## Thursday Afternoon, October 5, 2000

#### Surface Science Room 208 - Session SS1+MC-ThA

### **Oxidation and Molecule-Oxide Interactions**

Moderator: S.A. Joyce, Pacific Northwest National Laboratory

## 2:00pm SS1+MC-ThA1 Real Time TEM Observations of the Oxidation of Silicon, F.M. Ross, IBM Research Division INVITED

By making real-time observations of the progressive changes occurring at the silicon/oxide interface during oxidation, it is possible to examine the mechanism of the reaction and accurately measure the oxidation kinetics. In this presentation we will describe experiments carried out in a UHV transmission electron microscope which has been modified to allow images to be obtained before, during and after oxidation. By careful choice of imaging conditions we can follow the motion of the silicon/oxide interface in real time during oxidation, and in particular we can observe the configuration of interface steps. Our experiments show that passive oxidation, in which SiO@sub 2@ is formed, occurs in a layer-by-layer fashion with no flow of interface steps. Active oxidation is also a terrace reaction, although the SiO which is formed evaporates preferentially from surface steps. We will briefly discuss how the observation and analysis of step and terrace contrast is a powerful tool for examining the mechanism of other silicon surface reactions, such as epitaxial growth or silicide formation, as well as oxidation.

#### 2:40pm SS1+MC-ThA3 Comparison of Electrochemical Corrosion Properties and Oxidation Kinetics of Ozone- and Oxygen-formed Aluminum Oxide Films, A. Kuznetsova, I. Popova, V. Zhukov, G. Zhou, J.C. Yang, J.T. Yates, Jr, University of Pittsburgh

Ozone, O@sub 3@, has been employed to produce an aluminum oxide layer (thickness about 20 Å), on Al(111)and also on polycrystalline Al surfaces. It has been found, by electrochemical impedance spectroscopy, that the impedance of such films is about 10 times higher than films grown to similar thickness with O@sub 2@.Transmission electron microscopy studies have shown that the average pore size of Al@sub 2@O@sub 3@ films grown with O@sub 3@ (20 Å) is smaller than in films grown with O@sub 2@ (100 Å). In addition, electron diffraction studies of amorphous film have shown that the density of oxide film grown with O@sub 3@ is 10% greater than for oxide films grown with O@sub 2@. Thus the enhanced corrosion passivation properties of O@sub 3@-grown aluminum oxide films may be caused by the reduction of defect site density when O@sub 3@ is used.

#### 3:00pm SS1+MC-ThA4 Temperature Dependent Adsorption of Oxygen on TiO@sub 2@ (110): A Photoemission Study, H. Geisler, Xavier University of Louisiana; E.L.D. Hebenstreit, W. Hebenstreit, M. Li, U. Diebold, Tulane University; S.N. Thornburg, C.A. Ventrice, Jr., University of New Orleans; D.A. Hite, P.T. Sprunger, CAMD/ Louisiana State University

The Titanium dioxide (110) surface is one of the most thoroughly studied metal oxide systems. One of the primary reasons for this interest is the fact that TiO@sub 2@ is easily reduced by annealing in vacuum. During the annealing process, oxygen vacancies and titanium interstitial are created, which can increase the conductivity of the substrate sufficiently to allow characterization with electron and ion spectroscopies. In order to heal the surface region, the reduced crystals are exposed to oxygen at various temperatures and pressures. To determine the effect of oxygen adsorption on the electronic structure of reduced TiO@sub 2@ crystals, angular resolved photoelectron spectroscopy (UPS) measurements have been performed in conjunction with scanning tunneling microscopy (STM) measurements. STM indicates that the adsorption of oxygen on TiO@sub 2@ (110) at temperatures above 400 °C or below 200 °C results in an unreconstructed surface. However, adsorption between 200 °C and 400 °C results in a rosette-like structure that represents an incomplete restructured TiO@sub 2@ (110) surface with coordinatively unsaturated surface atoms.@footnote 1@ UPS measurements of the vacuum-annealed, reduced TiO@sub 2@ surface show emission from a defect state centered at approximately 1 eV below the Fermi level. The onset of emission from the TiO@sub 2@ valence band occurs ~3 eV below the Fermi level. After dosing oxygen at room temperature the defect state disappears with only slight modifications to the valence band structure. On the other hand, UPS spectra from the rosette- structured surface show an enhancement of the emission from the defect state and strong modifications of the TiO@sub 2@ valence band emissions. @FootnoteText@@footnote 1@ M. Li, W. Hebenstreit, L. Gross, et al., Surf. Sci. 437, 173-190 (1999)

3:20pm SS1+MC-ThA5 Water Reactions at Plutonium Oxide: Surface Chemistry, J.D. Farr, R.K. Schulze, M.P. Neu, L.A. Morales, Los Alamos National Laboratory

