Tuesday Afternoon, October 26, 1999

Surface Science Division Room 606 - Session SS1+EM-TuA

Oxides: Growth and Structure

Moderator: E.G. Seebauer, University of Illinois, Urbana

2:00pm SS1+EM-TuA1 Noncommutative Band Offset at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@(0001) Heterojunctions, S.A. Chambers, Y. Liang, Pacific Northwest National Laboratory

We have measured the valence band discontinuity at artificially structured, epitaxial heterojunctions of @alpha@-Cr@sub 2@O@sub 3@(0001) and @alpha@-Fe@sub 2@O@sub 3@(0001) grown on @alpha@-Al@sub 2@O@sub 3@(0001) substrates. Oxygen-plasma-assisted molecular beam epitaxy was the growth technique, and band offsets were measured by core-level and valence-band photoemission. Layered film structures of these two materials maintain the in-plane lattice parameter of @alpha@-Fe@sub 2@O@sub 3@(0001). Thus, the @alpha@-Cr@sub 2@O@sub 3@(0001) layers are under a 2.3% tensile stress. The valence band offsets are 0.3 ± 0.1 eV and 0.7 ± 0.1 eV when the top layer is Fe@sub 2@O@sub 3@ offset appears to be due to a growth-sequence-dependent interface dipole caused by different extents of intermixing for the two kinds of interfaces.

2:20pm **SS1+EM-TuA2 Ultrathin Iron Oxide Films**, *R.L. Stockbauer*, *J. Karunamuni, A. Koveshnikov, R. Madjoe, R.L. Kurtz*, Louisiana State University

Thin films of spin polarized conductors are receiving increased attention as potential contacts for devices such as spin-valves and high-sensitivity disk sensors. We have succeeded in producing ultra thin films of FeO and Fe@sub 3@O@sub 4@ and characterized their morphology using STM and LEED. The oxides are grown by depositing thin films of Fe on a Cu(100) surface at room temperature. The Cu substrate has terraces ca. 100Å wide with steps perpendicular to the [010] direction. The Fe grows layer-by-layer in islands uniformly distributed on the Cu terraces. The oxides are formed by heating to 840K in 10@super -6@ Torr O@sub 2@. The change in the morphology of the surface after oxidation is truly striking. At low Fe coverage (<2ML), FeO completely rearranges the Cu substrate. Large terraces up to 1µm wide are now observed. The FeO itself forms long stripes typically $0.2\mu m$ wide and up to $10\mu m$ long parallel to the [011] direction. Shorter stripes are observed in the perpendicular direction. The FeO stripes display two superstructures. A coarse structure consists of a series of dark bands parallel to the stripe direction and spaced at 360Å intervals. The fine structure is a 20.5Å hexagonal pattern. A comparison of LEED data and simulations indicates that the overlayer is FeO(111) with stripes aligned along the [110] directions. Oxidizing Fe films thicker than 2ML results in the oxide phase of device interest, Fe@sub 3@O@sub 4@. These patches show a 170Å banded structure and the same size hexagonal superstructure but rotated 30° from that observed for the FeO . LEED data, simulations, and thermochemistry are consistent with the overlayer being Fe@sub 3@O@sub 4@(111) rotated 15° from the [001] azimuth. Surprisingly, these highly oriented oxide films do not show strong angular dependence in photoemission. MOKE, circular dichroism, and spin polarized measurements are underway to determine the magnetic properties of the oxide films.

2:40pm SS1+EM-TuA3 Islanding, Facetting, and the Lattice Relaxation in the Growth of @alpha@-Fe@sub 2@O@sub 3@ on @alpha@-Al@sub 2@O@sub 3@, S.I. Yi, Y. Liang, S. Thevuthasan, S.A. Chambers, Pacific Northwest National Laboratory

