

Applied Surface Science Division

Room 307 - Session AS-MoA

Oxides and Insulators - Surface Characterization and Applications

Moderator: R.E. Davis, IBM Corporation, East Fishkill Facility

2:00pm AS-MoA1 Aqueous Leachability of Single Crystal and Polycrystalline Calcium Titanate, Z. Zhang, E.R. Vance, Australian Nuclear Sci. and Tech. Organisation, Australia

Calcium titanate (CaTiO_3) constitutes about 20% of Synroc-C, a titanate-based ceramic designed for the immobilization of high level nuclear waste from Purex-type reprocessing. The chemical durability of calcium titanate in an aqueous environment is, therefore, an important issue. We have investigated the aqueous leachability of both single crystal and polycrystalline CaTiO_3 primarily using X-ray Photoelectron Spectroscopy (XPS). Static leaching tests were conducted in doubly deionized water at room temperature (RT), 90°C and 150°C for various periods of time. A reduction in the surface concentration of Ca (with respect to Ti) was observed after all leaching tests. The calcium leach rate of single crystal CaTiO_3 is found to be slightly lower than that of polycrystalline CaTiO_3 at all leaching temperatures. For both single crystal and polycrystalline samples, the calcium leach rate increases with increasing leaching temperature: the leach rate at 90°C is slightly higher than that at RT, while the leach rate at 150°C is substantially higher than that at 90°C. The effect of surface cation impurities, resulting from thermally induced segregation from the bulk, on the leaching behavior will be discussed. Other techniques employed in the study include Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) of CaTiO_3 surfaces before and after leaching tests, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Emission Spectroscopy (ICP-AES) of the leaching solutions. These results will also be shown.

2:20pm AS-MoA2 XPS Investigations of the Chemistries of Soils, T.L. Barr, E.E. Hoppe, S. Hardcastle, University of Wisconsin, Milwaukee; S. Seal, University of Central Florida

The present study continues our XPS or ESCA investigations of silicate systems, particularly those in contact with biological materials. In the present case the investigations are extended to a detailed analysis of a wide variety of soil samples extracted from different locations around the world. The samples were selected from relatively pristine sites, pressed into wafers, and were examined without further modification. All of the materials were insulators and therefore analysis required extensive use of the electron flood gun. Careful XPS chemical shift arguments have been achieved for many silicate minerals. These have been exploited in the present study along with the detailed XPS analysis of organo-functional groups rendered by Beemson and Briggs. As a result a fairly detailed simultaneous non-destructive description is provided of both the humus and silt components of these soil samples. Substantial variations in the composition are demonstrated and questions are raised about our classifications of fertility.

2:40pm AS-MoA3 Problems in Surface Characterization of Oxides and Insulators, J. Cazaux, University of Reims, France

INVITED

Most of the oxides are insulators in which charging effects and radiation damage effects often coexist when they are investigated with incident particles. In electron irradiated insulators, charge phenomena result from a competition between the secondary electron emission which contributes to a positive charging and the trapping of incident electrons which tends the specimen to be negatively charged. The initial charge distribution (and the electric field it induces) may be estimated but self regulation processes rapidly take place. The final state equilibrium is difficult to predict because it is a function of the nature and of the density of trapping centers that may pre-exist or that are induced by the irradiation and then negative charging may be observed at primary beam energies where a positive charging is expected from the total yield approach. Various specific mechanisms may be involved in the chemical change of irradiated insulators and most of them are electric field dependent. There is first the migration of the mobile species driven by the electric field build-up. There is also the dissociation of some electron/hole pairs generated by the transport of energetic (photo) electrons. The third cause of damage results from the ionization of core electrons followed by (intra or inter atomic) Auger transitions. Each transition finally leaves the excited atom with two electrons missing and the lack of conduction electrons (in insulators) prevents the initial charge of this atom or of its surroundings to be quickly restored. Halogen ions change

sign while O^{2-} ions become neutral and they may be desorbed into the vacuum when they are located close to the surface. Examples of microscopic (Electric image effects and Schottky barrier lowering) and macroscopic (electric field function) calculations will be given. These calculations are supported by a significant number of recent experimental results. Practical consequences to minimize these effects or to take benefit of them (nanolithography ; controlled surface modifications) will be suggested

