

Applied Surface Science

Room 2005 - Session AS+SS-TuM

Environmental Materials and X-ray Spectroscopies

Moderator: D.J. Gaspar, PNNL

8:00am AS+SS-TuM1 Time-of-Flight SIMS in the Earth and Planetary Sciences, E.P. Vicenzi, D. Rost, Smithsonian Institution **INVITED**

Spatially-resolved chemical analysis of geological materials is typically performed by techniques that can best be described as near-surface methods, e.g. electron beam-induced X-ray microanalysis, or, laser ablation ICP-MS. A limited number of studies in recent years made use of legitimately surface sensitive techniques, such as Time-of-Flight Mass Spectrometry. The full mass spectrum imaging capability of ToF-SIMS has proved advantageous for extracting a high information content relative to the amount of sample consumed. The high information/sample mass ratios are particularly beneficial, even demanded in some cases, for the examination of extraterrestrial specimens. Over the past several years we have applied ToF-SIMS to the study of Martian meteorite specimens, particularly the alteration phases that formed in an aqueous environment at low temperatures. Through the analysis of these micrometer to submicrometer structures we have begun to address issues regarding the nature of fluid that flowed beneath the surface of Mars, as well as the number of fluid pulses that infiltrated rocks near the surface of the planet. Although no terrestrial analogues for the Martian meteorites are known, we will present results regarding the redistribution of the ultralight elements Li and B in similar Earth rocks by water-rich fluid alteration. NASA's highly successful STARDUST mission recently (January, 2006) returned the first samples of a comet to Earth, and is providing space science researchers with a first-hand look at some of the oldest material in the solar system. We anticipate receiving aliquots of Stardust from the curation facility at Johnson Space Center in mid 2006 and will report on our initial findings of this ultra-precious material.

8:40am AS+SS-TuM3 Characterization of Thin Films Produced by a Simulated Radioactive Dispersal Device, D.L. Blanchard, Jr., L.A. Snow, G.J. Lumetta, B.J. Cook, Pacific Northwest National Laboratory; F.T. Harper, Sandia National Laboratories

We have examined the surfaces of materials subjected to a simulated radioactive dispersal device (RDD), and find significant differences in the composition of the deposited surface films depending on the material and the distance from the blast. Coupons of aluminum, concrete, and other materials, roughly 1 cm square by 1 mm to 3 mm thick were placed at distances of 5, 10 and 25 feet from the center of the blast. The simulated RDD contained non-radioactive cesium (Cs) as a surrogate for radioactive Cs. X-ray Photoelectron Spectroscopy (XPS) reveals carbon films with incorporated Cs on the surface of the exposed materials. Depth profiling by ion sputtering shows that the thickness of the film, the character of the transition from carbon film to substrate material (abrupt or gradual), and the film composition vary greatly with distance from the blast and the material exposed.

9:00am AS+SS-TuM4 Characterization of Electrocoagulation Wastewater Treatment Floc and Aging Effects, J.A.G. Gomes, D.L. Cocke, H. Moreno, Lamar University; H.G. McWhinney, Prairie View A&M University; G.M. Irwin, E. Peterson, Lamar University

Analysis of contaminated water and the methods of water quality remediation, recycle and reuse are increasingly dependent on materials science. Metal poisoning in drinking water such as As has not only led to a health crises in third world countries such as Bangladesh and Mexico, but also threatens developed countries like the United States. Water dispersed materials containing iron or aluminum hydroxides /oxyhydroxide species can efficiently remove arsenic from water or wastewater. The detailed mechanisms of how this occurs are still being sought. Electrocoagulation (EC) is a very promising technique to produce such materials and remove arsenic and other heavy metals from aqueous media. In this paper, we discuss the characterization of these EC-flocs with and without metal pollutants using different analytical techniques, such as FT-IR, XRD, XPS, SEM/EDS and Mössbauer spectroscopy. Results reveal expected crystalline iron oxides (magnetite (Fe₃O₄), lepidocrocite (FeO(OH)), iron oxide (FeO)) and aluminum oxides (bayerite (Al(OH)₃), diaspore (AlO(OH)), mansfieldite (AlAsO₄·2H₂O)), as well as some interaction between the phases. New insight into the mechanisms of removal and the materials chemistry will be discussed along with the aging effects on the materials and on the compositional ratio of As(III) and As(V) ions in the floc.

