

Surface Science

Room 328 - Session SS2-FrM

Oxide Surfaces and Interfaces

Moderator: R.L. Kurtz, Louisiana State University

8:20am SS2-FrM1 Desorption Induced by Electronic Transitions (DIET) from a Lunar Sample and a Model Mineral Surface*, B.V. Yakshinsky, T.E. Madey, Rutgers University

We report recent results on an investigation of source mechanisms for the origin of alkali and alkaline earth atoms in tenuous planetary atmospheres, with focus on non-thermal processes (photon stimulated desorption (PSD), electron stimulated desorption (ESD), and ion sputtering). Whereas alkaline earth oxides (MgO, CaO) are far more abundant in lunar samples than alkali oxides (Na₂O, K₂O), the atmosphere of the Moon contains easily measurable concentrations of Na and K, while Ca and Mg are undetected there; traces of Ca have recently been seen in the Mercury's atmosphere (10¹⁰ of Na). Our experiments have included ESD, PSD and ion sputtering of alkali atoms from model mineral surface (amorphous SiO₂) and from a lunar basalt sample obtained from NASA. A comparison is made between ESD and PSD efficiency of monovalent alkalis (Na, K) and divalent alkaline earths (Ba, Ca). We find that bombardment of the alkali covered surfaces by ultraviolet photons or by low energy electrons ($E > 4$ eV) causes desorption of "hot" alkali atoms. This results are consistent with the model developed to explain our previous measurements of sodium and potassium desorption from a silica surface: electron- or photon-induced charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. A two-electron charge transfer to cause desorption of divalent alkaline earth atoms is a less likely process. A striking reversible temperature-dependent variation of PSD and ESD yields of alkalis from the lunar sample is found; these data have important implications for models of tenuous planetary atmospheres. The data support the suggestion that PSD by UV solar photons is a dominant source process for alkalis in the tenuous lunar atmosphere. * supported in part by NASA footnote 1@ BVY TEM, Nature (1999) 400, 642@ footnote 2@ BVY TEM, Surf. Sci.(2003) 528, 54.

8:40am SS2-FrM2 Temperature Dependence of the Noncommutative Valence Band Offset at α -Cr₂O₃/ α -Fe₂O₃ Epitaxial Heterojunctions, J.R. Williams, S.A. Chambers, Pacific Northwest National Laboratory

The valence band discontinuity at α -Cr₂O₃/ α -Fe₂O₃ interfaces in epitaxial heterojunctions grown on α -Al₂O₃ (0001) substrate has been measured as a function of deposition temperature. A prior study, conducted at a given temperature, showed a noncommutative band offset of -0.3 ± 0.1 and $+0.7 \pm 0.1$ eV in this system when the top layer is Fe₂O₃ and Cr₂O₃ respectively. This was attributed to an interface dipole that presumably depends on the growth sequence. In this study deposition temperatures of 500°C to 850°C have been investigated, and preliminary results show that this noncommutative band offset is largely independent of deposition temperature. This is an unexpected result, as the interface dipole is expected to change with deposition temperature due to interfacial mixing. Specifically we find that the binding energy difference between the Cr 3p and Fe 3p shallow core levels remains at 11.85 ± 0.08 eV (12.36 ± 0.20 eV) for structures with Fe₂O₃ (Cr₂O₃) as the top layer, and that these values are independent of deposition temperature. RHEED analysis of these structures shows that in all cases the Fe₂O₃ layer is unstrained, while the Cr₂O₃ layer is strained to match the lattice parameter of Fe₂O₃. This work was supported by U.S. DOE BES Department of Chemical Sciences.

9:00am SS2-FrM3 Electronic Structure at the Fe₃O₄/NiO Interface@footnote 1@, H.Q. Wang, W. Gao, E.I. Altman, V.E. Henrich, Yale University

