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Ion Mixing in Oxide-Sapphire Systems

D.L. Joslin, C.J. McHargue¹, and C.W. White²

Metals and Ceramics Division, Oak Ridge National Laboratory

Oak Ridge, TN 37831 USA

ABSTRACT

Ion beam mixing of thin oxide films on sapphire substrates has been studied in order to examine any role of equilibrium thermodynamic parameters on the mixing process. Mixing experiments were performed with polycrystalline oxide films deposited on single crystalline α -Al₂O₃ substrates. According to the equilibrium phase diagrams, Cr₂O₃ is completely soluble in α -Al₂O₃, while ZrO₂ is insoluble. The couples were irradiated with Cr ions (160 and 340 keV) or Kr ions to fluences of 4×10^{16} ions/cm² at temperatures between 20 and 900°C. Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy, and transmission electron microscopy were used to analyze samples before and after irradiation to determine the extent and nature of interface modifications. No long-range mixing was detected under any condition studied; the width of the "mixed" region in each case was consistent with recoil mixing. The absence of long-range mixing is rationalized in terms of the different ranges of oxygen ions and cations.

¹Consultant and Professor from the Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996-2000, USA; ²Solid State Division, Oak Ridge National Laboratory

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INTRODUCTION

The majority of studies of ion beam mixing phenomena have involved metal-metal or metal-silicon systems. Interest in these systems arose mainly from the observation that ion bombardment can enhance adhesion between a thin film and its substrate. Few investigations of metal-insulator systems have been made.

Several studies of metal-metal and metal-silicon systems have indicated that the thermochemical properties of the film/substrate combination influence mixing phenomena. For example, the compositions of layers formed at the interface between metal films and substrates are often those that form during thermal annealing [1-4].

The enthalpy of formation has been considered an important parameter in determining the nature of the interfacial reactions occurring during ion irradiation. Mixing rates have been linked with the solubility of metals in metal-metal couples; the solubility depends in part on the enthalpy of mixing, ΔH_m [5,6].

Differences in the amounts of mixing observed in collisionally similar but chemically different systems implies that cascade mixing is strongly influenced by local chemical processes. This point is illustrated by marker layer experiments on the systems Cu-Au and Cu-W, which are similar in terms of relative masses (and therefore implantation kinematics) but are chemically different. According to the equilibrium phase diagram, Cu and Au have extensive solid solubility, with the formation of ordered intermediate phases; Cu and W are virtually immiscible. In the Cu-W-Cu samples, the observed amount of mixing was of the magnitude predicted for recoil mixing alone, whereas the amount of mixing in the Cu-Au-Cu samples was an order of magnitude greater [7].

To explain the differences in collisionally similar but chemically dissimilar systems, Johnson et al. [7-10] developed a model in which the final distribution of the chemical species is determined by chemically biased diffusion within a thermal spike. The model uses the differences in ΔH_m and cohesive energies (ΔH_c) to analyze the variations in the amount of mixing observed. Data obtained for bilayers of 4d-5d metals irradiated with 600 keV Xe⁺⁺ at 77K correlated well with this model when the materials were assumed to behave as regular solutions and the values for $\Delta H_m/\Delta H_c$ used were those for a 50-50 mixture of the metals [10].

Farlow et al. [11] applied the enthalpy rule (mixing is expected only if the heat of reaction between the components is negative) in a study of mixing of 33 materials combinations. Mixing always occurred when predicted; however, mixing sometimes occurred when not predicted by the rule.

Ion beam induced mixing in systems containing insulators either as a substrate or as a deposited film is not well-understood. Few systems have been studied, and the range of

experimental conditions has been limited. This work is directed toward obtaining a better understanding of the roles of thermodynamics and kinetics in mixing of oxide-oxide bilayers. With this goal in mind, the systems $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2/\text{Al}_2\text{O}_3$ were chosen for study. The equilibrium phase diagrams show that Cr_2O_3 has complete solid solubility with Al_2O_3 , while ZrO_2 is completely insoluble in Al_2O_3 below 1710°C [12]. Solid solutions of Cr_2O_3 and Al_2O_3 have been formed by sintering the oxides as powders at temperatures between 1400 and 1500°C [13-15]. By studying these systems at room temperature and at elevated temperature, the role of thermodynamics and kinetics in any mixing obtained might be evaluated.

EXPERIMENTAL

The substrates were c-axis oriented, single crystal sapphire (Al_2O_3) disks supplied with an optical-grade polish by the manufacturer (Crystal Systems, Inc., Bedford, MA). Prior to film deposition, the substrates were annealed in flowing air at 1300°C for 120 h to remove residual polishing damage and surface contamination. Thin films (50 or 80 nm thick) of Cr_2O_3 or ZrO_2 were deposited from sintered oxide targets onto the substrates via rf sputter deposition. The as-deposited films were oxygen-rich; in order to obtain proper stoichiometry, the samples were annealed for 2 h at 500°C in an atmosphere of 96%Ar-4%H.

Implantations were carried out in a Varian Extrion 200 kV implanter. Samples were implanted with either 160 or 340 keV Cr^+ or with 475 keV Kr^+ to a fluence of 4×10^{16} ions/ cm^2 . Implantations were carried out at room temperature and near 900°C . The ion energies were chosen so that the majority of the implanted ions would come to rest relatively far from the film/substrate interface. A portion of each sample remained masked during implantation to provide an unimplanted region for comparison.