9:20am AS+SS-TuM5 Evolution of Metal-Core Oxide-Shell Iron Nanoparticles as a Function of Time in an Aqueous Environment, D.R. Baer, Pacific Northwest National Lab; P.G. Tratnyek, Oregon Health and Sciences Univ.; J.E. Amonette, C.M. Wang, M.H. Engelhard, Pacific Northwest National Lab; Y. Qiang, University of Idaho; J.T. Nurmi, V. Sarathy, Oregon Health and Sciences Univ.; J. Antony, University of Idaho

The high reactivity of metallic iron nanoparticles with contaminants such as chlorinated hydrocarbons, the possibility of solution based delivery to contamination zones and evidence of an ability of the nanostructure to alter reaction pathways have stimulated considerable research into the potential use of iron metal nanoparticles for environmental remediation. As part of our study of the chemical properties of nanoparticles, we are examining how metal-core oxide-shell iron nanoparticles evolve with time in aqueous environments. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and x-ray diffraction (XRD) are used to examine the particles at different times after exposure to water solutions with and without carbon tetrachloride. The influence of formation, processing and analysis conditions on the nature of the core/shell structure has been examined in some detail. The room temperature oxidation of these nanoparticles shows the formation of voids and in some circumstances hollow oxide nanoparticles. Other measurements show that an electron beam damages the oxide shell allowing oxidation to occur in the normal environment of a TEM. Aspects of particle reactivity have been examined by batch reactivity, electrochemical and electron paramagnetic resonance measurements. Studies measuring the reductive dechlorination of carbon tetrachloride (CT) have shown that nanoparticle properties (as well as solution chemistry and other experimental conditions) affect the distribution of products formed. Of particular interest are factors that favor degradation of CT by product formation pathways that do not produce chloroform (CF), which is a persistent and toxic byproduct.

9:40am AS+SS-TuM6 Effects of Dopant Concentration and Microstructures on Ionic Conductivity in Samaria Doped Ceria Thin Films, Z.Q. Yu, Nanjing Normal University; C.M. Wang, M.H. Engelhard, D.E. McCready, V. Shutthanandan, R. Shao, PNNL; P. Nachimuthu, UNLV; O. Marina, I. Lyubinetsky, L.V. Saraf, S. Thevuthasan, PNNL

Recently, samaria doped ceria (SDC) have received much attention in the literature due to its high ionic conductivity and high oxygen ion transport, and they are considered to be the most promising solid electrolytes for the intermediate temperature solid oxide fuel cells (SOFCs). Although SDC materials show promising results, there are controversies regarding the dopant concentration that provide higher values for ionic conductivity. The discrepancies in ionic conductivity are mostly due to different sample preparation methods and the crystalline quality associated with these methods. In addition, high quality single crystal ceria thin film work with dopants is limited in the literature. In this study, we have investigated the ionic conductivity as a function of samarium dopant concentration in high quality samaria doped ceria films that were grown on sapphire (0001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The structural properties of these films were characterized using in situ reflection high energy electron diffraction (RHEED) and exitu glancing angle x-ray diffraction. Thickness along with the compositional analysis was carried out using Rutherford backscattering spectrometry and x-ray photoelectron spectroscopy depth profiling. Microstructures in the films and at the interfaces were investigated by high resolution transmission electron microscopy (TEM) and TEM micrographs show sharp interfaces without grains and film/substrate epitaxial relationship as CeO@sub 2@ (111)// alpha-Al@sub 2@O@sub 3@ (0001) and CeO@sub 2@ [110]// alpha-Al@sub 2@O@sub 3@ [-2110]. Total conductivity measurements clearly show that the conductivity in these films is significantly higher than that in the polycrystalline material with the maximum values for the samarium concentration of 11 cation %. We will discuss these results along with the effects associated with grain boundaries in conductivity in these films.