The growth of @alpha@-Fe@sub 2@O@sub 3@ on c- and r-oriented @alpha@-Al@sub 2@O@sub 3@ by oxygen-plasma-enhanced molecular beam epitaxy has been investigated with reflection high-energy electron diffraction, non-contact atomic force microscopy, X-ray photoelectron spectroscopy, X-ray photoelectron diffraction, low-energy electron diffraction, and high-energy ion scattering. The epilayer is facetted due to compressional stress on the c-plane during growth of the first two monolayers. The epilayer structure is significantly distorted, with considerable in-plane strain. However, the film exhibits a constant Fe 2p binding energy with respect to the O 1s binding energy for all thicknesses, revealing the growth of phase-pure @alpha@-Fe@sub 2@O@sub 3@ throughout. A growth-mode transition begins at approximately two monolayers from strained wetting layer to the formation of clusters of rhombohedral islands when a relatively slow growth rate of 1 Å/min is used. However, this transition occurs over several monolayers at a growth temperature of 400 @super o@C. A film with high structural order and orientational stability grows as the islands coalesce to form new and larger terraces. This transition to island-mediated growth can be kinetically impeded for higher growth rates of 0.1-0.3 Å/sec.@footnote 1@ In contrast, the growth-mode transition will occur more rapidly if temperatures of 450 to 500 @super o@C are used along with the slower growth rate. However, sustained growth at temperatures in excess of 500 @super o@C results in the simultaneous formation of Fe@sub 3@O@sub 4@ (111) and/or @gamma@-Fe@sub 2@O@sub 3@ (111) along with @alpha@-Fe@sub 2@O@sub 3@(0001). In contrast to growth in the cplane, the epilayer shows only facetted growth on the r-plane, regardless of the deposition rate and substrate temperature. This result may be due to the lower surface symmetry of the r-plane compared to the c-plane. @FootnoteText@ @footnote 1@ S. I. Yi, Y. Liang, S. A. Chambers, to be published in JVST A, Jul/Aug, 1999

3:00pm **SS1+EM-TuA4 Surface Reconstructions of Fe@sub 3@O@sub 4@(001)**, *B. Stanka, W. Hebenstreit,* **U. Diebold**, Tulane University; *S.A. Chambers*, Pacific Northwest National Laboratory

We have investigated the structural changes to the Fe@sub 3@O@sub 4@(001) surface which are induced by different sample treatments. The samples consisted of ~5000 Å thick films of Fe@sub 3@O@sub 4@(001), grown with oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) on MgO(001) substrates. To study the surface termination, structure, morphology, and composition, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), low energy He@sup +@ ion scattering (ISS), and x-ray photoelectron spectroscopy (XPS) were used. A (@sr@(2) x @sr@(2))R45° reconstruction relative to bulk-terminated Fe@sub 3@O@sub 4@ is induced by heating in oxygen (10@sup -6@ - 10@sup -7@ mbar) at temperatures between 250°C and 500°C after a through-air transfer from the MBE chamber. Our STM results show an appearance consistent with a B-layer termination, which consists of a layer of octrahedrally coordinated Fe and tetrahedrally coordinated O, along with one O vacancy per unit cell. This surface is autocompensated, or charge neutral, and is therefore expected to be stable. Further annealing in UHV causes a transformation to either a (1 x n) or a (2@sr@(2) x @sr@(2))R45 structure. In both cases, a (@sr@(2) x @sr@(2))R45 reconstructed surface can be regained reproducibly by annealing in oxygen. Interestingly, at no time do we observe the other autocompensated termination, which consists of one-half monolayer of tetrahedrally coordinated Fe(III), despite its observation in other laboratories. Thus, it appears that the surface termination is critically dependent on the method of surface preparation.

3:20pm SS1+EM-TuA5 The Surface Structure of @alpha@-Al@sub 2@O@sub 3@(0001) Studied by LEED, C.F. Walters, Sandia National Laboratories; E.A. Soares, M.A. Van Hove, Lawrence Berkeley National Laboratory; K.F. McCarty, Sandia National Laboratories

The surface structure of @alpha@-Al@sub 2@O@sub 3@(0001) has been investigated using normal-incidence low-energy electron diffraction. High quality sapphire samples were produced by ex-situ annealing in air, followed by in-situ cleaning using atomic deuterium at an elevated sample temperature. To investigate the possible occurrence of different surface structures and/or stoichiometries, the samples were processed, subsequent to the atomic deuterium cleaning, using several different procedures. These included annealing the sample in oxygen, and exposing the cooled sample to atomic deuterium. The experimental data were compared to results of calculations performed using an automated tensor LEED program. Several different models were used as the starting point for the analysis. These included termination by: an oxygen layer, a single aluminum layer, a double aluminum layer, and a "hydroxyl" covered single aluminum layer. Additionally, we have analyzed mixtures of these terminations, with the mixtures including different species, as well as the same species but containing different crystallographic planes (i.e., terraced surfaces with fractional unit cell step heights). For each sample preparation, the best structural model was determined via an analysis of the Pendry R-factor that took into account the effect of the additional fitting parameters for the models containing mixed terminations. The bestfit models derived from the tensor LEED analysis will be discussed with respect to the preparation method used, as well as compared to the results of recent first-principles calculations. This work supported by USDOE-OBES-Division of Materials Sciences.

