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STRUCTURE, ADHESION, AND STABILITY OF
METAL/OXIDE AND OXIDE/OXIDE INTERFACES

Technical Progress Report
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Abstract

During the past six months, we have begun our studies of the fundamental properties of metal/oxide and oxide/oxide heterogeneous interfaces which are being prepared by epitaxial growth of ultra-thin films on single crystal TiO_2 and NiO surfaces. A new ultra-high vacuum film growth chamber was assembled and coupled to an existing surface analysis chamber; a sample transfer system, metal deposition sources, and a RHEED system with microchannel plate detection were constructed and implemented. Atomic Force Microscopy was used to characterize and refine the preparation procedures for the single crystal surfaces. The electronic structure of stoichiometric, oxygen-deficient, and potassium-covered TiO_2 (110) surfaces was investigated. Preliminary results on the Al/TiO_2 (110) system have been obtained. Two graduate students have begun thesis research on the project.

Equipment Development

A large effort has gone into constructing a new ultra-high vacuum chamber that is equipped with metal deposition sources for thin film growth and *in situ* RHEED analysis. A photograph of this new chamber and the accompanying surface analysis chamber are shown in Figure 1. A sample transfer system based on a magnetic transfer drive was designed and constructed. Samples can be installed via a small load-lock chamber and can be docked onto separate manipulators in the film growth and surface analysis chambers.

Since electron-induced damage to oxide surfaces is a well-known phenomenon, we are minimizing this effect by using a RHEED gun operating with nano-Amp beam currents and detecting the diffracted electrons with a microchannel plate detector. The VG Model LEG 110 Electron Gun was purchased due its superior stability characteristics at very low

beam current; we have independently verified the performance specifications in the nano-Amp beam current regime in our laboratory.

Other equipment development included design and construction of metal deposition sources and the channelplate RHEED detector. The deposition sources are shuttered Knudsen cells situated in a liquid nitrogen cooled shroud. The RHEED detector was constructed from a Microchannel Plate Assembly (Galileo Hot CEMA 6075) and custom phosphor screen manufactured by ITT Phosphor, Inc. As of January 1991, the first series of measurements with the RHEED system are just getting underway.

Figure 1 Photograph of the newly constructed film growth / RHEED chamber (on the left) which is coupled to the electron spectroscopies analysis chamber (on the right) in Prof. R.J. Lad's laboratory at the University of Maine.

Atomic Force Microscope Studies

We have used Atomic Force Microscopy to characterize the single crystal TiO_2 and NiO surfaces which are being used as substrates for the film growth and interface studies. The surfaces were prepared in ultra-high vacuum and then imaged by AFM in air. These measurements have provided a wealth of information about the surface microstructure and defect structure and have helped to refine our sample preparation procedures.

An AFM image of a TiO_2 (110) surface that was prepared by Ar^+ bombardment and high temperature oxidation in ultra-high vacuum is shown in Figure 2. This surface was believed to be nearly perfect since a sharp (1x1) LEED pattern was observed and no defect-induced electronic states were visible within the bulk band gap as measured by ultra-violet photoelectron spectroscopy (UPS). Yet, roughness is evident on a nanoscale. The 1000 Angstrom high features are suggestive of sputter cones similar to those reported on Ar^+ bombarded metallic alloys. After a repolishing treatment using 0.25 μm diamond particles, we discovered that particles were imbedded into the surface. After changing our polishing conditions, we obtained an extremely flat surface with a measured roughness of less than 30 Angstroms. This surface is now being used for our Al deposition experiments.

Figure 2 AFM image of a UHV-prepared TiO_2 (110) surface. The image size is 9 μm x 9 μm .

Results obtained on the TiO_2 (100) surface were quite different. After mechanically polishing and vacuum annealing at 800K, this surface became faceted as shown in Figure 3. Although the facets are approximately 3000 Angstroms in lateral dimension, they are less than 100 Angstroms high and because of this extremely low aspect ratio, no evidence was for faceting was detected by LEED. This faceted surface will provide an interesting template for film growth; we intend to study how a faceted interface structure influences adhesion.

