

Thursday Afternoon, November 5, 1998

Surface Science Division Room 309 - Session SS2-ThA

Oxide Growth and Structure

Moderator: W. Hebenstreit, Tulane University

2:00pm SS2-ThA1 Structural and Pt Adsorption Properties of Ultrathin Al@sub 2@O@sub 3@(001) Films on Al(111), Mo(110), and Ru(001)@footnote 1@, D.R. Jennison, C. Verdozzi*, P.A. Schultz, M.P. Sears, Sandia National Laboratories

Using first-principles LDA calculations, we explore Al@sub 2@O@sub 3@ ultrathin films on a variety of metallic substrates. A general principle of interface structure is proposed, which then affects the film-surface termination (i.e., Al or O) and the degree of surface polarity. Several film thicknesses are compared. In the thinnest films, we find a favored phase not observed in bulk crystals, having only four-fold coordinated Al-ions. For all studied substrate materials, this indicates that a structural transformation could occur during film growth, as the film bulk and interfacial energies compete. Large differences, ~50%, are found in the adhesion of a metallic overlayer (Pt) with two vs. three O-layer thicknesses. This is due to greater surface polarity in the latter, which in turn is related to decreased stability of the thinnest film phase. Diffusion barriers are presented for isolated Pt adatoms and predictions made of hop length and symmetry. Huge coverage dependences (five-fold) in the adsorption energy of Pt occur between 1/3 and 1 ML, the binding being ionic when the Pt atoms are isolated (Pt@super +1@ or greater), but image-polarization driven at 2/3 ML and higher coverages. Our results agree with experimental ISS and HREELS data on the thinnest films.@footnote 2@ @FootnoteText@*Current address: Univ. of Edinburgh, Edinburgh EH9 3JX, UK. @footnote1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000. @footnote 2@J. Libuda, et al., Surf. Sci. 318 (1994) 61.

2:20pm SS2-ThA2 Interaction and Growth of Rh on Hydroxylated Alumina Model Substrates, J. Libuda, S. Stempel, M. Heemeier, M. Frank, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; A. Sandell, Lund University, Sweden; S. Andersson, P.A. Brühwiler, N. M@ao@rtensson, Uppsala University, Sweden; M. Bäumer, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

In contrast to simple model surfaces, alumina supports employed in technical catalysis exhibit a variety of complex surface structures. In particular, depending on preparation, their surface can be covered to a large extent by hydroxyl groups, affecting the chemical behaviour not only with respect to adsorption of gases but also the interaction with the catalytically active metal component. In order to study the dependence of metal growth and metal oxide interaction on the surface properties of an alumina support, we have established a hydroxylation procedure based on Al deposition and subsequent water exposure, which is applied to a well ordered Al@sub 2@O@sub 3@ film grown on NiAl(110). The hydroxylated surface is characterized with respect to morphologic (Scanning Tunneling Microscopy (STM) and Spot-Profile Analysis-LEED (SPA-LEED)) and electronic properties (High Resolution Photoelectron Spectroscopy (PES)). Upon Al deposition, uniformly distributed small metallic aggregates are formed, which can be transformed to larger two-dimensional patches and three-dimensional islands by annealing. The small aggregates can be completely oxidized by water exposure. Following this treatment, characteristic features in the Al 2p and O 1s regions are observed. The growth of Rh on the modified surface has been investigated by STM and SPA-LEED and compared to previous results for the non-modified alumina support. In contrast to the non-modified support, no decoration of characteristic one-dimensional oxide defect structures is found. Instead, the formation of a high density layer of uniformly distributed aggregates is observed. The disappearance of the characteristic O 1s and Al 2p features upon metal exposure points to a direct chemical interaction between the surface hydroxyl groups and the Rh deposited.