The interfacial electronic structure between the metallic ferrimagnet Fe₃O₄ and the insulating antiferromagnet NiO has been investigated in the heteroepitaxial system Fe₃O₄/NiO (100) by growing from submonolayer to multilayer films of NiO (100) on single-crystal Fe₃O₄ (100) substrates. The lattice

mismatch in this system is only 0.55 %, and excellent superlattice structures have been grown previously by other groups. The presence of tetrahedral Fe³⁺ ions lying above the plane of O anions and octahedral Fe cations on Fe₃O₄ (100) results in unusually short Fe-Ni cation-cation distances in the stoichiometric interface structure with rocksalt NiO. The Fe₃O₄ surface prior to growth is characterized by LEED, RHEED and STM; both the (1x1) and (2x2)R45° surface reconstructions have been studied. The NiO growth morphology is measured with STM. The electronic structure is monitored versus overlayer thickness by using UPS, XPS, Auger and EELS spectroscopies, which were chosen because they sample several monolayers (ML) into the substrate/overlayer structure. The overlayer thickness dependence of spectral features is then used to separate interfacial states from those of the substrate and the overlayer film. The evolution of the density-of-states in the O 2p-Fe 3d-Ni 3d band has been observed during the first few ML of NiO deposition. Changes occur across the entire band (from E_F to about 12 eV below E_F). For NiO layers thicker than about 3 ML, the overlayer electronic structure is essentially that of bulk NiO. @FootnoteText@ @footnote 1@ This research was partially supported by U.S. Department of Energy Grant DE-FG02-00ER45844; and NSF equipment grant DMR-0075824.

9:20am SS2-FrM4 Understanding Fermi Level Pinning of SiO on GaAs(001)-(2x4), D.L. Winn, M.J. Hale, A.C. Kummel, University of California, San Diego

Scientists have been trying to develop a metal oxide semiconductor field-effect transistor (MOSFET) with GaAs in an effort to reduce standby power and gate leakage. In order to fabricate this device, it is important to understand the chemistry and physics at the oxide/semiconductor interface. It has been reported that a common cause of Fermi level pinning is the liberation of As, resulting from oxides bonding to Ga atoms on the surface. This has been directly observed using STM to monitor the reactions of O and O₂ on GaAs(001)-(2x4). In contrast, we have shown that SiO pins the Fermi level but does not liberate As when it is deposited on the GaAs(001)-(2x4) surface. Scanning tunneling microscopy (STM) images show that SiO inserts into the As dimers. SiO bonds in both trough and row dimers with a very small minority of the SiO molecules inserting into As-Ga backbonds. Using scanning tunneling spectroscopy (STS), we have observed that ~5% of a monolayer of SiO pins the Fermi level on GaAs(100)-(2x4) at mid-band gap. This is consistent with the SiO adsorbates withdrawing charge from the surface As atoms, causing charge on the As atoms to grossly deviate from the charge on bulk As atoms.

9:40am SS2-FrM5 Surface Phase Transitions Upon Reduction of WO₃(100) Thin Films, M. Li, E.I. Altman, A. Posadas, C.H. Ahn, Yale University

The evolution of surface morphology and reconstructions induced by reducing epitaxial WO₃(100) thin films grown on LaAlO₃(100) was studied using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). When the WO₃(100) surface was annealed in either O₂ or NO₂ at 620 K, the surface was predominantly covered by a p(2x2) reconstruction with a low density of elongated (1x1) islands. Raising the annealing temperature to 800 K led to a net reducing environment even in the presence of O₂ or NO₂. Under these conditions, the surface was dominated by a two domain p(4x2)/p(2x4) reconstruction, although a few small patches of the p(2x2) surface could still be detected. Further annealing at 800 K in oxygen led to the appearance of p(3x2) domains on the p(4x2) dominated surface and a more diffuse p(4x2) LEED pattern. The surface was exclusively populated by a p(3x2) reconstruction upon annealing in UHV above 800 K while a p(3x2) LEED pattern could also be observed. After further annealing in UHV above 800 K, (1x1) islands appeared on the surface and the p(3x2) LEED pattern became more diffuse. The (1x1) area increased with annealing time in UHV and eventually exclusively (1x1) terminated terraces with straight steps due to crystallographic shear planes were observed. The STM images of the p(4x2) and p(3x2) surfaces were dominated by 0.1 nm deep troughs separating bright rows with 4x and 3x spacings respectively between rows. The appearance of the rows was sensitive to the imaging bias with a 2x periodicity along the rows seen at high biases and a 1x periodicity at low biases. These results could be explained by a structural model based on incomplete (1x1) terraces that form as reduced W⁵⁺ ions migrate from the surface into the bulk.

