temperatures inferred from mass gain measurements. Accuracy of these experimental setups likely limited measurements to oxide films thicker than ~0.05 to 0.1  $\mu$  (50 - 100 nm). This is at the upper-limit of the thicknesses typically observed for plutonium oxide films. Little work has been published for studies of plutonium oxide thin-films (< 50 nm) on metal substrates. Additionally, very little is known about the role that gallium plays during the oxidation of the alloy other than it can significantly slow the rate.

We report here our studies of the initial stages of plutonium oxidation with O<sub>2</sub> in the thin-film regime with x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The results indicate that not only does a Pu<sub>2</sub>O<sub>3</sub> layer exist in thin plutonium oxide films, but that the sesquioxide exists as a substoichiometric species on a metal substrate, and is probably best described as Pu<sub>2</sub>O<sub>3-y</sub>. It also appears that the oxide thin-film is comprised mainly of the sesquioxide species, with PuO<sub>2</sub> accounting only for a relatively thin portion of the overall oxide film thickness. While the surface sensitive techniques employed here suffer from relatively high limits of detection, we have also been able to qualitatively, and in some cases quantitatively, study the behavior of gallium during the oxidation of the  $\delta$ -plutonium alloy. The gallium content relative to plutonium is observed to decrease within the oxide film during oxidation, with the

displaced gallium moving to the oxide/metal interface to form a thin gallium rich region. These new results will be compared and contrasted with existing literature. Additionally, how these results have altered our understanding of the Pu/O thin-film system and the oxidation/corrosion of plutonium will be discussed.

9:20am AC+SS-ThM5 **The Oxidation of Uranium Dioxide at High Pressures in Pure Oxygen**, J.C. Crowhurst, Z. Dai, J.M. Zaig, K.B. Knight, A.J. Nelson, W.J. Siekhaus, I.D. Hutcheon, Lawrence Livermore National Laboratory

The oxidation of uranium dioxide has received much experimental and theoretical attention over the last several decades in large part because of its relevance to the operation and storage of uranium-based nuclear fuel. The oxidation process is inherently complicated, involving the formation of multiple different phases via distinct mechanisms even at relatively low temperatures. In the range of a few hundred degrees centigrade oxidation is generally assumed to be a two step process[1]: UO<sub>2</sub> → U<sub>3</sub>O<sub>7</sub>/U<sub>4</sub>O<sub>9</sub> → U<sub>3</sub>O<sub>8</sub>. At low pressures the intermediate phases adopt crystal structures that are modifications of the UO<sub>2</sub> fluorite structure and are slightly denser. By contrast, U<sub>3</sub>O<sub>8</sub> forms a considerably less dense orthorhombic structure (by some 23%). The large volume expansion resulting from the oxidation of UO<sub>2</sub> to U<sub>3</sub>O<sub>8</sub> is a potentially serious concern in the event of oxidation of a fuel element, with consequent splitting of protective sheaths and the spalling of powder.

While attention has been focused on the oxidation of UO<sub>2</sub> at elevated temperatures, the associated experiments have all been performed at low partial pressures of oxygen. It is unclear how pressure affects the oxidation process – particularly in the context of the formation of U<sub>3</sub>O<sub>8</sub>, with its large volume change with respect to UO<sub>2</sub>. We have examined the oxidation of a nominal single crystal of UO<sub>2</sub> in pure oxygen at elevated pressures up to approximately 0.9 GPa (9000 atm) and temperatures of up to 450 °C. In-situ Raman scattering measurements were made as a function of temperature in order to monitor the oxidation. Recovered material was examined using electron based techniques including SEM, TEM, and electron diffraction and also using x-ray photoelectron spectroscopy.

Material synthesized under high pressure has a Raman spectrum that is different from both the UO<sub>2</sub> starting material and the common form of U<sub>3</sub>O<sub>8</sub>. Also, compared with common U<sub>3</sub>O<sub>8</sub>, we find that it has fewer crystalline defects and mostly adopts a hexagonal rather than orthorhombic form. Figure 1 of the supplemental document compares Raman spectra of UO<sub>2</sub> in oxygen with synthesized material. Fig. 2 compares electron diffraction obtained from recovered material with U<sub>3</sub>O<sub>8</sub> synthesized at ambient pressure.