2:40pm SS2-ThA3 Growth of Ultrathin β -MnO@sub 2@ on TiO@sub 2@(110) by Oxygen-Plasma-Assisted Molecular Beam Epitaxy, S.A. Chambers, Y. Liang, Pacific Northwest National Laboratory

We have used oxygen-plasma-assisted MBE to grow epitaxial rutile films of pyrolusite (@beta@-MnO@sub 2@) on TiO@sub 2@(110) for thicknesses of 1 to 6 bilayers (BL). We define a BL to be a layer of Mn and lattice O and an adjacent layer of bridging O within the rutile structure. The resulting

surfaces have been characterized in-situ by RHEED, LEED, XPS, XPD, and AFM. Well-ordered, pseudomorphic overlayers form for substrate temperatures between 400C and 500C. Mn-Ti intermixing occurs over the time scale of film growth for substrate temperatures in excess of 500C. Films grown at 400-500C exhibit classic Stranski-Krastanov growth whereas those grown at higher temperatures are atomically flat. 1-BL films grown at 450C form a well-ordered surface cation layer of Mn on the rutile structure with at most 10% indiffusion to the second cation layer. Thicker films rapidly disorder due to the simultaneous formation of pyrolusite and ramsdellite (@gamma@-MnO@sub 2@), which is orthorhombic and not lattice matched to TiO@sub 2@(110). However, thin films of rutile pyrolusite are preferentially stabilized by the TiO@sub 2@ substrate. @FootnoteText@ Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research - Environmental Management Science Program.

3:00pm SS2-ThA4 Ordered Cerium Oxide Thin Films Grown on Ru(0001) and Ni(111)@footnote 1@, D.R. Mullins, P.V. Radulovic, S.H. Overbury, Oak Ridge National Laboratory

Ultrathin oxide films grown on single crystal metal substrates are advantageous for studying the adsorption and reaction of gases on oxide surfaces. Ultrathin films have a high surface area relative to their bulk volume. Their composition can be controlled during growth. They can be grown as nearly single crystals, can be readily removed and replenished in situ and they don't suffer from sample charging when using electron or ion probes. Cerium oxide thin films between 1 - 10 ML thick have been grown in situ on the Ru(0001) and Ni(111) surfaces. Well ordered films were grown by dosing metallic Ce in an oxygen ambient of 10@super -8@ - 10@super -7@ torr while the substrate was at 700K. Fully oxidized films could be grown by using a higher oxygen pressure while substoichiometric films were grown by reducing the oxygen pressure. The relative amounts of Ce@super +3@ and Ce@super +4@ were determined by soft x-ray photoelectron spectroscopy. Ion scattering spectroscopy (ISS) and LEED indicate that the cerium oxide films have the same symmetry as the substrate on which they are grown, i. e. six-fold on Ru(0001) and three-fold on Ni(111). The principal azimuths of the oxide films are aligned parallel to the principal azimuths of the substrates. The lattice constant of the cerium oxide is nominally the same as cubic CeO@sub 2@. Angle resolved ISS indicated that the fully oxidized films were predominantly terminated by an oxygen layer, whereas the substoichiometric films had a significant amount of cerium in the top layer. The structure and composition of the films grown on Ru(0001) were stable at temperatures up to 1000K. The films grown on Ni(111) lost oxygen upon annealing to 1000K. @FootnoteText@ @footnote 1@ Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract number DE-AC05-96OR22464.

3:20pm SS2-ThA5 Evolution of Surface Morphology and Growth Modes for Epitaxial alpha-Fe@sub 2@O@sub 3@ on alpha-Al@sub 2@O@sub 3@, I. Yi, A. Chambers, Pacific Northwest National Laboratory

We have investigated how the surface morphology of epitaxial alpha-Fe@sub 2@O@sub 3@ evolves with film thickness on alpha-Al@sub 2@O@sub 3@ as a function of growth rate and surface orientation. The lattice mismatch of this materials system is 5.7%. The growth technique used was oxygen-plasma-assisted molecular beam epitaxy. Film surfaces were characterized as a function of thickness in situ using reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy and diffraction, and non-contact atomic force microscopy. Island formation is observed upon relaxation of the Fe@sub 2@O@sub 3@ film to its bulk lattice spacing. Relaxation begins at coverages of only ~1 full monolayer. Furthermore, the shape and size distributions of the islands are critically dependent on growth rate during the early stages of film growth. Sparsely populated, high-aspect-ratio islands form at higher growth rates, whereas more densely populated islands with lower aspect ratios form at lower growth rates. The former surface morphology is found to be a very poor template for further epitaxy, and gives rise to poorly ordered material, whereas subsequent epitaxy on the latter morphology produces very well ordered films and surfaces. The low-aspect-ratio islands formed at the initial stages of film growth coalesce within the first 50 Å. With a reduced number of islands, the surface becomes smoother. With additional growth, the surface morphology is greatly improved and the island-to-island height variation is reduced to few Ångströms.@footnote 1@ @FootnoteText@ @footnote 1@Work supported by the U.S. Department of Energy, Offices of Basic Energy

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Sciences and Biological and Environmental Research Environmental Management Science Program.

