

Surface Science

Room 203 - Session SS2-MoM

Oxide Surface Structure and Characterization

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:40am **SS2-MoM2 Thermodynamic Stability of Alumina Films on NiAl(110) and the Dynamics of Their Extended Defects**, *K.F. McCarty, N.C. Bartelt, J.P. Pierce*, Sandia National Laboratories; *C.B. Carter*, University of Minnesota

A well-studied oxide surface is the thin-film alumina formed by oxidizing a NiAl(110) surface [J. Libuda et al., Surf. Sci. 318 (1994) 61]. Here, we show how low-energy electron microscopy (LEEM) can determine the thermodynamic stability of these alumina films and image the formation and time evolution of extended crystallographic defects. At sufficiently high temperature, discrete islands of crystalline oxide form when NiAl is exposed to oxygen. Analysis by electron diffraction and scanning tunneling microscopy establish that these oxide islands are the same alumina produced by the literature "recipe." We directly measure the thermodynamic stability (Gibbs formation energy) of the alumina -- at a fixed temperature, the pressure of oxygen in equilibrium with the oxide is determined by finding the pressure at which individual alumina islands neither shrink nor grow. We find that the equilibrium oxygen pressure of the thin-film alumina is many orders of magnitude greater than bulk alumina. Analysis suggests that strain is the cause of the remarkable instability of the alumina film. We also investigate how two types of planar defects in the films, boundaries between rotational and translation domains, originate and evolve. Typically, domains in films are thought to originate from the nucleation stage of film growth. That is, domain boundaries occur where rotated or translated islands impinge. Indeed, we observe that rotational boundaries form in this manner. In contrast, translation ("antiphase") boundaries are observed to nucleate, grow, and even move within isolated oxide islands. The fact that translation boundaries form within isolated alumina islands strongly suggests that the boundaries are introduced to relieve strain. We will discuss how formation of translation domains reduces film strain. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:00am **SS2-MoM3 Growth and Properties of Vanadia on Anatase TiO₂(001) and (101) Surfaces**, *W. Gao*, Yale University; *R. Klie*, Brookhaven National Laboratory; *E.I. Altman*, Yale University

Inspired by its unique catalytic properties and elusive structure, we have been studying the structure of vanadia layers deposited onto epitaxial anatase (001) and (101) films. For anatase (001), a (1x4)/(4x1) reconstruction was observed by reflection high-energy electron diffraction (RHEED) and low energy electron diffraction (LEED). After depositing 1 ML at 525 K, X-ray photoelectron spectroscopy (XPS) showed predominantly V@super 5+@ and the (1x4)/(4x1) diffraction patterns were replaced by (1x1) patterns indicating that vanadia lifts the reconstruction and the monolayer is pseudomorphic. Continued growth caused the RHEED pattern to fade, suggesting that V@sub 2@O@sub 5@ epitaxy cannot be continued beyond 1 ML. At 750 K, however, VO@sub 2@ formed and the (1x1) pattern remained clear for 20 nm of vanadia. At 800 K, a c(2x2) termination was observed. These results suggest that the V@super 5+@ in the monolayer is due to 0.5 ML of terminal oxygen which allows epitaxy and the 5+ oxidation state. These results were compared with those for anatase (101) surfaces, the lowest energy anatase surface. The (101) surfaces were formed by depositing TiO@sub 2@ onto LaAlO@sub 3@(110). Although x-ray diffraction and scanning transmission electron microscopy indicated that the films grew with anatase (102) planes parallel to the interface, RHEED and LEED showed the surface diffraction patterns expected for a (101) surface and STM showed the oblique unit cell of the (101) surface. These conflicting results were attributed to the surface faceting to expose the lowest energy (101) surface. Similar to anatase (001), a (1x1) diffraction pattern is maintained after depositing 1 ML of V@sub 2@O@sub 5@; however, further vanadia deposition led to three dimensional vanadia clusters. STM is being used to further characterize the structure of the vanadia monolayers on the two anatase surfaces.

9:20am **SS2-MoM4 Oxide Nanolayers: Artificial Phases in Low Dimensions**, *F.P. Netzer, S. Surnev, J. Schoiswohl, G. Parteder, M.G. Ramsey*, Karl-Franzens-University Graz, Austria; *G. Kresse*, University of Vienna, Austria