10:00am SS2-FrM6 First Principles Calculations of the ZrO₂/Ni(111) Interface, J. He, S.B. Sinnott, University of Florida; E.C. Dickey, Pennsylvania State University

We report on first principle calculations of the equilibrium geometries, interfacial energies, and work of separation for the O- and Zr-terminated

Friday Morning, November 7, 2003

Ni(111)/cubic-ZrO₂(100) interfaces. The approach is density functional theory using the generalized gradient approximation combined with nonlocal, norm-conserving and ultrasoft pseudopotentials. The polar ZrO₂ surface slab is non-stoichiometric to remove artificial electric fields. Consequently, while the work of separation is relatively straightforward to calculate, determination of the interfacial energies depends on the chemical potentials of the system. The manner in which the oxygen and zirconium chemical potentials are calculated will be discussed. The results show the way in which the preferred termination, and thus the interfacial structure, depends on oxygen partial pressure. These results are helpful to better understand the nature of the bonding at metal-ceramic interfaces and to predict the atomistic structure and stoichiometry of the equilibrium interface at various environmental conditions. This work is supported by the NSF (DMR-9976851).

10:20am **SS2-FrM7 In situ-STM Experiments at Elevated Temperature (475K) on Growth, Atomic and Electronic Structure of Thin NiO Films on Ag(001)**, Ch. Hagendorf, H. Neddermeyer, Martin-Luther-University, Germany

New results will be presented on the growth behaviour as well as atomic and electronic structure of thin NiO films on Ag(001) by using scanning tunneling microscopy (STM) and spectroscopy (STS) at elevated temperatures. NiO films were deposited with a thickness of up to 3 monolayers by evaporation of Ni in an O₂ atmosphere of 10⁻⁶ mbar. Deposition and heating of the NiO films were followed by in situ-STM measurements which allowed us to identify the various stages of the growth mode. A (1x2) reconstruction is observed at substrate temperatures of less than 475 K and submonolayer coverages. They show a transition to (1x1) double layer NiO(001) after completion of the first monolayer. Only the latter one exhibits a pronounced bias dependent contrast reversal. The electronic structure of Ag(001), NiO(001) and the NiO precursor has been mapped using I(V)-STS at elevated temperatures and will be discussed in reference to results obtained on CoO /Ag(001). At coverages of more than one double layer areas with metallic behaviour are identified using STS. This indicates the formation of Ag islands in a height of several monolayers by segregation. Th. Bertrams et al., J. Vac. Sci. Technol. B 14 (1996), 1141. Ch. Hagendorf et al., Surf. Sci. (2003), in press.

10:40am **SS2-FrM8 Low Temperature Oxidation of Nitrided Surfaces**, J. Torres, C.C. Perry, S.J. Bransfield, D.H. Fairbrother, Johns Hopkins University

The oxidation of transition metal nitride coatings is an important process because the resultant oxidized interface plays a crucial role in determining the interfacial properties of these materials as well as their durability in extreme environments. The oxidation of iron nitrides, in particular, has received little attention despite its importance as a magnetic coating in the recording industry. In the present study, X-ray Photoelectron Spectroscopy (XPS), Reflection Absorption Infrared Spectroscopy (RAIRS) and Mass Spectrometry (MS) were used to probe the low temperature (< 150 K) oxidation of nitrided iron surfaces exposed to oxygen and water. By carrying out the reactions at these low reaction temperatures, new pathways and intermediates have been identified. During the exposure of nitrided iron surfaces to oxygen, iron oxynitride (Fe_xN_yO_z), nitrosonium ions (NO⁺) as well as nitrite(nitrito) and iron oxide(hydroxide) species were observed. Upon prolonged oxygen exposures, nitrate species were formed in the oxidized overlayer indicative of an O-insertion mechanism into the iron nitride lattice, a process that has not been observed in previous studies of nitride oxidation. In contrast to oxygen, the reactivity of nitrided iron surfaces towards water was limited to the production of adsorbed N-O species and iron oxide(hydroxide). No molecular nitrogen was produced during reactions with oxygen or water in contrast to oxidation studies on other transition metal nitrides. Upon annealing the oxidized overlayer from 150 K to 600 K, nitrogen desorbs exclusively as nitric oxide (NO) between 250-400 K, leaving a surface film of iron oxide on top of the iron nitride.