3:40pm **SS2-ThA6 The Nature, Growth and Stability of Vanadium Oxides on Pd(111)**, *F.P. Leisenberger, M.G. Ramsey, S.L. Surnev, F.P. Netzer*, Karl-Franzens-Universität Graz, Austria

The study of metal - oxide interfaces is at the cutting edge of present day surface science. This particular study is inspired by the fact that the vanadium oxide - palladium phase boundary is an important system in practical heterogeneous catalysis. In this work high resolution XPS and NEXAFS have been used to characterise the growth and stability of vanadium oxide on a Pd(111) single crystal surface as a model system. The vanadium oxides have been prepared by reactive evaporation of vanadium in $p \times 10^{-7}$ mbar at 250°C from submonolayer to 15 ML coverages. The oxide morphology has been gauged by the C 1s XPS following the adsorption of CO as a probe molecule for the bare palladium sites. The stoichiometry of the oxide phase varies as a function of coverage, V_2O_5 / VO_2 - like at low coverages to V_2O_5 for the thicker oxide layers as indicated by the characteristic NEXAFS fingerprints at both the V 2p and O 1s edges. The thermal stability of the oxides is dependent on the coverage: the decomposition onset temperatures range from 300°C for submonolayer coverage to $\geq 600^\circ\text{C}$ for 15 ML. The V 2p XPS data indicate that the oxides disproportionate into higher and lower oxidation state phases. For nominal oxide coverage of 1 ML two different LEED patterns are observed on annealing between 250°C to 350°C. The surface formed below 300°C has a complex pattern and allows the uptake of CO, while on heating to 300 - 350°C a simple $p(2 \times 2)$ structure evolves, on which CO cannot be accommodated. This behaviour suggests that initially ordered oxide island structures are formed with bare palladium in between. At the higher temperature (300 - 350°C) a more homogeneous passive surface layer evolves.

4:00pm **SS2-ThA7 Photoemission Study of Ultra-thin NiO(111) Films Grown on Au(111)**, *B.R. King, M. Howard, P.S. Robbert, H. Geisler, C.A. Ventrice, Jr.*, University of New Orleans; *D.A. Hite, P.T. Sprunger*, CAMD/Louisiana State University

Only a few systems are known where the polar surface of an ionic metal-oxide crystal can be grown without the introduction of surface impurities. One example of a stable polar surface is the growth of NiO(111) on Au(111) by evaporation of Ni in an O_2 atmosphere at $\sim 300^\circ\text{C}$. STM analysis of this surface has shown that the NiO(111) surface consists of a $p(2 \times 2)$ array of four-atom tripods with several missing-atom point defects on the surface as well as regions of bare Au. Angle-resolved photoelectron spectroscopy and x-ray absorption measurements have been performed to better understand the growth morphology and the resulting electronic structure of this system. Significant changes in the Au-5d photoemission intensity features are observed after the growth or the NiO which indicates that the Au regions observed with STM result from segregation, not NiO three-dimensional island growth into the Au substrate. The photoemission results also show a 1 eV shift in the Ni-3d emission to lower binding energy when compared to previously published results for single-crystal NiO(100). Since Ni deficient NiO results in a p-type substrate, this shift and the observation of missing-atom point defects with STM provide evidence that the (111) surface is Ni terminated. Analysis of structural changes in the Ni coordination upon oxidation is currently being performed by comparison of x-ray absorption features of Ni/Au(111) and NiO(111)/Au(111) systems. *Footnote 1*: C. A. Ventrice, Jr., et al., Phys. Rev. B 49, 5773 (1994). *Footnote 2*: S. Hüfner et al., Z. Phys. B 83, 185 (1991).