Transition metal oxides in ultrathin nanostructured layers on well-defined metal surfaces may form novel oxide phases, that do not occur in nature. These "artificial oxide phases" display new physical and chemical properties, which make them potentially interesting materials for nanotechnology applications. They derive their formation, on the one hand, from the interactions at the interface between the oxide overlayer and the metal substrate and, on the other hand, from kinetic constraints during the growth process. The growth of a variety of novel low-dimensional vanadium, nickel, and manganese oxide structures on Rh and Pd single crystal surfaces has been followed and the surface phase diagrams and the atomic structures of oxide nanolayer phases have been characterized by the interplay of various experimental and theoretical methods (STM, LEED, UPS and XPS, HREELS, ab initio DFT). The influence of energetic and strain effects at the interface is important and determines the particular structures, which are observed on different substrates. The oxide structures to be discussed comprise highly oxidised (nominally V@sub 3@O@sub 9@), mixed valent (VO@sub 1.6-2.09@), and reduced (nominally V@sub 2@O@sub 3@) vanadium oxide surface phases on Rh(111) and Pd(111) substrates, a c(4x2) wetting layer of an interfacial nickel oxide on Pd(100), which acts as an interlayer to cubic NiO growth, and various manganese oxide phases on Pd(100). It is shown that, in addition to the thickness confinement in the nanolayers, the lateral confinement as imposed by the regular step array on a vicinal substrate surface can promote the growth of novel oxide nanostructures. @FootnoteText@ Supported by the Austrian Science Fonds and the EU STREP Programme GSOMEN.

9:40am **SS2-MoM5 Metal Atoms and Clusters on Oxide Surfaces and Thin Films: Charging Mechanisms and Consequences**, *G. Pacchioni*, Universita' di Milano-Bicocca, Italy

INVITED

Metal clusters deposited on oxide surfaces exhibit specific chemical and physical properties often connected to their low dimensionality. The properties of truly nano-clusters a few atoms in size or even of isolated metal atoms are highly depending on the type of oxide support, adsorption site, surface morphology, etc. One of the aspects that can deeply modify the properties of the adsorbed metal atoms or clusters is the occurrence of charge transfers at the metal-oxide interface. Recent studies have shown that charged clusters, and in particular cluster anions, are catalytically more active than their neutral counterparts. Charging mechanisms of metal atoms and clusters on oxide surfaces is the topic of this talk. Using high quality electronic structure calculations in combination with experimental spectroscopic measurements, we will discuss in which conditions charging occurs and how to measure it. The systems considered are metal atoms like Cu, Au, Pd, on oxide substrates like MgO, SiO₂, and TiO₂ single crystals or in polycrystalline or amorphous form. We will show that a major role in charging of the deposited atoms is played by point defects at the oxide surface and discuss methods to prove the occurrence of the charge transfer. In the second part of the talk we will examine methods to induce charging even without implying the presence of defects. In particular, we will consider metal atoms deposited on ultra-thin oxide films epitaxially grown on metal single crystals. We will discuss the adsorption properties of Pd, Ag, and Au atoms on 1 to 5 layers thick films of MgO on Mo(100) and compare them to those of MgO(100) single crystals. On supported MgO thin films charging can occur from the metal substrate to adsorbed atoms with high electron affinities, like Au. We will discuss possible mechanisms for this charge transfer like direct tunneling or dielectric breakdown induced by an external electric field.

10:20am **SS2-MoM7 Growth of WO₃ Clusters on TiO₂(110)-(1x1)**, *O.A. Bondarchuk*, University of Texas at Austin; *Z. Dohnalek, B.D. Kay, J. Kim*, Pacific Northwest National Laboratory; *J.M. White*, University of Texas at Austin

Tungsten oxide clusters supported on Al@sub 2@O@sub 3@, SiO@sub 2@, ZrO@sub 2@ and TiO@sub 2@ are known to be catalytically active for a wide range of acid-catalyzed reactions including alcohol dehydrogenation, alkane hydrogenation, metathesis etc. In this work, we studied the growth of WO@sub 3@ nanoclusters on TiO@sub 2@-(110)-(1x1) surface using STM. Submonolayer amounts of WO@sub 3@ were deposited on TiO@sub 2@(110) via direct, thermal evaporation from WO@sub 3@. Using XPS we have determined that WO@sub 3@ deposited on TiO@sub 2@(110) is thermally stable and remains fully oxidized up to

Monday Morning, October 31, 2005

700 K. Atomically resolved studies of WO_3 deposited at room temperature on $\text{TiO}_2(110)$ show only fuzzy, poorly defined features indicating that the clusters are only weakly bound to the substrate. Subsequent annealing to 600 K results in the formation of bright WO_3 clusters that can be easily imaged. In case of low WO_3 coverages (< 0.25 ML) the STM images indicate that the majority of clusters have identical size (~ 0.6 nm in apparent diameter) and position with respect to the substrate registry. The amount of deposited WO_3 from a quartz crystal microbalance measurement together with the observed cluster density yields the upper bound of x for the number of W atoms in each cluster. Additionally, annealed WO_3 clusters exhibit preferential alignment across the $\text{Ti}4+$ rows suggesting attractive interactions between them.