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[1] R. J. McEachern and P. Taylor, *JNM*, **254**, 87, (1998).

9:40am AC+SS-ThM6 **Radiation Effects on Hydrogen Reactivity in Narrow Uranium-Uranium and Uranium-LiD (or Air) Gaps using MCNPX Code**, M.A. Schildbach, W.J. Siekhaus, Lawrence Livermore National Laboratory

Preferential uranium hydriding occurs frequently in narrow gaps. There are different hypotheses about its causes, one of which could be radiation-induced chemistry in gaps. Both <sup>238</sup>U and <sup>235</sup>U generate ionizing  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation capable of vibrationally or translationally exciting, ionizing, or dissociating H<sub>2</sub>, all of which increase the reactivity of H<sub>2</sub> with uranium. Dissociation of H<sub>2</sub> is necessary to initiate hydriding, and it has been shown that the sticking coefficient of H atom is about 1200 times higher than H<sub>2</sub>'s[1]. Here we use the MCNPX radiation transport code to calculate the energy dependent electron flux generated from the <sup>234m</sup>Pa  $\beta$  decay and from photoelectrons generated by brems-strahlung. We apply the code to gaps occurring in two <sup>238</sup>U cylindrical pieces welded together and filled on the inside with LiD with a 100 $\mu$ m gap between <sup>238</sup>U and LiD, and having a 100 $\mu$ m gap in <sup>238</sup>U itself, typical for step-joint-welded uranium shells.

The MCNPX Monte Carlo Code - as configured now - tracks the life cycle of electrons throughout the material and calculates the electron flux as a function of energy, putting results into "energy bins" 1 keV wide. We find that at 2 keV ( $\pm 5$  keV, the last energy bin) the calculated electron flux in the U-U gap is approximately 19 times larger than in the U-LiD gap, and fifty two times larger than in the U-air gap on the outside of the cylindrical

shells. Cross-sections for electron-hydrogen collisions peak, however, below 1 keV energy. We establish the upper limit of the effect of electron-hydrogen collisions by extrapolating the MCNPX electron flux results from the last bin to energies as low as 1 eV by fitting a function to the flux between 2 and 20 keV. To calculate the fraction of H<sub>2</sub> vibrationally or translationally excited, ionized, or dissociated per cm<sup>2</sup>/s, we integrate the product of the energy dependent cross sections (listed in reference [2]) and the energy dependent electron flux over the relevant energy range. The fraction of H<sub>2</sub> molecules calculated to be dissociated is small, but significant during long-time exposure. Future work will extend the MCNPX code below 1keV (as is done for biological radiation damage), to avoid energy extrapolation.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

#### References

1. Balooch M, Hamza AV. "Hydrogen and water vapor adsorption on and reaction with uranium." *Journal of Nuclear Materials*, **230**, 3, 259-270, 1996.
2. Yoon JS et al., "Cross sections for electron collisions with hydrogen molecules." *Journal of Physical and Chemical Reference Data*, **37**, 2, 913-931, 2008.

10:40am **AC+SS-ThM9 Study of the Gd<sub>5</sub>Ge<sub>4</sub> (010) Surface**, *C. Yuen, G. Miller, P.A. Thiel*, Ames Laboratory - US DOE