We have examined the surface chemistry of water at both monolithic and high surface area plutonium oxide using Auger and X-ray photelectron spectroscopy (AES and XPS). This work investigates the chemical reactions at the Pu oxide surfaces, primarily to help address issues that are critical for plutonium stabilization and 50-year storage. Interactions between PuO@sub 2@ particles and the adsorbed water vapor play a dominant role in potential catalytic gas generation reactions. Understanding the chemistry at this interface, particularly with respect to reactions with water and water vapor is crucial for predicting the storage behavior of Pu oxide powders. XPS indicates that water adsorbs initially at active sites to form surface hydroxyls groups. Upon saturation of these sites and at substantially higher exposures, particularly with high surface area oxides, the water adsorbs in molecular form as part of the surface layer. Heating the oxide to 200°C in vacuum results in removal of the adsorbed water and partial removal (conversion) of the hydroxyl. Above 400°C the oxide surface continues to undergo a transformation and the removal of hydroxyl is largely complete at 600°C. The tenacious nature of these surface groups suggests that most of the active sites at the surface are irreversibly saturated at room temperature and up to a temperature in excess of 200°C, with some of them irreversibly saturated up to 600°C, or greater. The surface reaction will be discussed in the context of reaction energetics for the active sites at the PuO@sub 2@ surface.

3:40pm SS1+MC-ThA6 Studies of Water Plasma Treatments on Silicon Oxide Films, N.A. Alcantar, University of California, Santa Barbara; T.L. Kuhl, University of California, Davis; A. Stacy, J. Au, E.S. Aydil, J.N. Israelachvili, University of California, Santa Barbara

Chemically active oxide surfaces can react with polymers to enhance their surface properties. Surfaces covered with polyethylene glycol have been shown to reject biological attack and protein adhesion. We activate silicon dioxide (i.e., silica) films by exposing them to water vapor plasma. These activated films are then reacted with polyethylene glycol (PEG, OH-(CH@sub 2@-CH@sub 2@-O)@sub n@-H) to make them biocompatible. We have characterized silica films prepared by plasma enhanced chemical vapor deposition (PECVD) before and after water plasma activation. We found that water plasma treatments chemically and physically modify the silica surface. For instance, water plasma fully saturates the silica surface with hydroxyl groups, significantly reduces their surface roughness without affecting the thickness of the deposited films and increases their cohesion force. This surface modification was monitored by in situ real time attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Other characterization techniques such as ellipsometry, atomic force microscopy (AFM), surface forces apparatus (SFA) and contact angle measurements were utilized to fully establish the effects of this surface modification. The optimal water plasma parameters for creating smooth, chemically reactive silicon oxide films were also obtained.

#### 4:00pm SS1+MC-ThA7 The Nature of Oxygen at Rocksalt and Spinel Oxide Surfaces, M.A. Langell, J.G Kim, S. Chapman, H.Y. Xu, University of Nebraska

The chemical environment of oxygen in mixed metal oxides with compositions M@subx@M'@sub(x-1)@O and M@subx@M'@sub(3x-1)@O@sub4@, (M, M' = Li, Mn, Fe, Ni, Co) has been studied by Auger electron spectroscopy, x-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy. While there is a single type of lattice oxygen in the bulk structure of simple rocksalt and spinel oxides, the nature of oxygen at the surface of the mixed-metal oxide materials is considerably more complex. Photoemission from core oxygen states in these materials often shows multiple peaks and satellite structure which have been attributed to a range of intrinsic and extrinsic oxygen states. Mixed-metal oxides form an ideal set of systems to investigate the nature of the lattice oxygen through their ability to tailor cation oxidation state and site occupancy within the crystal structure and thus affect the chemical environment of the lattice oxygen. All of these 3d transition metal oxides show a single, intense O1s core photoemission peak at approximately 529.6 eV. However, a second peak is often observed at about 1-1.5 eV higher binding energy, depending upon the types and distribution of the cations, and the history of the substrate surfaces. Surface hydroxylation, cation clustering and final state effects in the photoemission mechanism can all contribute to the O1s photoemission process and will be discussed in view of the data obtained for the mixed-metal oxides.