Tuesday Afternoon, October 26, 1999

3:40pm SS1+EM-TuA6 Formation of Epitaxial Al@sub 2@O@sub 3@ on Ni@sub 3@Al(111) Studied by STM, HREELS, UPS, @DELTA@@PHI@, and LEED, A. Rosenhahn, J. Schneider, J. Kandler, T. Pelster, Universität Bonn, Germany; R. Linke, Eindhoven University of Technology, The Netherlands; C. Becker, K. Wandelt, Universität Bonn, Germany

The formation of oxides on the Ni@sub 3@Al(111) single crystal surface has been studied in the temperature range from 300K to 1000K by STM, HREELS, UPS, @DELTA@@PHI@, and LEED. The experiments reveal a strong temperature dependence of the structure and the chemical composition of the resulting oxides, which is caused mainly by a rising aluminum mobility with increasing temperature. Adsorption of oxygen at room temperature creates a disordered surface which appears rough in STM images and shows a diffuse LEED pattern. At 600K STM images show patches of different appearance on the alloy surface. At low coverages the small oxidic nuclei possess a triangular shape, and HREELS measurements show a Al@sub 2@O@sub 3@-like composition. At higher coverages two areas with different appearance can be distinguished in STM, accompanied by the observation of mixed Ni/Al-oxide vibrations in HREELS. At 800K STM measurements show highly ordered triangular shaped oxidic islands. A moiré structure can be observed which corresponds to a superstructure due to an unrotated single O/Al overlayer, that has also been found by LEED and HREELS measurements. The electronic structure of the film being very similar to that of O/Al(111). Adsorption at 1000K finally leads to the growth of an oxidic film, that proceeds from steps exclusively. The oxide exists in two rotational domains that can be detected in LEED and STM. Both HREELS and UPS measurements show the formation of a Al@sub 2@O@sub 3@-doublelayer. Only at this temperature the chemical order of the underlying Ni@sub 3@Al(111) substrate is completely restored.

4:00pm SS1+EM-TuA7 Surface Structure Determination of Yttrium-Stabilized ZrO@sub 2@(001) Surface Using X-Ray Photoelectron Diffraction, S. Thevuthasan, S.I. Yi, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; T.T. Tran, S.A. Chambers, C.H.F. Peden, Pacific Northwest National Laboratory

The physical and chemical properties of oxide surfaces are strongly influenced by several structural properties. As such, there is a growing interest in determining surface termination and relaxation in single crystal oxides. The yttrium-stabilized ZrO@sub 2@(001) surface can in principle be either O terminated or Zr terminated. However, neither of these surfaces is autocompensated as a (1x1) structure. The Zr terminated @sr@2x@sr@2)R45@super o@ reconstruction is autocompensated. It was recently reported that the CeO@sub 2@(001)surface, which is similar to ZrO@sub 2@(001), is terminated with 0.5 monolayers of oxygen.@footnote 1@ We have carried out low-takeoff-angle x-ray photoelectron diffraction (XPD) measurements using Zr 3d, Y 3d and O1s core levels on a oxygen-plasma-cleaned ZrO@sub 2@(001) surface to determine the surface structure. Low-energy electron diffraction data show broad (1x1) spots that are characteristic of many oxide surfaces, and no half-order spots are visible. Currently single and multiple scattering simulations and R-factor analysis are being performed using model clusters generated using both O and Zr terminated surfaces. Preliminary analysis indicates that the surface is Zr terminated with the first layer spacing contracted by 23% relative to the bulk interlayer spacing. Detailed analysis is in progress and results will be presented at the meeting. @FootnoteText@ @footnote 1@G.S. Herman, Phys. Rev. B Rapid Comm. (in press). Work supported by the U.S. Department of Energy (DOE), Offices of Basic Energy Sciences, Division of Chemical Sciences and the DOE's Environmental Management Science Program.

