

# Monday Afternoon, October 18, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC+TF-MoA

### Actinide and Rare Earths Thin Films

**Moderator:** S.W. Yu, Lawrence Livermore National Laboratory

2:00pm **AC+TF-MoA1 EUV and in situ Spectroscopic Ellipsometric Analysis of the Oxidation of Uranium Thin Films, H. Dumais, D.D. Allred, R.S. Turley**, Brigham Young University

Uranium thin films have found a variety of uses: such as EUV mirrors for space application and driver layers on inertial confinement fusion microspheres. Uranium is chemically active and an unprotected surface oxidizes quickly. More is known about the oxidation of bulk than thin films. We have investigated the oxidation of uranium thin films and reactively sputtered uranium oxide films using spectroscopic ellipsometry, electron microscopy and XPS. We find that uranium magnetron sputtered (1-10 mtorr) in Ar/oxygen forms a UO<sub>2</sub> (fcc-structure) over a range of O<sub>2</sub> partial pressures. It is reasonably stable in air for several hours. On the other hand, thin uranium films (20nm) left to oxidize in air forms a higher oxide, probably U<sub>3</sub>O<sub>8</sub>. This observation may help interpret EUV optical data previously made on uranium films.

2:20pm **AC+TF-MoA2 Atomic Layer Deposition of Rare Earth Ion Co-doped Oxides for Optical Applications, J. Hoang, C. Pham, J.P. Chang**, University of California, Los Angeles

Rare earths (REs) exhibit unique shielded f-electrons giving rise to sharp spectral transitions. These transitions are dictated by the RE identity and can be manipulated by engineering the interactions of multiple RE ions. In this work, radical enhanced atomic layer deposition (RE-ALD) is used to design complex metal oxides with multiple dopants, whose concentration variation and spatial distribution control enable the synthesis of a wide range of multifunctional materials with tunable properties including magnetic, spectral, and electronic. Specifically, the control of sensitizer proximity and concentration is used to enhance amplification at 1.54  $\mu\text{m}$  ( $\text{Er}^4_{13/2} \rightarrow ^4_{15/2}$ ) for compact planar optical amplifier applications and promote Er upconversion at 535 nm ( $^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4_{15/2}$ ) and at 670 nm ( $^4\text{F}_{9/2} \rightarrow ^4_{15/2}$ ). The spatial distributions between  $\text{Er}^{3+}$  and RE (RE =  $\text{Yb}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$ ) are investigated with 1.54  $\mu\text{m}$  emission promotion via direct energy transfer for Yb sensitizers and via cross relaxation for Eu and Ce sensitizers. Polycrystalline thin films are synthesized by sequential radical-enhanced ALD of  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$  at 350°C using 2,2,6,6-tetramethyl-3,5-heptanedionato analog of the corresponding metal (e.g. RE(TMHD)<sub>x</sub>) and reactive oxygen atoms from a plasma. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films are determined by x-ray and Rutherford backscattering spectroscopies, electron microscopy and photoluminescence measurements. The effect of concentration is examined using a 8:1:x Y:Er:RE cycle sequence with x = 0, 1, 3, 5, 7, while the spatial distribution is investigated using a y:5:y:5 Y:Er:RE ratio with y = 0, 2, 4, 6, 8, 10. High resolution transmission electron microscopy on thin films deposited on nanotubes verify the construction of nanolaminates. Extended x-ray absorption fine structure Yb L<sub>2</sub> edge scans show that the Yb local environment possesses more 2nd nearest neighbor Yb ions as the Yb cycles increases. Photoluminescence (PL) spectra using both 488 nm and 980 nm laser excitations show sharp Er intra 4f peaks with peak intensity centered at 1535 nm at low pump powers (~50 mW for 980 nm excitation). ~8x luminescence enhancement is achieved using a 8:1:3 Y:Er:Yb cycle ratio, while a slight decrease in PL intensity is apparent as the Er and Yb distance increases. Individual PL studies of Eu and Ce codoped Er:Y<sub>2</sub>O<sub>3</sub> samples were found to require higher excitation powers, while tri-doped samples (Yb:Eu and Yb:Ce codoped Er:Y<sub>2</sub>O<sub>3</sub>) are currently under investigation to study further attainable PL enhancement and upconversion efficiency.