10:40am **SS2-MoM8 Imaging of Atoms on Oxide Surfaces by X-ray Standing Wave Fourier Inversion**, C.-Y. Kim, Northwestern University; J.W. Elam, Argonne National Laboratory; D. Goswami, M.J. Bedzyk, P.C. Stair, S Christensen, M.C. Hersam, Northwestern University

Supported metal oxides are among the most important of catalytic materials systems. However, there is a lack of experimental atomic-scale structural information for describing the relevant interfaces. We combine atomic layer deposition (ALD) and x-ray standing wave (XSW) atomic-imaging to address this challenge. As a first case, we determine the precise registry of W atoms on a rutile $\text{TiO}_2(110)$ surface. XSW results show that tungsten has an average adsorption height of 3.48 Å above the Ti-O plane. The direct-space image reveals that W occupies the Ti-site that would be occupied by Ti if the bulk structure were extended above surface. The tungsten atoms are vertically shifted upward from the ideal Ti-site location by +0.23 Å. We speculate that the sacrificial role of Si_2H_6 in removing surface species may apply to the TiO_2 substrate in addition to the W ALD film. This is the first atomic structure determination of a supported catalytic phase under ambient conditions. The results suggest that supported metal cations locate as if they were the next layer in the bulk structure. The ALD method for supported catalyst material preparation provides a bridge over the "materials preparation gap" that typically separates practical, high-surface-area and single crystal model catalytic materials.

11:00am **SS2-MoM9 Terminal Oxygen Structures on $\text{WO}_3(100)$ Thin Films**, M. Li, A. Posadas, C. Ahn, E.I. Altman, Yale University

Scanning tunneling microscopy (STM) was used to characterize the surface reconstructions on epitaxial $\text{WO}_3(100)$ thin films on $\text{LaAlO}_3(100)$ in a reducing environment. As the films were annealed between 600-770 K, a myriad of surface structures related to terminal oxygen were observed. Upon initial reduction the surface was covered with small $c(2 \times 2)$, $p(2 \times 2)$, $c(4 \times 2)$, and poorly ordered terminal oxygen terraces all coexisting with (1×1) islands. Further reduction caused large flat terraces of poorly ordered terminal oxygen to coexist with strand terminated $p(n \times 2)$ terraces with $n = 3-5$. Continued reduction led to a zigzag arrangement on top of the $p(n \times 2)$ surface, half-height $p(2 \times 2)$ and $c(4 \times 2)$ islands, and a local (15×2) structure. The latter three structures could only be explained by crystallographic shearing of the surface plane. In contrast to higher annealing temperatures, the exclusively $p(n \times 2)$ terminated surface characterized by alternating strands and troughs was not observed, suggesting that at lower temperatures crystallographic shear competes with the bulk migration responsible for trough formation as the dominant surface reduction mechanism.

Author Index

Bold page numbers indicate presenter

— A —

Ahn, C.: SS2-MoM9, 2

Altman, E.I.: SS2-MoM3, 1; SS2-MoM9, **2**

— B —

Bartelt, N.C.: SS2-MoM2, 1

Bedzyk, M.J.: SS2-MoM8, 2

Bondarchuk, O.A.: SS2-MoM7, **1**

— C —

Carter, C.B.: SS2-MoM2, 1

Christensen, S.: SS2-MoM8, 2

— D —

Dohnalek, Z.: SS2-MoM7, 1

— E —

Elam, J.W.: SS2-MoM8, 2

— G —

Gao, W.: SS2-MoM3, **1**

Goswami, D.: SS2-MoM8, 2

— H —

Hersam, M.C.: SS2-MoM8, 2

— K —

Kay, B.D.: SS2-MoM7, 1

Kim, C.-Y.: SS2-MoM8, **2**

Kim, J.: SS2-MoM7, 1

Klie, R.: SS2-MoM3, 1

Kresse, G.: SS2-MoM4, 1

— L —

Li, M.: SS2-MoM9, 2

— M —

McCarty, K.F.: SS2-MoM2, **1**

— N —

Netzer, F.P.: SS2-MoM4, **1**

— P —

Pacchioni, G.: SS2-MoM5, **1**

Parteder, G.: SS2-MoM4, 1

Pierce, J.P.: SS2-MoM2, 1

Posadas, A.: SS2-MoM9, 2

— R —

Ramsey, M.G.: SS2-MoM4, 1

— S —

Schoiswohl, J.: SS2-MoM4, 1

Stair, P.C.: SS2-MoM8, 2

Surnev, S.: SS2-MoM4, 1

— W —

White, J.M.: SS2-MoM7, 1