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

Technical Progress Report
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Abstract

Fundamental studies of the structural, electronic, and chemical properties of metal/oxide and oxide/oxide interfaces were performed on well-defined interfaces that were created by depositing ultra-thin potassium and aluminum films and their oxides onto single crystal TiO₂ and NiO surfaces. The work focused on (i) determining the structure, growth mechanisms, and morphologies of metal and oxide films as they are deposited on single crystal oxide surfaces using RHEED and atomic force microscopy (ii) probing the electronic structure, bonding and chemical interactions at the interfaces using x-ray and uv photoelectron spectroscopies (XPS, UPS) and Auger electron spectroscopy (AES) and (iii) understanding the important factors that affect stability and reactivity of the interface regions including the role of defects and impurities. The results indicate that kinetic effects have a very important influence on interface structure and composition, and they also show that defects in the oxide substrate induce new electronic states at the interface which play a major role in cation-anion bonding and interface interactions. Our results establish a link between the electronic and chemical bonding properties and the interface structure and morphology, which is basic knowledge required to successfully manipulate the interfacial properties of advanced ceramic materials.
Highlights of Research Results

The major research activities have focused on several metal-ceramic interfaces that were formed by depositing metals onto single crystal TiO$_2$ and NiO surfaces. The experiments were designed to study (i) interface bonding and adhesion (ii) interface structure and morphology (iii) the influence of defects on interface properties and (iv) interface stability and interdiffusion. The systems studied to date include potassium / TiO$_2$, potassium / NiO, aluminum / TiO$_2$, and aluminum / NiO. In general, the interactions at these interfaces follow the oxidation - reduction reactions predicted by bulk thermodynamics. However, exceptions to the thermodynamic predictions are observed, particularly in the Al / NiO system, and kinetic effects are found to be very important in determining the interface structure and composition. Results also show that defects in the oxide substrate induce new electronic states at the interface that play a major role in cation - anion bonding and interface structure. The main results for the specific systems are summarized below, and the details are provided in the reprint and preprints enclosed as appendices to this report.

(1) Properties of Potassium / TiO$_2$ Interfaces - Potassium interacts strongly with stoichiometric TiO$_2$ (110) surfaces. At submonolayer coverages, the potassium donates charge to the oxygen anions causing a reduction of the Ti cations in the TiO$_2$. At larger doses, stable K$_2$O multilayers are formed at room temperature via oxygen diffusion from the substrate, leaving behind an oxygen deficient TiO$_{2-x}$ composition at the interface. The K$_2$O layers are stable to at least 600 °C but have no epitaxial order with respect to the substrate. On defective TiO$_2$ surfaces, the surface titanium cations are already in the Ti 3+ valence state and the potassium is found to be less reactive.

(2) Properties of Aluminum / TiO$_2$ Interfaces - Aluminum interacts strongly with both stoichiometric and sub-stoichiometric TiO$_2$ (110) surfaces at room temperature. For monolayer Al doses, charge transfer occurs from the aluminum to the surface Ti cations
thereby reducing the TiO$_2$ and oxidizing the aluminum layer. At larger Al doses, an aluminum oxide film continues to grow by extracting oxygen anions from the TiO$_2$ substrate. When oxygen diffusion becomes rate limiting, a heterogeneous mixture of metallic and oxidized aluminum is created on top of the oxygen-deficient TiO$_{2-x}$ substrate. This mixed layer is unstable upon heating and is converted completely to aluminum oxide. In addition, the annealing treatment causes a re-oxidation of the reduced Ti species at the interface via diffusion of oxygen anions from the bulk TiO$_2$ crystal.

(3) Properties of Potassium / NiO Interfaces - The interaction between potassium and NiO (100) surfaces is very similar to that observed on TiO$_2$ (110). At monolayer coverages, charge transfer to the NiO surface causes a large decrease in work function and an increased population of Ni 3d valence states indicating that the NiO becomes reduced. Following larger doses of potassium, a K$_2$O layer forms but the growth rate of the overlayer is slower than that on TiO$_2$, which we attribute to differences in diffusion rates and the degree of nonstoichiometry that can occur in NiO versus TiO$_2$.

(4) Properties of Aluminum / NiO Interfaces - Aluminum does not become oxidized as it is deposited onto a NiO (100) surface, in contrast to the Al / TiO$_2$ system. Although aluminum oxide formation is predicted by the relative free energies of formation of the oxides, we observe an intermetallic Ni$_3$Al phase at the interface. The Ni$_3$Al grows epitaxially with the same (100) orientation as the NiO substrate and the reaction is controlled by the extraction of Ni out of the NiO subsurface region. At large doses of aluminum, metallic aluminum is formed on top of the Ni$_3$Al phase and the overlayer has a very heterogeneous morphology. The Ni$_3$Al interphase layer is very stable upon heating in vacuum. Defects on the NiO surface help to promote the Ni$_3$Al growth, but induce some structural disorder in the overlayer.
Issues currently being addressed

In the remaining 9 months of the project, the work will examine several key areas. From our results thus far, we have determined that the following issues play a significant role in controlling interface properties. Work is already underway in each of these areas.

