

Monday Morning, October 18, 2010

Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC+SS-MoM

Surface Science of Actinides

Moderator: J.G. Tobin, Lawrence Livermore National Laboratory

9:00am **AC+SS-MoM3 High Resolution Auger Electron Spectroscopy of Plutonium Metal and Oxide Surfaces**, *D.P. Moore, A.L. Broach, D.L. Pugmire*, Los Alamos National Laboratory, *H.G. Garcia Flores*, University of Nebraska-Lincoln, *P. Roussel*, Atomic Weapons Establishment

There has been considerable new study of the oxidation of plutonium in recent years. Much of this study has focused on the properties of the thin film oxide layers that form on the plutonium metal surface under exposure to oxygen. For these studies, x-ray photoelectron spectroscopy (XPS) has typically been the technique of choice as it is ideally suited for the study of oxidation states by analyzing XP peak shape and position changes. This allows for the identification of relative changes in the Pu 4f manifold in going from Pu metal, to the Pu sesquioxide (Pu_2O_3), to the Pu dioxide (PuO_2). But there are advantages of other surface science techniques, specifically Auger electron spectroscopy (AES), over XPS for certain types of studies. Prime among them is that AES has a much higher spatial resolution than XPS allowing for analysis of specific areas and features on a surface down to a few tens of nanometers. And although AES typically suffers from less sensitivity and specificity to chemical state differences in its peak shape and position, modern Auger systems with field emission sources and hemispherical electron analyzers have alleviated much of this shortcoming.

For plutonium, Auger peaks for the metal and dioxide have been used for investigation whereas the Auger peaks for the sesquioxide have not received the same study. Peak positions from derivative spectra have been used for distinguishing between metal and oxide with quantification of the oxides from peak-to-peak heights and estimates of relative sensitivity factors. In order to more fully utilize AES for the study of the oxidation of plutonium surfaces, the relative changes in the Auger peaks in going from Pu metal to all its oxides must be quantified. We have used high resolution AES to identify the Auger peak structure of Pu metal, PuO_2 , and Pu_2O_3 . We have studied the OPP and OVV Auger transitions in the 80 – 110 eV range as well as the NOV transitions at approximately 315 eV via oxygen dosing on Pu metal surfaces. Oxygen doses from less than a Langmuir up to over 500 Langmuirs have been investigated. Relative changes in both the integrated and derivative Auger peak structures for Pu metal, PuO_2 , and Pu_2O_3 have been identified and will be presented. Using this new information we will be able to take advantage of the higher spatial resolution of AES to further study plutonium oxide properties such as layer structure, oxidation kinetics, and auto reduction on polycrystalline plutonium samples.

9:20am **AC+SS-MoM4 The Behavior of Gallium During the Initial Stages of Plutonium/Gallium Alloy Oxidation**, *D.L. Pugmire*, Los Alamos National Laboratory, *H.G. Garcia Flores*, University of Nebraska-Lincoln, *D.P. Moore, A.L. Broach*, Los Alamos National Laboratory, *P. Roussel*, Atomic Weapons Establishment

An area of significant importance to the oxidation of any alloy is the role that the constituent metals play. It has been previously shown that the oxidation rate for the δ -phase stabilized, plutonium/gallium alloy can be significantly affected by the gallium content as well as composition of the oxidizing atmosphere (O_2 , $\text{O}_2/\text{H}_2\text{O}$, H_2O). Reasons for the observed rate changes upon alloying with gallium are not understood. A previous study of a variety of δ -plutonium alloys shows that the significant structure difference between unalloyed α -plutonium and alloyed δ -plutonium cannot be the sole cause of different oxidation rates. This implies that the alloying metal must play some role in the slower oxidation rates observed for gallium-stabilized δ -plutonium. In order to elucidate the oxidation mechanism of this commonly employed alloy, it is important to understand the role gallium plays during oxidation. The relatively low concentrations of alloying metals used, typically several atomic percent, can make the activities of gallium during oxidation of δ -plutonium difficult to follow. This complication is compounded by the fact that the initial stages of oxidation are inherently a surface phenomenon, thereby significantly limiting the relative amount of affected material. Significant questions remain as to what is a realistic description for the Pu/Ga-oxide, thin-film system during the initial stages of oxidation.