3:20pm AS-MoA5 ESCA Depth Profiling of Insulating Thin Film Structures, J.S. Hammond, J.F. Moulder, D.J. Hook, Physical Electronics, Inc.; H.M. Dunlop, Pechiney, Centre de Recherches de Voreppe, France

Recent advances in ion gun technology have allowed ESCA to surpass AES as the routine, quantitative depth profiling technique for thin film structures. To effectively utilize the potential of ESCA to provide chemical state information, accurate and reproducible charge neutralization for insulating and mixed insulator/conductor samples is required. Results will be presented comparing traditional, floating, and biased sample mounting techniques, to obtain an optimized process for reproducible, stable charge referencing. Depth profiling data will be presented from doped aluminum oxide thin films, architectural glass coatings, and silicon ONO thin films. Only by using the optimized charge neutralization approach can subtle acid-base chemistry in the aluminum oxide films and chemical states in the oxidized silicon films be elucidated.

3:40pm AS-MoA6 Quantification of Nitrogen in Silicon Oxynitride Thin Films by XPS, J.R. Shallenberger, D.A. Cole, Evans East, US; S.W. Novak, Evans East

There has been a considerable effort in the past several years to incorporate nitrogen into oxides in order to improve the electrical properties of ultra-thin (2-10 nm) gate oxides. The nitrogen in-depth distribution, concentration and local bonding all affect the electrical properties of the dielectric layer. To date at least five different nitrogen environments have been reported in the XPS literature. All have the general formula: $\text{N}(\text{Si})_x(\text{O})_y(\text{H})_z$, where $x+y+z = 3$ and $x \leq 3$, $y \leq 1$, $z \leq 2$. This paper focuses primarily on determining the concentration (to a detection limit of 1×10^{13} atoms/cm²) and local coordination of nitrogen in oxynitrides by XPS. Both Secondary Ion Mass Spectrometry and Nuclear Reaction Analysis are used as complementary tools for quantifying nitrogen; SIMS is also used to determine the in-depth N distribution.

4:00pm AS-MoA7 XPS Characterization of Nitrogen Profile and Chemical States in Ultrathin Silicon Oxynitrides, J.P. Chang, M.L. Green, V.M. Donnelly, R.L. Opila, Bell Laboratories, Lucent Technologies

Continuous scaling of the gate dielectric thickness to $\approx 40 \text{ \AA}$ makes X-ray photoelectron spectroscopy (XPS) a viable technique for analyzing the composition and stoichiometry of a thin film and its interface with silicon, since the film thickness is comparable to the escape length of photoelectrons. Photoemission of various species is acquired at different take-off angles, and the maximum entropy method is employed to convert the angular dependent photoemission intensities to compositions as a function of depth. Angular resolved XPS (ARXPS) analysis permits nondestructive characterization of the nitrogen profile and interfacial compositions of ultrathin silicon oxynitride films grown by furnace oxidation. The incorporation of nitrogen in SiO_2 improves the electrical reliability and prevents boron penetration. In this work, nitric oxide (NO) and oxygen gases have been used to engineer the nitrogen profile in SiO_2 films. With furnace growth at 800°C, 1-4 at. % of nitrogen can be incorporated in the ultrathin ($\approx 40 \text{ \AA}$) oxide films. Additional nitrogen can be incorporated by plasma ion nitridation. The nitrogen profile and nitrogen chemical bonding states are analyzed as a function of the depth to understand the mechanism of nitrogen incorporation during the NO/ O_2 thermal growth process. Reoxidation of a thermal oxide grown in NO leads to a peak nitrogen concentration at the upper oxide interface, ideal to prevent boron penetration. Annealing of thermal oxide in NO leads to a peak concentration of nitrogen at the SiO_2/Si interface. Nitrogen bonds primarily to silicon at low total nitrogen content (1-4 at. %), but also bonds to oxygen at higher total nitrogen content. The improved reliability as determined by charge to breakdown (Q_{bd}) measurement will be correlated with compositions and stoichiometry of the bulk film and its interfaces. The mechanism of nitrogen incorporation in NO or plasma ion nitridation will be discussed. @FootnoteText@ @footnote 1@G. C. Smith and A. K. Livesey, Surf. and Interface Anal. 19, 175 (1992). @footnote 2@N. Layadi, V. M. Donnelly, and J. T. C. Lee, J. Appl. Phys., 81, 6738 (1997).