10:40am AS+SS-TuM9 Getting Atomic-Scale Information from Complex Surfaces using Synchrotron Radiation, D.P. Woodruff, University of Warwick, UK **INVITED**

"Chemical shifts" in core-level photoelectron binding energies are an important feature of conventional laboratory-based x-ray photoelectron spectroscopy (XPS) and indeed are why the technique was originally referred to as ESCA - electron spectroscopy for chemical analysis. For surface studies, however, this ability to exploit XPS chemical shifts is greatly enhanced through the use of modern synchrotron radiation facilities to

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achieve enhanced spectral resolution and surface specificity. There are now many examples of how such core level shifts alone can distinguish and give insight into the nature of adsorbed and coadsorbed species on surfaces. In addition, however, these chemically-shifted photoemission peaks can be used to provide quantitative chemical-state-specific local structural information by using them to monitor photoelectron diffraction and absorption in x-ray standing waves. For both methods the high spectral brightness, tunability, and ability to provide light in the vacuum ultra-violet and soft x-ray ranges are essential features provided only by synchrotron radiation. These capabilities will be illustrated by a small number of case studies of adsorption and coadsorption systems where the ability to distinguish atoms of the same element in different chemical or structural local environments proved essential to understanding the systems.

11:40am AS+SS-TuM12 X-ray Spectrometry with the NIST Transition Edge Sensor Microcalorimeter, *T. Jach, N.W.M. Ritchie, J. Ullom*, National Institute of Standards and Technology

We report on the use of the NIST Transition Edge Sensor Microcalorimeter to obtain high-resolution x-ray spectra over extended energy ranges for materials analysis. The microcalorimeter is a detector with dimensions of $400\ \mu\text{m} \times 400\ \mu\text{m}$ oper deposited by individual photons by means of a resistive sensor ated at a temperature of 70 mK. It detects the energy operating at its superconducting-normal transition. The resolution of the detector is determined by the energy range for which it is designed. Our current detector has demonstrated a resolution of 4.4 eV over an energy range of 7 keV. The spectra were obtained from samples excited by the high-energy electron beam in an electron microprobe. We have performed quantitative analyses on two NIST reference glasses in which we are able to characterize the concentrations of multiple elements to an accuracy of less than 2%. The resolution of the lines in their spectra was such that we are able to identify the transitions in a series and their satellites. In transitions where the initial state is the valence band, our energy resolution is starting to allow identification of features in the density of states. We foresee detectors which will permit the chemical identification of species in x-ray fluorescence similar to what is now done with ESCA, but without the need for ultra high vacuum.

12:00pm AS+SS-TuM13 Dynamical XPS Measurements, *A. Dana, S. Suzer*, Bilkent University, Turkey

Photoelectron spectra of a clean silicon sample and another one containing 10 nm oxide layer are recorded while the sample rod is subjected to 10.0 V square pulses with varying frequencies in the range of 0.001 to 1000 Hz to probe the dynamical response of the samples. For the clean silicon sample the Si2p(Si0) peak is twinned and appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) at all frequencies measured. However, although the Si2p (Si4+) of the oxide is also twinned, the measured difference between the peaks is smaller than 20.0 eV and exhibits a strong frequency dependence due to charging of the oxide layer. The frequency dependence of the oxide layer can be experimentally simulated by the clean silicon tied through an external RC circuit. The frequency dependent shifts of the peaks, their broadening, and other related experimental parameters can be reproduced by modeling the various currents involved as a voltage controlled current source to yield a powerful extension of XPS for dynamical measurements of charging/discharging processes of surface structures. As a simple application of the technique we will show that the two O1s components, which can be assigned to SiOx and TiOy domains in a composite film, exhibit different dynamical behavior. Other applications fro probing dielectric properties of various surface structures will be presented and discussed.

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