Certain intermetallics of Gd, Ge, and Si exhibit giant magnetocaloric effects, yet very little is known about their surfaces. We have investigated one such system, Gd<sub>5</sub>Ge<sub>4</sub>, with the goal of elucidating its clean and oxidized surface structure, using STM and XPS. The clean Gd<sub>5</sub>Ge<sub>4</sub> (010) surface exhibits a step-terrace morphology after repetitive sputtering and annealing at 900 K. Step heights are equal to half the bulk unit cell length in the <010> direction, consistent with the existence of an equivalent plane in the middle of the unit cell. Surface compositions of Gd and Ge are close to the bulk composition. However, at higher temperatures—between 900 K and 1200 K—the surface becomes Gd poor by 10 at.%. In STM, at these temperatures, the fine structure on the terraces changes, and a different type of terrace with a different step height emerges. We propose that the preferred surface termination is rich in Gd (which has lower surface energy than Ge), and that this termination is exposed after annealing at 900 K. At higher temperature, we propose that Gd (which has higher vapor pressure than Ge) evaporates preferentially, leading to the changes described above and exposing a Ge-rich surface termination. Finally, we find that Gd oxidizes preferentially.

11:00am **AC+SS-ThM10 Using Spatially Controlled Thin-Films Coatings Around Rare-Earth doped Nanophosphors for High Efficiency Energy Applications**, *J.A. Dorman, A. Joshi, G. Kuzmanich, J.H. Choi, J.P. Chang*, University of California Los Angeles

The development of rare-earth (RE) doped phosphors allows for the conversion of photons to energies that are more usable for the desired application. Additionally, these RE phosphors have long lifetimes, on the order of ms, which offer potential in many energy conversion and energy transfer devices. Currently, RE phosphors are used in fiber optics amplifiers, broad absorption solar cells and various other lighting applications. Energy transfer mechanisms of the excited RE states, such as defect quenching and sensitizer/emitter interactions, must be understood in order to achieve high efficiency energy conversion and propagation.

In order to increase the efficiency of solar cells, high efficiency phosphors need to synthesize in order to convert photons at the edge of the absorption band into higher energy photons while avoiding undesired quenching effects. In effort to produce these high efficiency phosphors, spatially controlled RE doped thin films are deposited around nanoparticles (NP) to produce a core-shell nanophosphor. Reduction in luminescent quenching can be achieved by increasing the distance between the surface quenching site and active ions through the deposition of a precisely controlled thin film around the NP. Secondly, the luminescent fingerprint can be further controlled through doping of the shell structure by increasing the absorption spectrum or the introduction of emission peaks. Deposition of a thin film around an Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup> core NP is achieved via atomic layer deposition or sol-gel synthesis to compare the effect of a spatially controlled vs. a random dopant distribution. Primarily, this work focuses on the emission of visible photons through upconversion, making them ideal components in broad absorption solar cells. By spatially controlling the position and concentration of the RE ions within the nanostructure, increased luminescence is observed due to energy transfer between the dopant ions within a critical interatomic distance. Passivation of surface sites with increasing film thickness was shown to increase luminescent lifetimes up to 53%, with a critical shell thickness of 8 nm, while lowering the theoretical lifetimes extracted from Judd-Ofelt parameters. The effect of the spatially

controlled Yb ions was probed through the extraction of the upconversion photon requirement, showing a statistical decrease in photons from 2.16 to 1.43, or ~30 %. Finally, the effective energy transfer distance and energy transfer coefficients were studied as a spacer layer is added to the system, showing energy transfer up to ~3 nm, confirming the Förster-Dexter theory.

11:20am **AC+SS-ThM11 Growth and Characterization of Scandia Stabilized Zirconia and Samaria Doped Ceria Multi-Layer Thin Films**, *S. Thevuthasan*, Pacific Northwest National Laboratory, *M.I. Nandasiri*, Western Michigan University, *T. Varga, V. Shuthanandan, S.P. Sanghavi, S.V.N.T. Kuchibhatla*, Pacific Northwest National Laboratory, *A. Kayani*, Western Michigan University

Recent studies showed a colossal enhancement in the ionic conductivity of multi-layer oxygen-ion conducting thin films compared to most commonly used solid oxide fuel cell (SOFC) electrolytes. It has been observed that, the oxygen ionic conductivity of nano-scale hetero-structures increases with the increase in number of layers. However, some of these findings were questioned due to the inability to distinguish electronic and ionic conductivity. Thus, here we investigated the scandia stabilized zirconia and samaria doped ceria (SDC/ScSZ) multi-layer system to understand the oxygen-ion conductance in multi-layer hetero-structures.