An ultra-high vacuum (UHV) system equipped with surface sensitive techniques, such as x-ray photoelectron spectroscopy (XPS) and Auger

electron spectroscopy (AES), provides a controlled environment ideally suited to study the behavior of gallium during the initial stages of Pu/Ga oxidation. In addition to information about the oxidation states of the plutonium species in the near surface region provided by XPS, both XPS and AES are very useful for studying the relative atomic concentration of elements present at the sample surface (such as oxygen and gallium). While these surface sensitive techniques suffer from relatively high limits of detection, we have been able to qualitatively, and in some cases quantitatively, study the behavior of gallium during the oxidation of the δ -plutonium alloy. The gallium content relative to plutonium is observed to decrease within the oxide film during oxidation, with the displaced gallium apparently moving to the oxide/metal interface to form a thin gallium rich region. The results of these studies and their implications on the mechanism of gallium-stabilized, δ -plutonium oxidation will be discussed.

9:40am **AC+SS-MoM5 Angle-Resolved Photoemission and the 5f Electronic Structure of Pu Materials**, *J. Joyce, T. Durakiewicz, K.S. Graham, E.D. Bauer, J.N. Mitchell, D.P. Moore, J.A. Kennison, T.M. McCleskey, A.K. Burrell, E. Bauer, Q. Jia*, Los Alamos National Laboratory

INVITED

The electronic structure of Pu compounds ranging from Mott insulators to strongly correlated metals is investigated using angle-resolved photoemission (ARPES). The electronic properties of the Pu compounds PuCoGa_5 , PuSb_2 , and PuO_2 are compared with angle-integrated and temperature-dependent photoemission results for Pu metal. The balance in strongly correlated materials between the central and periodic potentials is directly probed through ARPES. For the strongly correlated metals, details of the sharp quasiparticle peak at the Fermi energy are presented, including crystal momentum dispersion, giving insight into the self-energy and ground state properties of these Pu materials. In PuSb_2 , the ARPES data at a photon energy of 21.2 eV, indicates a quasiparticle peak that disperses through the Fermi energy. At 40.8 eV photon energy, PuSb_2 shows f-electron intensity periodic with the lattice. Photoemission results for the Fermi level spectral intensity as well as the more localized 5f states well-removed from the Fermi energy are used to quantify adaptive character for these materials. Both PuSb_2 and PuCoGa_5 ARPES data show a dispersive peak which crosses the Fermi energy at a photon energy of 21.2 eV where the conduction states have a larger cross section than the 5f states. The results for 40.8 eV photon energy, with enhanced 5f strength, indicate a peak dispersing through the Fermi energy for PuCoGa_5 but the PuSb_2 data indicate an intensity modulated peak near the Fermi energy. The first ARPES results for the Mott insulator PuO_2 show substantial dispersion consistent with hybrid functional calculations which predict significant covalency for PuO_2 compared with the earlier ionic actinide dioxides such as UO_2 . The ARPES, photon energy dependence, and the temperature dependent data for Pu materials will be discussed in terms of 5f adaptive character and the implications for Pu ground state properties.

Work supported by the U.S. Department of Energy, Basic Energy Sciences, the Los Alamos National Laboratory LDRD program, and Campaign II.

10:40am **AC+SS-MoM8 Novel Band Renormalization Mechanism in f-electron Systems**, *T. Durakiewicz, J. Joyce*, Los Alamos National Laboratory, *P.S. Riseborough*, Temple University, *P.M. Oppeneer*, Uppsala University, Sweden, *J.-C. Griveau*, ITU, Germany, *E.D. Bauer*, Los Alamos National Laboratory, *E. Guzikiewicz*, Polish Academy of Sciences, Poland