2:40pm **AC+TF-MoA3 Electronic Structure and Surface Reactivity of Actinide Systems, Th. Gouder, A. Seibert**, European Commission, JRC, Institute for Transuranium Elements, Germany **INVITED**

Actinide research is motivated by the peculiar properties of the 5f states which are on the verge from itinerancy to localization. These states confer to the actinides rich, yet often unpredictable chemical and physical properties. In this context surface science, focusing on the few topmost atomic layers, plays a particularly important role. In this region decreased bonding leads to 5f-band narrowing and enhances localization effects. On the other hand, the interaction of actinide surface atoms with the environment dominates the reactivity of spent nuclear fuel. Detailed

knowledge of these surface reactions is required for the prediction of the long term storage behavior of spent fuel.

In the talk we will discuss the evolution of the electronic structure of actinide elements confined to thin films. We will describe film preparation by sputter deposition from elemental targets (Th, U, Np, Pu and Am) on strongly and weakly interacting substrates (Mg, Al, Si). Information on the electronic structure is obtained by photoemission spectroscopy. 5f localization occurs both with increasing Z and with decreasing layer thickness. In Pu, which is the last actinide where in the bulk the 5f states are itinerant, the 5f states become localized at one monolayer. For thicker films, photoemission shows precursor effects manifesting as final state multiplets. For Np, the 5f states are always itinerant, even at the submonolayer level, but also here, deviation from the pure band behaviour is observed.

We will then compare actinide surface compounds, focusing on the oxides. The difference between surface and bulk oxides, and the specific contribution of the 5f states will be discussed. In late actinides oxides (down to Pu) the 5f states are well localized and only rare-earth like (An<sub>2</sub>O<sub>3</sub>) sesquioxides and (AnO<sub>2</sub>) dioxides are observed. There is no higher oxide. With decreasing Z, the increasingly bonding 5f states destabilize the An<sub>2</sub>O<sub>3</sub> favoring AnO<sub>2</sub>, and simultaneously enable higher oxidation states beyond AnO<sub>2</sub>. Here again, the presence of the surface with its lowered coordination and increased tendency for 5f localization leads to oxidation states different from the bulk.

Finally, we will give a brief overlook on actinide surface reactions with the environment, where 5f states are involved (catalysis and photochemistry). We will present the surprising surface reduction of PuO<sub>2</sub> thin films by water, which we attribute to a photochemically driven surface reaction involving 5f states. Such processes may fundamentally influence the long term storage properties of spent fuel.

3:40pm **AC+TF-MoA6 Observation of Strong Resonant Behavior in the Inverse Photoelectron Spectroscopy of Ce Oxide, J.G. Tobin, S.W. Yu, B.W. Chung**, Lawrence Livermore National Laboratory, G.D. Waddill, Missouri University of Science and Technology, L. Duda, J. Nordgren, Uppsala University, Sweden

X-ray Emission Spectroscopy (XES) and Resonant Inverse Photoelectron Spectroscopy (RIPES) have been used to investigate the photon emission associated with the Ce3d<sub>5/2</sub> and Ce3d<sub>3/2</sub> thresholds. Strong resonant behavior has been observed in the RIPES of Ce Oxide near the 5/2 and 3/2 edges. Inverse Photoelectron Spectroscopy (IPES) and its high energy variant, Bremstrahlung Isochromat Spectroscopy (BIS), are powerful techniques that permit a direct interrogation of the low-lying unoccupied electronic structure of a variety of materials. Despite being handicapped by counting rates that are approximately four orders of magnitude less than the corresponding electron spectroscopies (Photoelectron Spectroscopy, PES, and X-ray Photoelectron Spectroscopy, XPS) both IPES [1,2,3,4,5] and BIS [6,7,8] have a long history of important contributions. Over time, an additional variant of this technique has appeared, where the kinetic energy (KE) of the incoming electron and photon energy (h $\nu$ ) of the emitted electron are roughly the same magnitude as the binding energy of a core level of the material in question. Under these circumstances and in analogy to Resonant Photoelectron Spectroscopy, a cross section resonance can occur, giving rise to Resonant Inverse Photoelectron Spectroscopy or RIPES. [9-13] Here, we report the observation of RIPES in an f electron system, specifically the at the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> thresholds of Ce Oxide.

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4:00pm **AC+TF-MoA7 Growth and Reactivity of CeO<sub>2</sub>(100) Thin Films**, *D.R. Mullins, T.-L. Chen, F.C. Calaza, S.H. Overbury, M.D. Biegalski, H.M. Christen*, Oak Ridge National Laboratory

Cerium oxide is a principal component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. The different crystallographic faces of ceria present significantly different surface structures and compositions that may alter the catalytic reactivity. The structure and composition determine the availability of adsorption sites, the spacing between adsorption sites and the ability to remove O from the surface.

