Applied Surface Science Division
Room 6A - Session AS-WeA

Oxides and Insulators

Moderator: C. Pantano, Pennsylvania State University

2:00pm **AS-WeA1 The Pleasure and Pain of Working with Insulators***, **D.R. Baer**, S.A. Chambers, G.C. Dunham, M.H. Engelhard, S.A. Joyce, A.S. Lea, T.M. Orlando,* Pacific Northwest National Laboratory **INVITED**

The detailed understanding of the surface properties of insulating materials is considerably less well developed then that for metals and semiconductors. Some of the reasons for this include the difficulty in getting clean well defined surfaces, the fact that many analysis methods use beams that damage the materials and complications in data collection and analysis due to charge buildup on the samples. The good news is that these materials are very interesting, they are technologically and environmentally important and not as many people are examining them as other materials. Even for analysis of "real" materials and solving applied problems, understanding damage processes, having relevant "reference" spectra, and appropriately dealing with charging effects can mean the difference between success or failure. This presentation will describe some of our research interests involving insulating materials along with a selection of the problems (some with solutions) we have encountered. The presentation will give some examples of deliberate and unintentional beam damage, consequences of heating surfaces, creating and observing defects, methods to prepare "good" and "bad" surfaces, handling charging on difficult materials, and consequences of ion depth profiling. Materials to be discussed will include oxidized forms of Ti, Fe, Pb, Al, and Mg. Examples will include uses of AES, XPS, MBE, and SPM. This work is supported by the Division of Geosciences, Office of Science, U. S. Department of Energy and most of the research performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

2:40pm **AS-WeA3 Surface Segregation in NixCo(1-x)O and MnxCo(1-x)O Solid Solutions***, **M.A. Langell**,* University of Nebraska*; M.W. Nydegger,* Pace Analytical Corporation*; F. Gevrey,* Univ. Framche Comte, France*; G. Couderc,* Univ. Lyon, France

Because of the similarity in crystal structure and compatible nature of their cations, many transition metal oxides systems are miscible over a wide range of composition. For these systems, the bulk structure was investigated by powder x-ray diffraction as early as the mid 1940's, and they are generally observed to follow Vegard's law. We have measured the surface composition of two rocksalt monoxide systems, NiO/CoO and MnO/CoO, which form bulk homogeneous solid solutions over the entire range M@subx@Co@sub(1-x)@O (M =Ni or Mn) of 0@<=@x@<=@1. Surface analysis has been performed with Auger and x-ray photoelectron spectroscopy, the latter of which also provides information on the chemical nature of the cations at the surface of the solid solution. Unlike the bulk material, the surface of both systems shows distinct evidence for segregation of one cation at the expense of the other and appears to be related to the formation of a spinel phase. In the case of the NiO/CoO system the spinel composition is NiCo@sub2@O@sub4@, and for the MnO/CoO system the composition agree with the spinel CoMn@sub2@O@sub4@. Information is also obtained on the octahedral and tetrahedral site occupancy of the cations and on their formal oxidation states.

3:00pm **AS-WeA4 Dynamics of CO Adsorption on O-ZnO: a Molecular Beam Study***, Th. Becker, Ch. Boas, **U. Burghaus**, Ch. Woell,* Ruhr-Universität Bochum, Germany

We present measurements of the initial adsorption probability, S@sub 0@, as well as its coverage dependence, S(@THETA@@sub CO@), of CO on oxygen terminated ZnO(0001) surfaces. Two different substrates with significantly different density of defects, as determined by He atom scattering, were investigated. Using a well defined molecular beam of CO seeded in He the He atom reflectivity could be monitored simultaneously with the flux of backscattered CO molecules. These results allow to separately determine the total sticking coefficient averaged over the whole surface (using the King and Wells method) and the sticking coefficient on flat terraces. Measurements were carried out for different impact energies (48 meV < E@sub i@ < 0.74 eV) and surface temperatures (77 K < T@sub s@ < 800 K). The crystallographic structure and chemical composition of the surfaces have been characterized by LEED, He atom scattering, and XPS. The shape of the S(@THETA@@sub CO@,T@sub s@) curves points to a precursor mediated adsorption, since, for medium (100 - 180 K) surface temperatures S(@THETA@@sub CO@) remains approximately constant up to saturation coverage, @THETA@@sub sat@. For low adsorption temperatures (70 - 90 K) a rather unique shape of S(@THETA@@sub CO@) has been observed, namely an increase of S(@THETA@@sub CO@) with @THETA@@sub CO@ followed by an abrupt decrease when approaching @THETA@@sub sat@. S@sub 0@ is essentially independent of T@sub s@ and decreases linearly with E@sub i@, consistent with a precursor-mediated adsorption and a decreasing probability of adsorption into the precursor state, respectively. The results indicate that the presence of defects does affect the CO sticking probability.