11:00am **SS2-FrM9 Surface Characteristics of the Remote Plasma-treated ITO**, S. Kim, H. Seo, Hanyang University, Korea; Y. Kim, Pusan National University, Korea; K. Kim, Y. Tak, LG Electronics; H. Jeon, Hanyang University, Korea

Indium tin oxide (ITO) is an essential material in fabrication of organic light emitting devices (OLEDs). ITO functions as a hole injector into organic material and the injection efficiency is influenced by the work function of ITO anode surface. Work function of the ITO surface primarily depends on carbon and oxygen concentration. Particularly, carbon contaminants of ITO

surface should be removed as much as it could be, because it results in the defect of bonding structure and increases in the sheet resistance of ITO. We investigated the removal of surface carbon contaminants using the oxygen and hydrogen plasma and examined the change of chemical composition and electrical properties of ITO after plasma treatments. ITO film was coated on glass to a thickness of about 1600 Å and had a sheet resistance of about 10 Ω/□. And these ITO glass specimens were not pre-cleaned before plasma cleaning to demonstrate effects using plasma treatments only. The remote RF plasma cleaning chamber and the surface analysis system were connected each other by an ultra-high vacuum transfer system for the in-situ analysis. The carbon residues were almost removed below the detection limit of XPS after remote plasma cleaning at 50W. In XPS analysis for Sn3d_{5/2}, Two peaks were completely resolved. These resolved peaks indicated respectively Sn²⁺ and Sn⁴⁺. The peak intensity of Sn⁴⁺ was reduced on ITO surfaces which was treated by plasma. Work function on ITO surface increased by oxygen plasma treatment and decrease by hydrogen plasma treatment. It also showed that the oxygen concentration affected much more than carbon contamination at the work function of the ITO surfaces. Y. Yu, X.D. Feng, D. Grozea, and Z. H. Lu, R. N. S. Sodhi, A-M. Hor and H. Aziz, Appl. Phys. Lett., 78, 2595-2597 (2001).

11:20am **SS2-FrM10 Temperature Dependent Water Adsorption on BSCCO Single Crystal**, X.F. Hu, D.A. Human, C.J. Hirschmugl, University of Wisconsin-Milwaukee

Infrared Reflection adsorption spectroscopy and Temperature Programmed Desorption studies of water adsorption on the surface normal to ab-plane of BSCCO single crystal reveal the molecular adsorption of water. The monolayer and multilayer desorption temperature is approximately 167 K. The absorption bands occur between 3200-3500 cm⁻¹ for the OH stretching, suggesting hydrogen bonding. The OH stretching bands change their absorption signatures as a function of temperature. For 2 L exposure, one asymmetric broad band is observed at approximately 3350 cm⁻¹ at 80 K, and becomes symmetric at 140K. At 150K, less water is adsorbed, exhibiting a sharper feature at 3250 cm⁻¹ with both high and low frequency shoulders. Below 140K, the adsorbed water forms clusters, and above 150K, it forms clusters with more bulk-like character.

Author Index

Bold page numbers indicate presenter

— A —

Ahn, C.H.: SS2-FrM5, **1**
Altman, E.I.: SS2-FrM3, **1**; SS2-FrM5, **1**

— B —

Bransfield, S.J.: SS2-FrM8, **2**

— C —

Chambers, S.A.: SS2-FrM2, **1**

— D —

Dickey, E.C.: SS2-FrM6, **1**

— F —

Fairbrother, D.H.: SS2-FrM8, **2**

— G —

Gao, W.: SS2-FrM3, **1**

— H —

Hagendorf, Ch.: SS2-FrM7, **2**

Hale, M.J.: SS2-FrM4, **1**

He, J.: SS2-FrM6, **1**

Henrich, V.E.: SS2-FrM3, **1**

Hirschmugl, C.J.: SS2-FrM10, **2**

Hu, X.F.: SS2-FrM10, **2**

Human, D.A.: SS2-FrM10, **2**

— J —

Jeon, H.: SS2-FrM9, **2**

— K —

Kim, K.: SS2-FrM9, **2**

Kim, S.: SS2-FrM9, **2**

Kim, Y.: SS2-FrM9, **2**

Kummel, A.C.: SS2-FrM4, **1**

— L —

Li, M.: SS2-FrM5, **1**

— M —

Madey, T.E.: SS2-FrM1, **1**

— N —

Neddermeyer, H.: SS2-FrM7, **2**

— P —

Perry, C.C.: SS2-FrM8, **2**

Posadas, A.: SS2-FrM5, **1**

— S —

Seo, H.: SS2-FrM9, **2**

Sinnott, S.B.: SS2-FrM6, **1**

— T —

Tak, Y.: SS2-FrM9, **2**

Torres, J.: SS2-FrM8, **2**

— W —

Wang, H.Q.: SS2-FrM3, **1**

Williams, J.R.: SS2-FrM2, **1**

Winn, D.L.: SS2-FrM4, **1**

— Y —

Yakshinskiy, B.V.: SS2-FrM1, **1**