Monday Afternoon, November 2, 1998

4:20pm **AS-MoA8 Ultra Shallow Depth Profiling by ESCA and SIMS**, *J.F. Moulder, S.R. Bryan*, Physical Electronics, Inc.

The next generation of semiconductor devices will contain shallow implants and other ultra thin structures. SIMS has been the traditional choice for analysis of these ultra thin layers. Because of the nature of these layers, significant challenges are being encountered in the interpretation and quantification of the SIMS data from them. A shallow 250eV boron implant for example, resides completely within the native oxide at the surface of a silicon wafer, complicating quantification by SIMS. ESCA depth profiles obtained with low energy ions (100-500V) and shallow photoelectron take-off angles provide quantitative chemical state information from these ultra thin film structures. ESCA and SIMS data will be presented from shallow boron implants and thin silicon oxy-nitride (ONO) structures. The data suggests that ESCA depth profiles may be very useful for calibrating and interpreting SIMS depth profiles of these ultra thin film structures.

4:40pm **AS-MoA9 Valence Band X-ray Photoelectron Spectroscopic Studies to Distinguish Between Oxidized Aluminum Species**, *J.A. Rotole, P.M.A. Sherwood*, Kansas State University

The determination of the detailed chemical nature of oxidized aluminum species is an essential requirement for the study of many important practical aspects of aluminum metal. While thick oxidized films on aluminum metal can be easily characterized by X-ray powder diffraction when the films are crystalline, thin amorphous films are very difficult to characterize. In this paper a study of the valence band X-ray photoelectron spectrum of aluminum oxides, hydroxides and oxyhydroxides is reported using monochromatized aluminum K α X-radiation. The valence band spectra obtained are shown to have significant differences for different oxidized aluminum species, and a spectrum that can be well understood by calculations. The calculated spectra are generated by cluster calculations using multiple scattered wave X α calculations, together with spectra generated by band structure calculations. This study compliments earlier published studies from this research group using achromatic radiation, and the use of monochromatized X-radiation can be seen to allow a more conclusive distinction between the oxidized aluminum species.

5:00pm **AS-MoA10 Influence of Mg on the Oxide Formation on Al**¹, *D.R. Baer, C.F. Windisch, Jr., M.H. Engelhard, M.J. Danielson*, Pacific Northwest National Laboratory

In an effort to increase the strength of lightweight, non-heat treatable Al alloys, Mg is a common alloy addition. However, particularly due to changes in alloy structure and chemical distribution during processing and welding, these alloys can be susceptible to grain boundary dissolution, stress corrosion cracking or hydrogen induced cracking. In an effort to understand the influence of Mg segregation and second phase formation on the electrochemical behavior and corrosion behavior of Al, we have exposed freshly cleaned surfaces of Al, Mg-implanted Al and Al₃Mg₂ to a salt solution. These cleaned surfaces are moved to the solution through a transfer system that exposes the cleaned specimens only to vacuum or a nitrogen environment (with some water vapor) before immersion into the salt solution. The open circuit corrosion potential is measured for each sample. After a short exposure, the specimens are quickly rinsed with clean water, pumped to vacuum conditions and moved into a spectrometer for XPS analysis. Specimens are also analyzed by SEM imaging and AES in a different spectrometer. Measurements show that Mg influences the corrosion potential of the material and changes the nature of the film. When Mg is present in the alloy at levels of approximately 4 at%, the oxides that form are no longer smooth but rumpled. The outer oxide that formed during solution exposure contains no observable Mg, but regions below this alumina layer are rich in oxidized Mg. This film is compared to those that form on pure Al and the beta phase Al₃Mg₂.
¹This research was conducted at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) with funding provided by the U.S. Department of Energy, Office of Basic Energy Sciences. The EMSL is a new DOE scientific user facility located at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. PNNL is operated by Battelle for the Department of Energy.

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