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4:20pm SS1+MC-ThA8 Direct Observation of Native Hydrogen Adatoms on Rutile TiO@sub 2@(110) Surface, *T. Fujino, K. Inudzuka, T. Okuno, M. Katayama, K. Oura,* Osaka University, Japan

Titanium dioxide (TiO@sub 2@) surface has received considerable attention because TiO@sub 2@ is the material of photocatalyst such as the photodecomposition of water. Over the past few years a considerable number of studies have been made on the analysis of rutile TiO@sub 2@(110) surface composition and structure. Most of these studies were conducted using microscopic techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). However, the information of hydrogen atoms adsorbed on TiO@sub 2@(110) surface seems to be lacking because it is difficult to detect the surface hydrogen using STM or AFM. In the present study, we have investigated the structure and composition of the rutile TiO@sub 2@(110) using coaxial impact collision ion scattering spectroscopy (CAICISS), time-of-flight elastic recoil detection analysis (TOF-ERDA) and low energy electron diffraction (LEED). CAICISS and TOF-ERDA have been proved to be useful techniques for in situ observation of surface structure and composition, in particular, for the determination of the amount of surface hydrogen atoms. When the sample was introduced into ultra high vacuum (UHV) chamber without any treatments, a large quantity of hydrogen and oxygen atoms adsorb on the surface. These atoms can be attributed to water molecules. After annealing the sample at 800°C in UHV, the clean surface of TiO@sub 2@(110) with the LEED pattern of a sharp 1x1 spots was obtained. It was found from the CAICISS measurement that this surface formed bulk terminated structure, known as bridging oxygen rows model. However, it was also found from the TOF-ERDA measurement that the hydrogen atoms still resided on the surface. These hydrogen atoms are not components of water molecules but directly chemisorb on the TiO@sub 2@(110)1x1 surface. Thus, native hydrogen adatoms on the TiO@sub 2@ surface was directly observed and evidenced. Detailed results will be discussed in the presentation.

# 4:40pm SS1+MC-ThA9 Work Function Changes and Surface Chemistry of Oxygen and Hydrogen on Indium Tin Oxide, J.A. Chaney, P.E. Pehrsson, Naval Research Laboratory

Indium tin oxide (ITO) is used as a transparent, semiconducting substrate for many device applications. However, there is an inadequate understanding of ITO surface properties, its interaction with gaseous species, and the physical/electronic changes imposed by its surface chemistry. The surface physics and chemistry of oxygen plasma treated ITO were investigated under ultra high vacuum conditions. The work function (@PHI@) of ITO was determined by a vibrating Kelvin probe calibrated with a graphite standard. Sample composition, electronic structure and chemistry were examined by Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). Commercial ITO films were heated in-vacuo to remove physisorbed species and then exposed in-situ to oxygen or deuterium activated with a hot metal filament. Oxidation increased the work function from 5.2 to 5.6 eV, but @PHI@ then decayed to <5.2 eV, possibly due to oxygen diffusion into the bulk along defects and grain boundaries. The AES oxygen level was stable after oxidation, and the ELS spectrum consistently showed a strong feature at 0.7 eV for oxidized samples. Deuteration visibly metallized the film and sharply reduced the surface oxygen level. The ELS feature simultaneously disappeared, and the work function decreased to 4.6 eV. The HREELS of clean ITO revealed substantial C-H contamination, which persisted after heating to ~300°C. Even substantial oxygen treatment did not remove the hydrogen signal, suggesting that C-H permeates the ITO film.

# 5:00pm SS1+MC-ThA10 Adsorption of Atomic Hydrogen on Both Polar Surfaces of ZnO, *Th. Becker, M. Kunat, Ch. Boas, U. Burghaus, C. Wöll,* Ruhr-University Bochum, Germany

The interaction of atomic hydrogen with Zn-ZnO and O-ZnO surfaces has been investigated by LEED, He atom scattering, He atom reflectivity measurements (as a function of H exposure and surface temperature, T@sub s@), and XPS. Furthermore, measurements of adsorption probabilities of CO on the two polar surfaces of ZnO are presented (see [1] for CO/O-ZnO) as well as the effect of pre-exposed atomic hydrogen on the adsorption dynamics of CO. He atom diffraction measurements indicate the formation of a well ordered H overlayer structure. The strong attenuation of the specular He atom reflectivity by hydrogen exposure indicates, however, a second competing reaction pathway; since extensive exposure to atomic hydrogen leads to a high degree of disorder on the surface. Values for the heat of adsorption for H were estimated from He-atom reflectivity curves, measured as a function of T@sub s@. The shape of the coverage dependent adsorption probability curves, S(@theta@gsub Thursdeu Afterneen October 5, 2000 CO@), of CO are for both surfaces consistent with a precursor mediated adsorption; adsorbate assisted adsorption dominates the adsorption. The He atom reflectivity measurements point to the influence of an intrinsic precursor state. A comparison of He atom reflectivity with S(@theta@@sub CO@) curves, respectively, showed that CO initially populates defect sites. The coadsorption of H and CO can be explained by a site blocking mechanism; leading to an estimate of @theta@esub H@. [1] Th. Becker, Ch. Boas, U. Burghaus, Ch. Wöll, Phys. Rev. B 61(7) (2000) 4538.

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