Figure 3 Facet morphology observed on a vacuum annealed TiO_2 (100) surface. The image size is $9\ \mu\text{m} \times 9\ \mu\text{m}$.

The AFM measurements also provided valuable information about the preparation of NiO (100) surfaces. Figure 4 shows an image of a cleaved NiO surface. Cleavage steps higher than 200 Angstroms are visible, indicative of branching crack propagation during fracture. These results revealed how important it is to precisely orient the crystal by Laue x-ray diffraction and cut notches in order to initiate crack propagation along the (100) plane. Surfaces that were prepared in this manner were extremely flat, which will improve the sensitivity of our RHEED measurements.

Figure 4 Fracture morphology of a cleaved NiO (100) surface imaged by AFM. The image size is $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$.

The Atomic Force Microscope has already provided significant information about the microstructure and morphology of the single crystal oxide substrates.

We anticipate that the direct imaging capability of the AFM will also aid in addressing questions such as wetting, homogeneity, defect structure, and morphology of overlayers grown on the oxide surfaces, which should nicely complement the RHEED and photoemission results. The load-lock and sample transfer capabilities of the new UHV chamber that we have constructed should facilitate the realization of these measurements.

Properties of Potassium-Modified TiO_2 Surfaces

The interaction of potassium with stoichiometric and oxygen-deficient TiO_2 (110) and (100) surfaces has been studied by UPS, XPS, and LEED. These studies were carried out in order to investigate ways of modifying the TiO_2 surfaces prior to film growth with the goal of improving adhesion. Potassium, being very electropositive, has been known to strongly influence the surface electronic structure of metals, but no data had yet been reported on oxides or other insulator surfaces.

Our results show that a submonolayer amount of potassium strongly reduces stoichiometric TiO_2 surfaces; these surfaces are generally very stable and inert towards other species. UPS and XPS measurements indicate a large charge transfer from the potassium to the surface oxygen anions and a reduction of the Ti^{4+} surface cations to the Ti^{3+} state. Figure 5 shows UPS spectra measured as a function of potassium coverage. New potassium-induced surface states develop within the bulk band gap and their intensity saturates at a coverage of one monolayer. These same band gap states are visible on oxygen-deficient surfaces following Ar^+ or electron bombardment.

Figure 5 UPS spectra of the TiO_2 (110) valence band as a function of potassium coverage. The potassium-induced states near the Fermi level exist within the bulk band gap.

With increasing potassium coverage, we also measured a large decrease in work function and a downward shift of the valence and conduction bands. Our model of this phenomenon is illustrated in Figure 6. In this energy level diagram the Fermi level on the stoichiometric TiO_2 surface is pinned just below the conduction band edge as a consequence of a reduced semiconducting bulk composition. The potassium adsorption induces a downward band bending, pulling conduction band states below the Fermi level where they become populated as the Ti^{4+} cations are reduced to Ti^{3+} .

Figure 6 Schematic energy level diagram which accounts for the creation of surface states within the bulk band gap following potassium adsorption.

Surfaces that were Ar^+ bombarded prior to potassium deposition surprisingly interacted very weakly with the adsorbed potassium. The Ar^+ bombardment procedure created an oxygen deficiency which reduced the surface cations to Ti^{3+} and populated the band gap states. After potassium adsorption no additional band bending or work function change occurred.

The results of these potassium adsorption experiments were presented at the 1990 National Meeting of the American Vacuum Society in Toronto. Currently we are studying the electronic structure of Al layers deposited on the stoichiometric and Ar^+ bombarded TiO_2 surfaces with and without potassium present.

