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

Technical Progress Report
for Period August 1, 1991-July 31, 1992

R. J. Lad

University of Maine
Orono, ME 04469

January 1992

Prepared for
THE U. S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-90ER45417

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

DMG MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Table of Contents

<u>Page</u>	
1	Abstract
2	Highlights of Research Progress
2	Properties of Potassium / TiO_2 Interfaces
2	Properties of Potassium / NiO Interfaces
3	Properties of Aluminum / TiO_2 Interfaces
4	Influence of Defects on Interface Properties
6	Equipment Development
7	Graduate Students Working on the Project
8	Presentation of Results at National Meetings
8	Publications
8	Current and Pending Support for R.J. Lad
9	Appendix I: Abstract from the American Ceramic Society Symposium
10	Appendix II: Abstract from the 38th American Vacuum Society Symposium
11	Appendix III: Abstract for the Fall Meeting of the Materials Research Society
12	Appendix IV: Preprint of paper submitted to Proc. Mat. Res. Soc.

Abstract

Studies of several model metal/oxide and oxide/oxide interfaces were carried out by depositing ultra-thin metal films on single crystal oxide substrates. The specific systems that were characterized include K / TiO_2 , $\text{K}_2\text{O} / \text{TiO}_2$, Al / TiO_2 , $\text{Al}_2\text{O}_3 / \text{TiO}_2$, and K / NiO . The interface electronic structure and bonding interactions were determined with x-ray and uv photoelectron spectroscopies (XPS and UPS) and the structure and morphology was analyzed with low energy and high energy electron diffraction (LEED and RHEED) and atomic force microscopy (AFM). The two metal overlayers studied, K and Al, were found to strongly interact with the single crystal oxide substrates. Given adequate thermal energy, the metals became oxidized and substoichiometric TiO_2 and NiO compositions were created near the interface. Defects were found to have a major influence on interface structure.

The construction of the thin film deposition / RHEED analysis chamber was completed during the past year, and a versatile sample transfer and heating system was implemented. Three graduate students participated in the project, the results were presented at three national meetings, and one manuscript was submitted for publication.

HIGHLIGHTS OF RESEARCH PROGRESS

Properties of Potassium / TiO_2 Interfaces

During the past year, the work on the potassium / TiO_2 (110) system was completed and the results were published in the Proceedings of the Materials Research Society (see Appendix IV). The experiments probed the electronic and structural interface properties (i) for submonolayer potassium depositions on TiO_2 surfaces and (ii) following the growth of films ranging up to about 100 Å in thickness.

In summary, the potassium / TiO_2 (110) interfaces were investigated using x-ray and uv photoelectron spectroscopies (XPS and UPS), Auger electron spectroscopy (AES), and low energy and high energy electron diffraction (LEED and RHEED). Potassium was found to strongly interact with the oxygen anions of the TiO_2 and partially reduce the valency of the Ti cations. A large charge transfer to the substrate causes a sharp drop in work function, a population of electronic states within the bulk bandgap, and band bending across the interface. After large potassium doses, multilayers of K_2O form by diffusion of oxygen anions from the TiO_2 substrate, creating a substoichiometric TiO_{2-x} composition at the interface. These potassium oxide layers remain stable at least up to 900 K. LEED indicates little long range order in the potassium oxide films, while RHEED analysis is limited by the roughness of the TiO_2 surface. The importance of interfacial defects and surface roughness are discussed in more detail below.

Properties of Potassium / NiO Interfaces

Interfaces created by potassium deposition on NiO (100) surfaces were studied and the results were similar to those obtained on TiO_2 (110). The first aspect of this work involved determining the proper method for preparing a stoichiometric NiO (100) surface. Previous studies by several groups have shown that stoichiometric NiO surfaces cannot be prepared by a mechanical polishing and vacuum annealing treatment; however, stoichiometric surfaces can be created by in-vacuum cleaving. We found a method to prepare and regenerate stoichiometric surfaces without the need for in-vacuum cleaving. Our preparation method involves cleaving in air followed by Ar^+ bombardment, annealing in UHV at 500 °C, and annealing at 200 °C in 1×10^{-6} Torr O_2 . As shown in Fig. 1, this method yields a UPS valence band spectrum that is free of defect states and the spectrum is identical to spectra recorded from NiO surfaces cleaved in-vacuum. The stoichiometric surface can be regenerated several times eliminating the need for difficult in-vacuum cleaving procedures.