3:20pm **AS-WeA5 Compositional Heterogeneity in Cerium-Based Mixed Oxides Observed by XPS***, **G.W. Graham**,* Ford Motor Company, US*; C.L. Roe,* GE Lighting Division*; L.P. Haack, A.M. Straccia,* Ford Motor Company

It is argued that compositional heterogeneity in certain reducible mixed oxides, like Ce@sub1-x@Zr@subx@O@sub2@, can be inferred from a variation in the metals ratio, as measured by XPS, between fully oxidized and partially reduced states of the oxide, provided that the characteristic linear dimension of the heterogeneity is at least as large as the typical electron inelastic mean free path. The argument is supported by experimental results from two examples involving mixed phases, one in which the length scale is 100 nm and the other in which the domains are too small for detection by standard x-ray diffraction.

3:40pm **AS-WeA6 The Formation of Magnesium Oxide Layer using the MgO Precursor Solution and its Secondary Electron Emission***, **J.H. Lee**,* Samsung Advanced Institute of Technology, Korea*; T.W. Jeong,* Myong Ji University, Korea*; S.G. Yu, H.W. Son, S.H. Jin, W. Yi, Y.S. Choi,* Samsung Advanced Institute of Technology, Korea*; D. Jeon,* Myong Ji University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

The thin layer magnesium oxide having a secondary electron emission coefficient (@delta@) value over 5 is obtained by a spin coating of the MgO precursor solution. The solutions are prepared as an aqueous base using magnesium formate and poly vinly alcohol, or as an organic base using magnesium acetate in 1,3-propanediol which is polymerized by magnesium methoxide. Alkali metal ions including Cs ion are doped by dissolving metal formate or acetate salts additionally in the above solutions. The firing condition, 450 C for 2 hours, is determined by the thermogravimetric analysis data of the dried bulk solution. The XRD measurement of the powder from a firing of the bulk solution at this temperature confirms the MgO crystal structure. The MgO films on Si(100) or ITO glass substrates prepared by a spin coating at 4000 rpm for 40 sec followed by firing at 450 C for 2 hours result in the thickness of 300 Å with a good roughness for a @delta@ value over 5. The doping effect of alkali metal ions of the MgO film is discussed on the regards of the secondary electron emission. The surface morphology and composition are characterized by SIMS, AFM, and SEM. This method allows an easy processing approach with a relatively high @delta@ value, as well as a variety of application into many kinds of structural device such as a microchannel plate with high aspect ratio.

4:00pm **AS-WeA7 Reactivity of Formic Acid (HCOOD and DCOOH) at Uranium and UO2 Surfaces***, **M.T. Paffett**, W.L. Manner,* Los Alamos National Laboratory

Interactions of DCOOH and HCOOD with uranium and UO2.0 surfaces have been examined using surface specific techniques of thermal desorption mass spectroscopy (TDMS), x-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectroscopy (SSIMS). Formic acid dissociates on both surfaces below 100 K to yield surface formate in relatively high yield. On the clean uranium surface a wide range of products are observed after annealing to 200 K which include formate, hydroxyl, and C-Hx (C-Dx,), Oads, and Hads(Dads) groups. Adsorbed formate decomposes by 300 K increasing the concentration of the remaining surface products (especially C-Hx (C-Dx) type moieties). The only gaseous species created in high yields from the clean surface upon annealing are H2, HD, and D2. A small amount of water and methane desorb at higher temperatures. Between 100 and 300 K the predominant species on the UO2.0 surface is surface formate and hydroxyl groups. The presence of surface oxygen stabilizes the formate groups to further dissociation in comparison to the clean uranium surface. Hydroxyl groups react between 300 and 350 K to release water from the surface. Adsorbed formate groups decompose between 400 and 500 K to release CO, COH2 (COD2) groups. Carbon was not detected on the surface by XPS after annealing to 500 K indicating that all carbon containing species either desorb in the form of CO-containing products or dissolve into the surface.