Several mechanisms may lead to band renormalization in strongly correlated systems. Inter-band scattering was recently shown to produce significant renormalization effects in high temperature superconductors. Here we show, for the first time, that inter-band processes may lead to strong band renormalization in the vicinity of Fermi level in a 5f-electron system, USb_2 . The Fermi surface of this compound consists of several uniaxial cylindrical sheets. We show that the bare band LDA calculation over-counts the number of sheets, because it lacks the renormalization part. But our high resolution angle resolved photoemission (ARPES) experiments demonstrate that one of the calculated cylinders shrinks below the Fermi level, forming a closed cigar-shaped Fermi surface rather than an open cylindrical one. In normal emission experiments, we measure the dispersion of the bands of interest in the Gamma-Z direction. The measured results disagree with the LDA result, but the bare LDA bands can be renormalized by using a low order self-energy expansion in three-band inter-band scattering model, and very good fit is obtained. We conclude that inter-band scattering in USb_2 influences the fermiology of this system in terms of changing the shape and number of Fermi sheets.

11:00am **AC+SS-MoM9 The Initial Oxidation of Polycrystalline Thorium**, *M. Bagge-Hansen, R.A. Outlaw, D.M. Manos*, College of William & Mary

The initial oxidation of clean, polycrystalline α -Th from background CO/CO₂ and saturation of the Th surface by O₂ has been examined in ultrahigh vacuum ($p < 2 \times 10^{-11}$ Torr, H₂) by angle resolved Auger electron spectroscopy (ARAES) and time of flight secondary ion mass spectrometry (ToF-SIMS). Following dissociative adsorption of background CO/CO₂, the accompanying oxygen surface population increased at a rate roughly one third that of the carbon, suggesting significant oxygen incorporation into the bulk. The admission of O₂ following heating and sputter cleaning of the Th, showed similar behavior in that some oxygen atoms continued to diffuse into the bulk until formation of stoichiometric ThO₂ was observed at ~ 37 L. The thickness of the oxide complex was determined by both ARAES and ToF-SIMS and found to be ~ 5 nm. The thermal stability of the ThO₂ over the temperature range of 25 – 1000°C was also studied. Rapid decomposition of the oxide by CO desorption and subsequent oxygen dissolution into the bulk was observed to occur within a temperature range of ~ 550 -750°C.

11:20am **AC+SS-MoM10 The Non-Equilibrium Nature of Uranium Oxide Surfaces**, *R.K. Schulze, D.P. Johnson, M.A. Hill*, Los Alamos National Laboratory

We examine the surface reactions of bulk single crystal uranium oxide (UO₂) and thin films of uranium oxide on metal using Kelvin probe (surface work function and chemical potential) measurements and x-ray and ultraviolet photoelectron spectroscopy. The processes of surface and sub-surface reactions with small gas phase molecules are examined through *in situ* work function measurements (dynamic) while the surface chemistry and configuration are probed with photoemission and LEED measurements (equilibrium). The hyperstoichiometric uranium oxide (UO_{2+x}) is shown to be composed of, in the surface region, labile interstitial oxygen that can be moved relatively easily in and out of the fluorite structure lattice through control of the headspace oxygen activity. The transport of oxygen in this near surface region of the oxide is examined through changes in the surface work function with exposure to various partial pressures of oxygen. The amount of excess oxygen in the oxide lattice of the surface is shown to affect the reactivity of this surface with small gas phase molecules directly. A measurement and description of the band structure of the uranium oxide surface for different levels of oxygen content (UO₃, UO_{2+x}, UO₂, UO_{2-x}) is presented.

11:40am **AC+SS-MoM11 Characterization of the Surface Changes During the Activation of Erbium/Erbium Oxide for Hydrogen Storage**, *M.T. Brumbach, K.R. Zavadil, C.S. Snow, J.A. Ohlhausen*, Sandia National Laboratories

Erbium is known to effectively load with hydrogen when held at high temperature in a hydrogen atmosphere. To make the storage of hydrogen kinetically feasible, a thermal activation step is required. Activation is a routine practice, but very little is known about the physical, chemical, and/or electronic processes that occur during Activation. This work presents *in situ* characterization of erbium Activation using variable energy photoelectron spectroscopy at various stages of the Activation process. Modification of the passive surface oxide plays a significant role in Activation. The chemical and electronic changes observed from core-level and valence band spectra will be discussed along with corroborating ion scattering spectroscopy measurements.

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