Fig.1 UPS valence band spectra from a NiO (100) surface. The defect peak near the top of the valence band becomes populated by Ar^+ bombardment or K adsorption.

The interaction of potassium with the NiO (100) surface is comparable to that with TiO_2 . At monolayer coverages, charge transfer to the NiO surface causes a large decrease in work function and a population of the defect state near the top of the valence band, leading to a reduction in the NiO composition. Following larger doses of potassium, a K_2O layer forms but the growth rate of the overlayer is slower than on TiO_2 . This effect may be related to differences in diffusion rates and the degree of nonstoichiometry that can occur in TiO_2 and NiO.

Properties of Aluminum / TiO_2 Interfaces

The most important result of our aluminum deposition studies on TiO_2 (110) surfaces is that an Al_2O_3 layer is formed and a reduced TiO_{2-x} interface composition is created upon dosing the surface with metallic Al at room temperature. This result is inferred from the UPS, XPS and AES data shown in Fig. 2 measured from a TiO_2 surface dosed with 50 Å of Al. The lineshape of the Al MVV Auger transition (Fig. 2a), the UPS valence band (Fig. 2b), and the Al 2p XPS binding energy (Fig. 2c) are all characteristic of Al_2O_3 . Furthermore, the Ti 2p XPS lineshape (Fig. 2d) shows a low binding energy peak which we associate with the formation of Ti 3+ cations and a reduced TiO_{2-x} composition near the interface. The Al 2p

Fig. 2 (a) AES spectrum (b) UPS spectrum (c) Al 2p XPS spectrum and (d) Ti 2p XPS spectrum measured from a TiO_2 (110) surface dosed with 50 Å of Al.

XPS lineshape does, however, contain a low binding energy component suggesting that metallic Al is still present in the film. Since the electron mean free path is much longer in the XPS experiment, we conclude that the film is heterogeneous containing both a mixture of Al_2O_3 and metallic Al. We are currently doing similar experiments at several different temperatures and film thicknesses to determine the relative importance of kinetic versus thermodynamic effects on these results.

Influence of Defects on Interface Properties

Defects were found to have a major influence on the structure of the various surfaces and interfaces that we studied, as determined by low energy and high energy electron diffraction (LEED and RHEED) and atomic force microscopy (AFM). TiO_2 and NiO were chosen as the substrate oxides for our investigations primarily because a large database of surface properties already exists from numerous studies on these materials. However, most structural information to date has been inferred from LEED. What we have found with

RHEED and AFM is that even carefully prepared TiO_2 and NiO surfaces still contain many structural defects and these in turn dictate the structure of our prepared interfaces.

RHEED analysis was performed on a carefully prepared TiO_2 (110) surface that was judged to be "nearly-perfect" based upon the absence of any defect states in the UPS spectra, the absence of surface contaminants in the XPS and AES spectra, and the presence of a sharp (1x1) LEED pattern. The RHEED patterns measured along two different azimuths are shown in Fig. 3. Because of a large degree of surface roughness, these sharp diffraction features are not caused by reflected electrons but rather by transmission through the highest regions on the surface. The indexed patterns are precisely what would also be observed in a TEM experiment. The surface roughness and shadowing effects of the RHEED beams were confirmed by atomic force microscopy (AFM). Fig. 4 shows a $2\ \mu\text{m} \times 2\ \mu\text{m}$ image of the surface which contains 100 - 200 Å high ridges running parallel to the bridging oxygen direction of the lattice. The origin of these ridges is not completely understood, but they may be related to changes in the bulk stoichiometry of TiO_2 after prolonged thermal treatments. A possible mechanism for their formation is the intersection of crystallographic shear planes

Fig. 3 RHEED patterns from a clean TiO_2 (110) surface. The diffraction features are the result of electron transmission rather than reflection due to surface roughness effects.

formed in the substoichiometric bulk with the surface; the shear mechanism is well known in bulk substoichiometric TiO_2 . By carefully controlling the thermal history, we have found a way to prepare TiO_2 surfaces without these large structural defects for our future metal deposition experiments.

Although numerous structural defects may be present on the TiO_2 and NiO substrates, the local coordination and surface stoichiometry is satisfied. It is the local environment which appears to control the electronic structure and bonding, the focus of most of our work to date. In the future, our emphasis will be on the geometric structure of our prepared interfaces. The characterization of defects is difficult but will be possible using RHEED and AFM.