In this study, the growth of SDC and ScSZ multi-layer thin films was carried out using the optimized growth conditions, dopant concentrations and film properties established for single-layer SDC and ScSZ epitaxial thin films. The epitaxial SDC and ScSZ multi-layer thin films were grown on Al<sub>2</sub>O<sub>3</sub>(0001) substrates by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) at 650°C. The number of layers in the multi-layer hetero-structures was varied from 2 to 20 by keeping the total film thickness constant at 140 nm. Following the growth, thin films were characterized by various in-situ and ex-situ characterization techniques including reflection high energy electron diffraction (RHEED), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and x-ray photoelectron spectroscopy (XPS). The initial streaky RHEED pattern indicates the epitaxial growth of SDC/ScSZ multi-layer thin films. Furthermore, RHEED patterns indicate the transition of the initial smooth surface to a rough surface with the increase in number of layers. The individual layer thickness was found to be approximately 7 nm for the twenty-layer film as confirmed by x-ray reflectivity data. RBS was also used to find the composition and thickness of the films. HRXRD patterns of ScSZ/SDC thin films exhibit only CeO<sub>2</sub>(111) and ZrO<sub>2</sub>(111) reflections, indicating the growth of epitaxial SDC(111) and ScSZ(111) multi-layers. XPS depth profile confirmed the uniform dopant concentration in both SDC and ScSZ layers, which was found to be 7 and 6 atom % for Sc and Sm, respectively. In the near future, the ionic conductivity of SDC and ScSZ multi-layer thin films will be measured by four probe conductivity method.

# Authors Index

**Bold page numbers indicate the presenter**

**— B —**

Bagus, P.S.: AC+SS-ThM1, **1**  
Broach, A.L.: AC+SS-ThM3, **1**

**— C —**

Chang, J.P.: AC+SS-ThM10, **2**  
Choi, J.H.: AC+SS-ThM10, **2**  
Crowhurst, J.C.: AC+SS-ThM5, **1**

**— D —**

Dai, Z.: AC+SS-ThM5, **1**  
Dorman, J.A.: AC+SS-ThM10, **2**

**— G —**

Garcia Flores, H.G.: AC+SS-ThM3, **1**

**— H —**

Hutcheon, I.D.: AC+SS-ThM5, **1**

**— I —**

Ilton, E.S.: AC+SS-ThM1, **1**

**— J —**

Joshi, A.: AC+SS-ThM10, **2**

**— K —**

Kayani, A.: AC+SS-ThM11, **2**  
Knight, K.B.: AC+SS-ThM5, **1**  
Kuchibhatla, S.V.N.T.: AC+SS-ThM11, **2**  
Kuzmanich, G.: AC+SS-ThM10, **2**

**— M —**

Miller, G.: AC+SS-ThM9, **2**  
Moore, D.P.: AC+SS-ThM3, **1**

**— N —**

Nandasiri, M.I.: AC+SS-ThM11, **2**  
Nelin, C.J.: AC+SS-ThM1, **1**  
Nelson, A.J.: AC+SS-ThM5, **1**

**— P —**

Pugmire, D.L.: AC+SS-ThM3, **1**

**— R —**

Roussel, P.: AC+SS-ThM3, **1**

**— S —**

Sanghavi, S.P.: AC+SS-ThM11, **2**  
Schildbach, M.A.: AC+SS-ThM6, **1**  
Shutthanandan, V.: AC+SS-ThM11, **2**  
Siekhaus, W.J.: AC+SS-ThM5, **1**; AC+SS-ThM6,  
**1**

**— T —**

Thevuthasan, S.: AC+SS-ThM11, **2**  
Thiel, P.A.: AC+SS-ThM9, **2**

**— V —**

Varga, T.: AC+SS-ThM11, **2**

**— Y —**

Yuen, C.: AC+SS-ThM9, **2**

**— Z —**

Zaug, J.M.: AC+SS-ThM5, **1**