(1) **Role of oxygen activity** - An important question to consider is what is the relative importance of kinetic versus thermodynamic factors in determining the chemical bonding and reactivity at the interfaces. The critical experiments to clarify this issue involve changing the oxygen activity during film growth by varying the oxygen partial pressure and performing controlled annealing studies.

(2) **Importance of substrate roughness** - One of the problems that limits our diffraction studies of film growth mechanisms and interface morphology is the substrate roughness. TiO$_2$ and NiO substrates were originally chosen because a large database of surface properties already exists for these surfaces. However, our RHEED and atomic force microscopy results have shown that the structure and morphology of the clean surfaces are surprisingly complex. We have developed processing methods which improve the perfection of the prepared surfaces and we will determine how substrate roughness influences the interface morphology and the heterogeneity of the overlayers.

(3) **Influence of impurities at the interface** - Trace amounts of impurity atoms on surfaces often act as a surfactant and strongly influence the wetting behavior of deposited overlayers. We will investigate whether trace amounts of potassium or carbon have any effect on interface composition and morphology in the Al / TiO$_2$ and Al / NiO systems.
(4) **Synchrotron radiation experiments** - During spring 1993, we will perform photoemission and fluorescence synchrotron radiation experiments as a general user on beamline U16 at the National Synchrotron Light Source (NSLS). We have 18 days of beamtime and the specific experiments will include valence band and resonant photoemission to further probe the interface region in the Al / TiO$_2$ and Al / NiO systems. Fluorescence / absorption and total yield measurements will also be carried out to identify electronic excitations and defect states at the interfaces.

**Equipment Development**

The experimental approach for the project involves growing ultra-thin metal and oxide films on single crystal TiO$_2$ (110) and NiO (100) surfaces, thereby creating well-defined interfaces that can be probed with surface analysis techniques. To accomplish this procedure, a large effort went into constructing a new ultra-high vacuum chamber that is equipped with metal deposition sources for thin film growth and *in situ* Reflection High Energy Electron Diffraction (RHEED) analysis and coupling it to a surface analysis chamber. This construction phase took approximately a year to complete.

Fig. 1 shows a schematic diagram of the coupled film growth and surface analysis vacuum chambers. A versatile sample transfer and sample heating system was designed and implemented which allows samples to be installed via a small load-lock chamber and either docked onto separate manipulators in front of electron beam heaters in each chamber or onto a sample storage stage. The sample load-lock facility also allows samples to be transferred out of vacuum and immediately imaged with an Atomic Force Microscope (AFM).

Characterization of film epitaxy and interface morphology is carried out in the film growth / RHEED chamber. To minimize electron beam-induced damage to the
oxide surfaces, the RHEED system is operated with nanoamp beam currents and using a microchannel plate detector in front of the phosphor screen.

In the analysis chamber, the chemical bonding, composition, interdiffusion, and electronic structure information is probed with X-ray and Ultra-violet Photoelectron Spectroscopies (XPS and UPS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). During this past year, a new VG x-ray source was acquired which increased the XPS signal by a factor of 50. In addition, a quartz crystal oscillator was added to monitor the deposition rate from the metal evaporator.

**PI's Time Commitment to the Project**

Prof. Lad devotes at least the equivalent of four months per year working directly on the project. The University of Maine cost shares 2 months academic year salary to enable Prof. Lad to fulfill this commitment.
Students Working on the Project


Yu Yan, Ph.D. candidate in Physics, "Interaction of Metal Overlayers with Aluminum Oxide Surfaces," (enrolled Sept. 1992, expected completion June 1996)

Thomas Cole, senior project in Physics, "Design, Fabrication, and Calibration of a Metal Evaporation Source for Use in Ultra-high Vacuum" (Spring 1990)

Elizabeth Dyer, undergraduate student in Physics, "Preparation and Characterization of Polished NiO Single Crystal Surfaces" (Fall 1992)

Presentations at National Meetings

"Electronic Structure of Surface Defects on TiO\textsubscript{2}(110) Studied by Resonant Photoemission," Meeting of the American Physical Society, Anaheim, CA, March 1990 (Talk given by R.J. Lad)

"Properties of Potassium Modified TiO\textsubscript{2}(110) Surfaces," American Vacuum Society 36th National Symposium, Toronto, Canada, October 1990 (Poster given by R.J. Lad)


"Electronic and Structural Properties of Interfaces Created by Potassium Deposition on TiO\textsubscript{2}(110) Surfaces," Fall Meeting of the Materials Research Society, Boston, MA, December 1991 (Poster given by R.J. Lad)

"Electronic and Chemical Interactions at Aluminum / TiO_2 Interfaces," Conference on the Physics and Chemistry of Metal/Oxide Interfaces, Rutgers University, Piscataway, NJ, September 1992 (Poster given by L.S. Dake)

"Structure and Morphology of Aluminum Overlayers on NiO (100) Interfaces," Conference on the Physics and Chemistry of Metal/Oxide Interfaces, Rutgers University, Piscataway, NJ, September 1992 (Poster given by S. Imaduddin)


"Structure and Composition of Al / NiO Interfaces," S. Imaduddin and R.J. Lad, Meeting of the American Ceramic Society, April 1993 (submitted)

Publications from the Project


Related Publications Not Emanating Directly from the Project