Fig. 4 Atomic force microscope image of a stoichiometric TiO_2 (110) surface showing 100 - 150 Å high ridges. The image area is 2 μm x 2 μm .

Equipment Development

During the past year, the RHEED / thin film deposition chamber and sample transfer system was completed. The main components and the present capabilities of our surface analysis system are shown schematically in Fig. 5. Specific improvements done in year 2 include the installation of (i) a retractable quartz crystal film thickness monitor and (ii) a Ti sublimator pump and cryoshroud which gives us a 1×10^{-10} Torr base pressure in both vacuum chambers. We are currently fabricating a sample docking stage to store several samples in vacuum and are assembling a photodetector system to measure the intensities of the RHEED beams during film growth.

Fig. 5 Schematic drawing of the ultra-high vacuum surface analysis and thin film growth chambers. The main capabilities of each chamber are listed.

Graduate Students Working on the Project

The following students have directly worked on the project during the past year as part of their Ph.D. thesis research. One student (X. Chen) transferred to the University of Illinois due to personal reasons and his position was filled by a transfer student from Idaho State (S. Imaduddin). The new student already has an M.S. in Physics with relevant experience in surface science and has completed nearly all of his required course work.

Linda S. Dake, Candidate for Ph.D. in Physics. "Structure, Adhesion, and Stability of Metal / TiO_2 Interfaces," (enrolled Sept. 1989, expected completion Dec. 1993).

Xiao-zhuang Chen, Candidate for Ph.D. in Physics, "Properties of Metal Overlayers Deposited on Nickel Oxide Surfaces," (enrolled Jan. 1990, transferred to University of Illinois in June 1991 due to personal reasons).

Syed Imaduddin, Candidate for Ph.D. in Physics, "Electronic and Structural Properties of Interfaces Created by Thin Film Deposition on Nickel Oxide Surfaces," (enrolled Aug. 1991 as a transfer student from Idaho State University with an M.S. in Physics, expected completion June 1994).

Presentation of Results at National Meetings

The following papers were presented at National Meetings. Abstracts are included in Appendices I - III.

1. "Structure, Adhesion, and Stability of Metal Overlayers on TiO_2 and NiO Surfaces," American Ceramic Society Symposium on Atomic Structure, Bonding, and Properties of Ceramics, Marco Island, FL, October 1991. (Talk)
2. "Structure and Chemical Bonding of Metal Overlayers on NiO and TiO_2 Surfaces," American Vacuum Society 37th National Symposium, Seattle, WA, November 1991. (Talk)
3. "Electronic and Structural Properties of Interfaces Created by Potassium Deposition on TiO_2 (110) Surfaces," Fall Meeting of the Materials Research Society, Boston, MA, November 1991. (Poster)

Publications (Preprint enclosed as Appendix IV)

"Electronic and Structural Properties of Interfaces Created by Potassium Deposition on TiO_2 (110) Surfaces," R.J. Lad and L.S. Dake, to be published in the Proceedings of the Materials Research Society, Vol 238, Structure and Properties of Interfaces in Materials.

Current and Pending Support for R.J. Lad

Current Support:

"Structure, Adhesion, and Stability of Metal/Oxide and Oxide/Oxide Interfaces,"
Funded by DOE Basic Energy Sciences, August 1990 - July 1993, \$221,760.

"Direct Imaging of the Surface Microstructure of Dielectric Materials Using an Atomic Force Microscope," Co-investigator: W. N. Unertl. Funded by AFOSR, May 1990 - April 1993, \$216,000.

Pending Support:

"Microstructural Effects in Thin Film SnO_2 and WO_3 Gas Sensor Materials," Co-Investigators: S. Semancik, R.E. Cavicchi, and J.F. Vetelino. NSF Materials Synthesis & Processing Initiative, 3 years, \$607,000.

"An Atomic Force Microscope for Use in Ultra-High Vacuum", Co-investigator: W. N. Unertl. NSF Instrumentation for Materials Research, 1 year, \$61,000.

"Nomination for Young Investigator FY 1992 Award Program," NSF, 5 years, up to \$100,000 per year.

(abstracts removed)

END

DATE
FILMED

3126192

I