4:20pm **SS2-ThA8 The Effects of High Temperature Annealing on the Surface Reconstruction of NiO(111)**, *M.A. Schofield, A.K. Hicks, M. Gajdardziska-Josifovska*, University of Wisconsin, Milwaukee

NiO is an ionically bonded solid with a rocksalt structure. In the crystallographic direction, NiO consists of alternating close-packed planes of nickel and oxygen. The bulk terminated (111) surface, therefore, is a polar surface with theoretically predicted infinite surface energy. Consequently, adsorption of charged species at the surface or a considerable rearrangement of the atomic ordering is expected to occur to stabilize the surface. While microscopic faceting into neutral planes has been the accepted model for polar oxide surfaces, recent theoretical and experimental studies have reported a 2×2 reconstruction as a stabilization mechanism for the NiO(111) surface. In essence, the 2×2 structure (also known as octapolar, or nanofaceting structure) is the smallest possible scaling of the faceting model. In the present work we report two new

reconstructions of annealed NiO(111) surfaces which cannot be readily explained by nanofaceting. Electron transparent single-crystal NiO samples were prepared for study of the (111) surface in plan view by transmission electron microscopy (TEM) and diffraction (TED) techniques. Annealing experiments were performed under high vacuum and atmospheric conditions over a wide range of temperatures and times. Under high vacuum annealing conditions a preferential desorption of oxygen from the sample surface resulted in the formation of epitaxial nickel islands. Conversely, for annealing experiments performed under atmospheric conditions, the NiO(111) samples exhibited surface reconstructions. Two reconstructions were observed and identified as having $(\sqrt{3} \times \sqrt{3})R30^\circ$ and (2×2) surface periodicities from TED patterns obtained after annealing above 800°C in air. Both reconstructions were stable in air even after prolonged exposure of several weeks to atmospheric conditions.

4:40pm **SS2-ThA9 Morphology of MgO (111) Surfaces: Artifacts Associated with the Faceting of Polar Oxide Surfaces into Neutral Surfaces**, *R.A. Plass, J. Feller, M. Gajdardziska-Josifovska*, University of Wisconsin, Milwaukee

We have found using optical, atomic force, scanning and transmission electron microscopies that the polar ionic MgO (111) surface does not facet into neutral (100) type planes upon high temperature annealing, as has been commonly believed, rather it appears to be stabilized by surface reconstructions containing cyclic ozone. The triangular pyramidal pits which Henrich associated with this presumed faceting turn out to be artifacts of the acid etch used in the sample preparation process. We have determined that the pits have walls sloped at $10.8^\circ \pm 2.8^\circ$ with respect to the (111) surface, not the 54.7° expected for faceting to (100) type planes. The pit edges were confirmed by transmission electron microscopy to be along the three equivalent type directions. The morphology of this surface before and after annealing as well as transmission electron diffraction data and proposed atomic structures of three native surface reconstructions seen after annealing will be discussed. *Footnote 1*: V.E. Henrich, Surf. Sci., 57 (1976) 385

5:00pm **SS2-ThA10 Surface Phonons and Surface Phase Transitions in KTaO₃ (001)**, *J.A. Li, E.A. Akhadov, T.W. Trelenberg, S.A. Safron, J.G. Skofronick*, Florida State University; *L.A. Boatner*, Oak Ridge National Laboratory

Phase transitions of the (001) surface of KTaO_3 , prepared by cleaving a single crystal sample in situ, have been investigated by high-resolution Helium Atom Scattering (HAS). Angular distribution measurements of the diffractive scattering show that thermal cycling of the sample from room temperature to low temperatures (≤ 140 K) and back to ≥ 220 K induces the (1×1) surface found after cleaving at ~ 300 K to reconstruct to a (2×1) surface. The reconstruction appears to occur much more rapidly, minutes vs. days, when the temperature is cycled to above ~ 250 K. The (2×1) phase appears to be stable until ~ 365 K at which point the surface reverts partially to the (1×1) structure. A time-of-flight technique was employed to measure the helium atom-single phonon creation/annihilation scattering events in order to examine the surface phonon dispersion of this surface. Experiments were carried out over the temperature range of 80 to 220 K. For bulk KTaO_3 considerable softening near the Brillouin zone center of the transverse optical phonon branch had been reported as the temperature was reduced. For the surface, the observed softening in the surface phonon branches is not as great, but it appears to become more pronounced as the temperature is raised from 80 to 220 K. The implications of the temperature behavior of the surface lattice dynamics and the surface phase transitions are discussed. *Footnote 1*: *Footnote 2*: Work supported in part by US DOE grant No. DE-FG02-97ER45635.

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