4:20pm SS1+EM-TuA8 Epitaxial Growth and Characterization of Zirconium-Doped CeO@sub 2@(111) Thin Films on Yttria-Stabilized Zirconia(111), T.T. Tran, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; S. Thevuthasan, G.S. Herman, Pacific Northwest National Laboratory

Doning of the ceria lattice with 7r has been shown to enhance the oxygen storage capacity and the rate of oxygen release, and thus the catalytic properties of noble metals supported on these oxides.@footnote 1@ The ability to obtain a detailed knowledge of the effect of the surface structure and zirconium doping levels on oxygen exchange rates requires high-quality single crystalline materials. In a previous study, pure and Zr-doped CeO@sub 2@(001) thin films were grown on SrTiO@sub 3@(001).@footnote 2@ Due to the good lattice match and identical crystal structure, yttria-stabilized zirconia (YSZ) was chosen as the substrate for the growth of CeO@sub 2@(111) in this study. Both pure and Zr-doped CeO@sub 2@(111) thin films were grown on YSZ(111) by oxygen-plasmaassisted molecular beam epitaxy. After deposition, the films were compositionally and structurally characterized by in-situ reflection highenergy electron diffraction (RHEED), low-energy electron diffraction (LEED), x-ray photoelectron diffraction (XPD), and x-ray photoelectron spectroscopy (XPS), as well as by ex-situ Rutherford backscattering spectrometry. RHEED, LEED, and XPD results indicated that the materials are well-ordered at the surface for zirconium doping levels up to 40%. Furthermore, a +4 oxidation state was confirmed for both Zr and Ce using XPS. RBS results showed that Zr was found to incorporate substitutionally at cation sites in the ceria lattice. @FootnoteText@ @footnote 1@ P. Fornasiero, G. Balducci, J. Kaspar, S. Meriani, R. Di Monte, and M. Graziani, Catal. Today, 29, 47 (1996); Hamada, H., Catal. Today, 22, 21 (1994); Ozawa, M., M. Kimura, and A. Isogali, J. Alloys Comp., 193, 73 (1993). @footnote 2@ Y. Gao, G.S. Herman, S. Thevuthasan, C.H.F. Peden, and S.A. Chambers, J. Vac. Sci. Technol. (in press).

4:40pm SS1+EM-TuA9 Structure and Dynamics of KTaO@sub 3@(001) via Elastic and Inelastic Helium Atom Scattering@footnote 1@, J.A. Li, T.W. Trelenberg, E.A. Akhadov, S.A. Safron, J.G. Skofronick, Florida State University; L.A. Boatner, Oak Ridge National Laboratory

Although bulk KTaO@sub 3@ is considered an incipient ferroelectric which remains cubic at all temperatures, He diffraction on the (001) surface, cleaved in situ, shows reconstruction of the (1x1) surface to (2x1). The surface behavior, however, seems to depend on its thermal history as, for example, in the following observations: 1)After the sample is cleaved at about 300K and cooled to about 190K, He diffraction reveals a (1x1) surface which appears to be stable indefinitely. 2) If the target is then warmed from 190K to about 220K, reconstruction to the (2x1) phase takes place gradually over a period of about 2 days, whereas if it is warmed to about 260K, the (2x1) phase becomes evident after about 3 hours. 3)When the target is instead taken from 190K to approximately 60K and then to about 260K, the (2x1) surface is apparent immediately. 4)Restoration to (1x1) can be achieved (a) in a few hours or (b) immediately by warming the surface to about 330K or to about 360K, respectively. In addition, there is considerable hysteresis in the intensities of the He diffraction spots for the (2x1) surface over the thermal cycle from 260 K to 50 K to 260 K. Helium time-of-flight (TOF) spectra were obtained to determine the surface phonon dispersions of the (1x1) and (2x1) surfaces for several surface temperatures between 80K and 300K. These appear very similar over the entire surface Brillouin zone. The dominant peaks in the TOF spectra correspond to a dispersionless mode at about 13.5meV, which stiffens slightly as the temperature is raised. However, the lowest energy branch which is quite flat at low temperatures seems to soften near the zone center as the temperature increases. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

5:00pm SS1+EM-TuA10 Deposition of Highly Oriented Mg@sub 3@(VO@sub 4@)@sub 2@ Thin Films for Use in Catalysis Studies, J.A. Ruffner, A.G. Sault, Sandia National Laboratories