Presentation of Results at National Conferences

Abstract from the 37th Annual American Vacuum Society Symposium
Toronto, Canada; October 10, 1990

PROPERTIES OF POTASSIUM MODIFIED $\text{TiO}_2(110)$ SURFACES, R.J. Lad and L.S. Dake, Laboratory for Surface Science and Technology and Physics Department, University of Maine, Orono, ME 04469 and K.E. Smith, Physics Department, University of Oregon, Eugene, OR 97403

The influence of potassium on the electronic and structural properties of stoichiometric and oxygen-deficient $\text{TiO}_2(110)$ surfaces has been studied by UPS, XPS, LEED, and resonant photoemission. The adsorption of submonolayer amounts of potassium on $\text{TiO}_2(110)$ strongly reduces the oxide surface giving rise to Ti^{3+} derived states within the bulk band gap and a corresponding shift in the Ti core levels. The potassium induced Ti^{3+} states exhibit the same resonance profiles across the 3p-3d optical absorption edge as the defect states on oxygen-deficient $\text{TiO}_2(110)$. In addition, the charge transfer from the potassium to surface oxygen anions causes a large downward surface band bending and a 3 eV drop in the work function. The potassium induced Ti^{3+} derived states are responsible for enhanced adsorption of O_2 and CO on the otherwise inert stoichiometric surface. Preliminary results on the nucleation and growth of Al films on potassium covered $\text{TiO}_2(110)$ will also be presented.

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Abstract from Meeting on Scanning Probe Microscopy
Greater New York Chapter of the American Vacuum Society
Rutgers University, November 7, 1990

MICROSTRUCTURE OF SINGLE CRYSTAL OXIDE SURFACES STUDIED BY ATOMIC FORCE MICROSCOPY

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Images of insulating single crystal oxide surfaces were obtained at length scales ranging from 10 μm to 1 nm using a Park Scientific Instruments Atomic Force Microscope operating in the constant scanning force regime. The surfaces that were studied include NiO (100) and Cr_2O_3 (1012) which were cleaved in air, and TiO_2 (100) and TiO_2 (110) which were prepared in ultra-high vacuum by Ar^+ bombardment / O_2 annealing treatments. The cleaved Cr_2O_3 (1012) surface was extremely flat with single atomic height steps spaced approximately 1 μm apart. The steps were oriented predominantly along a single crystallographic direction but occasional jogs were observed. The cleaved NiO (100) surface was much rougher and exhibited characteristic features of a fracture surface. Flat ~ 500 nm wide terraces were separated by 50 nm high steps; single atomic height steps were rarely visible. The TiO_2 (100) and (110) surfaces were prepared and characterized in ultra-high vacuum. Relatively sharp (1x1) LEED patterns were observed and no defect states within the bulk band gap were detected by UPS. Imaging of these surfaces in air revealed gross roughness on the submicron scale. The TiO_2 (110) surface contained 100 nm high features suggestive of sputter cones that have been reported on Ar^+ bombarded metallic alloys. This texture was also observed on the 20 nm scale; flat terraces and single atomic height steps were not visible. The TiO_2 (100) surface was also extremely rough and contained facets approximately 200 nm in size. Atomic resolution was achieved on all of the surfaces using a large repulsive force between the cantilever and the surface.

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Abstract Submitted
for the 1991 March Meeting of the
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Suggested Session Title
Adhesion, Fracture, and Interfaces

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151

Morphology and Structure of Fractured
Cr₂O₃ (1012) and NiO (100) Surfaces Imaged by
Atomic Force Microscopy. M. A. ANTONIK and R. J.
LAD, University of Maine. -- The surface microstructure
of air-fractured Cr₂O₃ and NiO single crystal surfaces
was studied by Atomic Force Microscopy. Cr₂O₃
(1012) cleavage surfaces were found to be extremely
flat with single atomic height steps spaced greater
than 1 μm apart. The steps were oriented
predominantly along the most densely packed step
directions but occasional jogs were observed. NiO
(100) cleavage surfaces were much rougher and
contained ~500 Å high cleavage steps resulting from
branching crack propagation during fracture. Results
of nanoindentation measurements which reflect the
adhesive force interactions between the surfaces and
the Si₃N₄ microcantilever tips will also be discussed.
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Prefer Standard Session

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