To investigate the role of surface orientation on reactivity, CeO<sub>2</sub> films were grown with two different orientations. CeO<sub>2</sub>(100) films were grown ex situ by pulsed laser deposition on Nd-doped SrTiO<sub>3</sub>(100). The structure was characterized by RHEED, XRD and reflectometry. CeO<sub>2</sub>(111) films were grown in situ by thermal deposition of Ce metal onto Ru(0001) in an oxygen atmosphere. The structure of these films has been studied by LEED and STM. Attempts to grow CeO<sub>2</sub>(100) in situ by physical vapor deposition on Pt(100) and Pd(100) failed due to preferential growth of CeO<sub>2</sub>(111) on these supports.

The chemical reactivity was characterized by the adsorption and decomposition of methanol and 2-propanol. Reaction products were monitored by TPD and surface intermediates were determined by soft x-ray photoelectron spectroscopy and infrared spectroscopy. Both of these alcohols readily chemisorbed on either surface in UHV. The decomposition of methanol was less selective on CeO<sub>2</sub>(100) than on CeO<sub>2</sub>(111) with CO and H<sub>2</sub> resulting even from a fully oxidized surface. Water was also produced as on CeO<sub>2</sub>(111), and the CeO<sub>2</sub>(100) surface could be reduced by exposure to methanol at 700 K. Unlike on reduced CeO<sub>x</sub>(111), methanol adsorption on reduced CeO<sub>x</sub>(100) produced only a small increase in reactivity and inhibited formaldehyde formation. 2-propanol produced primarily propene and water with a small amount of acetone.

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4:20pm **AC+TF-MoA8 Photoemission Study of Au-Schottky Barrier Formation on YbGaN Thin Films using Synchrotron Radiation**, *S.R. McHale, J.W. McClory, J.C. Petrosky*, Air Force Institute of Technology, *Y.B. Losovyj*, Louisiana State University

Au-YbGaN Schottky barrier formation was observed using Au evaporation on multiple concentrations of Yb<sub>x</sub>Ga<sub>1-x</sub>N thin films deposited on (111) Si substrates. Low Energy Electron Diffraction was performed to verify the integrity of the Au deposition. Energy dependent, synchrotron generated photoemission spectroscopy ranging from 15 to 26 eV under UHV conditions clearly determined a valence band shift of up to 0.62 eV.

The experiments were conducted at the Louisiana State University (LSU) Center for Advanced Microstructures and Devices (CAMD), using synchrotron radiation dispersed by the 3m toroidal grating monochromator (TGM) beamline, where resolution of the experimental apparatus is approximately 70 meV. Thin films were fabricated using RF plasma-assisted molecular beam epitaxy (PAMBE) at the University of Nebraska (Lincoln) Center for Materials and Nanoscience (NCMN). Yb temperatures during deposition were 500 °C, 700 °C, and 860 °C, resulting in slightly coarse, uniform, and very coarse grained films, respectively. The XRD patterns show a high degree of order in the films.

A least squares fit was used to calculate the valence band maximum (VBM) for each spectrum. Comparing the calculated VBM values for the bare YbGaN sample spectra with those following Au deposition shows that Au clearly affects the YbGaN electronic structure by shifting the valence band

toward the Fermi energy by a maximum value of 0.62 eV at a monolayer of Au coverage. This valence band shift yields a calculated Schottky Barrier,  $\phi_{\text{SB}}$ , of 0.83 eV, determined by the relationship  $E_{\text{g}} - (E_{\text{F}} - E_{\text{VBM}})$ , where the energy gap,  $E_{\text{g}}$ , was approximated at 3.5 eV.

SB calculation via direct spectroscopic data will be supplemented by SB calculation via I-V measurements of the sample surface, using a Keithley 4200 Semiconductor Characterization System and a Signatone Probe Station.

Our research efforts are motivated by radiation detection materials and devices. Radiation detector diodes typically operate in the reverse bias mode, where Schottky contacts are desirable to optimize the signal-to-noise ratio. Therefore, we intend to extend these results to facilitate additional measurements using other Lanthanide-doped III-nitride compounds in a future research endeavor involving potential radiation detection materials. We anticipate that this effort will improve researchers' determination of suitable combinations of materials, and will produce novel, efficient, and more accurate neutron detection devices than currently available.

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