Magnesium vanadates are potentially important catalytic materials for the conversion of alkanes to alkenes via oxidative dehydrogenation. However, little is known about the active sites at which the catalytic reactions take place. It may be possible to obtain a significant increase in the catalytic efficiency if the effects of certain material properties on the surface reactions could be quantified and optimized through the use of appropriate preparation techniques. Given that surface reactivity is often dependent upon surface structure and that the atomic level structure of the active sites in these catalysts is virtually unknown, we desire thin film samples consisting of a single magnesium vanadate phase and a well defined crystallographic orientation in order to reduce complexity and simplify the study of active sites. We report on the use of reactive RF sputter deposition to fabricate very highly oriented, stoichiometric Mg@sub 3@(VO@sub 4@)@sub 2@ thin films for use in these surface analysis studies. Preliminary depositions of Mg@sub 3@(VO@sub 4@)@sub 2@ onto amorphous substrates resulted in amorphous thin films. However, deposition of Mg@sub 3@(VO@sub 4@)@sub 2@ onto well-oriented, lattice-matched thin film "seed" layers such as Ti (0002), Au (111) or Pt (111) resulted in very strong preferential (042) crystallographic orientation (pseudo-hexagonal planes parallel to the substrate). This strong preferential growth of the Mg@sub 3@(VO@sub 4@)@sub 2@ suggests epitaxial (single-crystal) growth of this mixed metal oxide on the underlying metal seed layer. The effects of the substrate material, seed layer material, deposition temperature, and post-deposition anneal temperatures on thin film properties such as stoichiometry, crystallographic orientation, and chemical interactions will be reported.

Author Index

-A-Akhadov, E.A.: SS1+EM-TuA9, 2 — B — Becker, C.: SS1+EM-TuA6, 2 Boatner, L.A.: SS1+EM-TuA9, 2 - C -Chambers, S.A.: SS1+EM-TuA1, 1; SS1+EM-TuA3, 1; SS1+EM-TuA4, 1; SS1+EM-TuA7, 2 — D — Diebold, U.: SS1+EM-TuA4, 1 -H-Hebenstreit, W.: SS1+EM-TuA4, 1 Herman, G.S.: SS1+EM-TuA8, 2 — K — Kandler, J.: SS1+EM-TuA6, 2 Karunamuni, J.: SS1+EM-TuA2, 1 Kim, Y.-J.: SS1+EM-TuA7, 2; SS1+EM-TuA8, 2 Koveshnikov, A.: SS1+EM-TuA2, 1

Bold page numbers indicate presenter

Kurtz, R.L.: SS1+EM-TuA2, 1 -1-Li, J.A.: SS1+EM-TuA9, 2 Liang, Y.: SS1+EM-TuA1, 1; SS1+EM-TuA3, 1 Linke, R.: SS1+EM-TuA6, 2 -M-Madjoe, R.: SS1+EM-TuA2, 1 McCarty, K.F.: SS1+EM-TuA5, 1 — P — Peden, C.H.F.: SS1+EM-TuA7, 2 Pelster, T.: SS1+EM-TuA6, 2 — R — Rosenhahn, A.: SS1+EM-TuA6, 2 Ruffner, J.A.: SS1+EM-TuA10, 2 — S — Safron, S.A.: SS1+EM-TuA9, 2 Sault, A.G.: SS1+EM-TuA10, 2 Schneider, J.: SS1+EM-TuA6, 2

Skofronick, J.G.: SS1+EM-TuA9, 2 Soares, E.A.: SS1+EM-TuA5, 1 Stanka, B.: SS1+EM-TuA4, 1 Stockbauer, R.L.: SS1+EM-TuA2, 1 - T -Thevuthasan, S.: SS1+EM-TuA3, 1; SS1+EM-TuA7, 2; SS1+EM-TuA8, 2 Tran, T.T.: SS1+EM-TuA7, 2; SS1+EM-TuA8, 2 Trelenberg, T.W.: SS1+EM-TuA9, 2 -v-Van Hove, M.A.: SS1+EM-TuA5, 1 -w-Walters, C.F.: SS1+EM-TuA5, 1 Wandelt, K.: SS1+EM-TuA6, 2 -Y-Yi, S.I.: SS1+EM-TuA3, 1; SS1+EM-TuA7, 2