4:20pm **AS-WeA8 Characterisation of Ceramics Thin Films Deposited by Plasma Assited CVD***, **G. Ceccone,*** European Commission Joint Research Centre, Italy*; P. Colpo,* European Commission, Joint Research Centre, Italy*; M. Baker, P.N. Gibson, P. Sauvageot, F. Rossi,* European Commission Joint Research Centre, Italy

The use of ceramics in biomedical applications has received large attention during the last two decades. In particular, ceramics and glasses have important applications as orthopedic and dental implants. However, since most of bioactive ceramics and glasses are relatively brittle they have to be applied as a coating on high-strength material such as titanium. In this paper, we report the possibility to depositing zirconia coatings by using Inductively Coupled Plasma Assisted CVD technique. Deposition have been performed in a cylindrical ICP reactor from tetra (tert-butoxy)-zircon precursor diluted in argon and oxygen. A 13.56 MHz generator was used for sustain the plasma, whilst the substrate negative bias voltage was controlled by an independent RF generator. The coating microstructural characteristics were investigated by SEM/EDX; XRD was used to assess the coating crystal structure, whereas the coating composition and stoichiometry was investigated by AES and XPS. The mechanical properties of the films have been assessed by nanoindentation and scratch tests. Zirconia coatings having a thickness between 1 and 10µm, and with a maximum hardness of 13GPa have been deposited under different plasma conditions. Correlation between the deposition parameters, such as the gas composition, RF biases, and RF power, and coating properties have been investigated. AES measurements indicate that films having a stoichiometric composition can be deposited over a large range of gas composition, whilst the crystalline structure and mechanical properties of the film are strongly dependent on the ion bombardment energy. The possibility of tailoring the coating characteristics by controlling the ion energy, i.e. the substrate negative bias is presented and discussed.

4:40pm **AS-WeA9 XPS and UPS Characterization of Single Crystal NaNO@sub 3@ and NaNO@sub 2@: Influence of Laser Irradiation at 248 nm***, **C. Bandis**, S.C. Langford, J.T. Dickinson,* Washington State University

Inorganic nitrates are susceptible to radiation damage, including laser and x-ray irradiation. The critical role of radiation induced chemistry is studied utilizing monochromatised X-ray photoelectron spectroscopy (XPS) and He II (40.8 eV) ultraviolet photoemission spectroscopy (UPS). Photoelectron emission from single crystal NaNO@sub 3@ and NaNO@sub 2@ cleaved and laser or x-ray irradiated surfaces shows that the observed changes in the spectra due to laser irradiation are similar with those observed due to X-ray exposure. Our observations suggest that in both cases (laser and X-ray irradiation) the NaNO@sub 3@ decomposition is initiated by the pi-pi* transition in the NO@sub 3@@super -@ anion. Direct comparison of our experimental UPS and XPS valence band electron energy distributions with recent calculations of the total density of states shows good agreement between theory and experiment for both NaNO@sub 3@ and NaNO@sub 2@. We also report on the influence of such surface modification on the laser desorption of ions and neutrals from cleaved NaNO@sub 3@ single crystal surfaces. This work was supported by the Department of Energy (DE-FG03-98ER14864) and the National Science Foundation (DMR-9503304).

5:00pm **AS-WeA10 Surface Defects on Amorphous Aluminum Oxide Films as Corrosion Initiation Sites***, **K.R. Zavadil**, J.C. Barbour, K.-A. Son,* Sandia National Laboratories

The surface activity of chloride ions is viewed as one parameter responsible for corrosion initiation and subsequent breakdown of native aluminum oxide films on aluminum surfaces. One approach to understanding the role of chloride, as well as other corrosion initiators and inhibitors, is to study the surface of tailored oxides that mimic the properties of naturally occurring passive oxides on aluminum. We generate amorphous oxides ranging from tens to hundreds of angstroms thick by exposing electron beam deposited Al films to an O@sub2@ electron cyclotron resonance (ECR) plasma. Surfaces defects in the form of oxygen vacancies are generated at low energy doses of both electron (electron stimulated desorption) and ions (preferential O sputtering). A comparison is made between the activity of vapor phase and solution phase H@sub2@O and Cl at the defective oxide surface by conducting vacuum and solution experiments with a contiguous electrochemical cell. Irradiation and hydration effects are tracked using a combination of Auger electron and x-ray photoelectron spectroscopies as well as temperature programmed desorption. We show that vacancies are active toward vapor phase Cl sorption resulting in surface Cl concentrations of 10@super13@ to 10@super14@ atoms×cm@super-2@. Cl is desorbed from these vacancies at temperatures below 570 K and is displaced by H@sub2@O vapor at room temperature. Defective surfaces show a greater susceptibility to corrosion as measured by a lowering in the pitting potential in 50 mM NaCl solutions. The role of the vacancies in solution appears to be an increase in surface charge resulting in enhanced Cl@super-@ sorption. We find measurable increases in surface oxygen for defective, hydrated alumina surfaces consistent with a surface charge increase. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

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