After implantation, all samples were examined using Rutherford backscattering spectroscopy (RBS) with He^{2+} ions at an energy of 2.3 MeV. Spectra were taken in glancing exit angle geometry ($\theta = 40^\circ$) to enhance depth resolution when examining the specimens for evidence of mixing.

Selected samples were analyzed using x-ray photoelectron spectroscopy (XPS), and analytical electron microscopy (AEM). The XPS analyses were performed in either a V.G. ESCALAB II system or a Perkin-Elmer Model 5600 ESCA system. The base pressure was approximately 1×10^{-7} Pa. The analyzing radiation was either Mg K_α x-rays (1253.6 eV) or Al K_α x-rays (1486.6 eV); the analyzer pass energy was 100 eV for all analyses, and the analysis area on the sample was 300 μm in diameter. Sputter depth profiling was

used to track the components from the film through the film/substrate interface and into the substrate.

Specimens for the analytical electron microscopy (AEM) were prepared by mounting in cross section, mechanical grinding and dimpling to a thickness of $\sim 20\text{ }\mu\text{m}$, and ion milling to electron transparency with Ar^+ . The samples were carbon coated ($< 10\text{ nm}$) to minimize charging in the microscope. The AEM was performed at 100 keV in a Philips EM 400T/FEG TEM-STEM analytical electron microscope. Energy Dispersive Spectrometry (EDS) was performed with the microscope in scanning transmission mode for both stationary probes and analogue line scans (2 nm diameter full width half maximum). The samples were placed in a cooling stage at liquid nitrogen temperature (-196°C) to minimize contamination.

RESULTS AND DISCUSSION

Examination of the films by RBS yielded inconclusive evidence concerning the amount of mixing observed; however, the appearance of the spectra indicated that no long-range mixing had occurred.

X-ray photoelectron spectroscopy depth profiles from the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples implanted at room temperature and at elevated temperature with $4 \times 10^{16}\text{ Cr}^+/\text{cm}^2$ at 160 keV are shown in Fig. 1. In both samples, there is a small amount of Al present at the sample's surface. In the sample implanted at room temperature, the Cr extends at least 40 nm into the Al_2O_3 substrate. Curve-fits of Cr spectra taken in this sample at positions in the film and in the substrate near the interface indicate the presence of multiple charge states, from Cr^0 to Cr^{6+} (Table 1). In the film, the major contribution is from Cr metal; at the interface, Cr^{3+} is the major component, but the amount of Cr^0 is significant. In the substrate near the interface, the Al appeared is present as Al^0 and Al^{3+} .

In the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample implanted at 860°C (160 keV Cr, $4 \times 10^{16}\text{ Cr}^+/\text{cm}^2$), the Cr extends only about 20 nm into the Al_2O_3 substrate (Fig. 1). Results from curve-fitted Cr spectra from positions in the film and in the substrate near the interface are listed in Table 1. In the film, Cr is present in various states of oxidation, as in the specimen implanted at room temperature. These peaks persist through the interface region, with the relative amounts changing slightly. The major contribution at all positions is from Cr^{3+} . The Al at the interface was shown to be present only as Al^{3+} .

Depth profiles from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted at 20°C and at 860°C with $4 \times 10^{16}\text{ Cr}^+/\text{cm}^2$ at 160 keV are shown in Fig. 2. There is no evidence of Al near the surface in either of these samples. In the sample implanted at room temperature, the Zr appears to extend approximately 25 nm into the Al_2O_3 substrate, and at higher levels than

those found in the sample implanted at elevated temperature. Results from curve fits of spectra obtained on both samples are shown in Table 1. In the sample implanted at 20°C, Zr is present as Zr^0 and Zr^{4+} in the film and at the interface, and the Al at the interface is present as Al^0 and Al^{3+} . However, in the sample implanted at 860°C, Zr is present as Zr^{2+} and Zr^{4+} , and the Al is present only as Al^{3+} .

Depth profiles from a ZrO_2/Al_2O_3 film bombarded with $4 \times 10^{16} \text{ Kr}^+/\text{cm}^2$ (475 keV, 20°C) revealed somewhat more extensive mixing in this sample than that observed after the other implantations. After implantation, the Zr extends at least 120 nm (~45 min sputter time) into the Al_2O_3 substrate. Curve fits of the spectra revealed that this sample's ZrO_2 film was not stoichiometric, probably due to a mistake in annealing. The results from the curve fits are listed in Table 1. In contrast, comparison of implanted and unimplanted XPS depth profiles from the ZrO_2/Al_2O_3 sample implanted at 825°C (475 keV, $4 \times 10^{16} \text{ Kr}^+/\text{cm}^2$) show the sample to be virtually unchanged from the unimplanted condition except that some of the film was sputtered away during implantation. This sample was also nonstoichiometric. The results from the curve fitted data are listed in Table 1.

Figures 3-5 are micrographs obtained from cross-sections of some ZrO_2/Al_2O_3 specimens. An unimplanted ZrO_2/Al_2O_3 couple is shown in Fig. 3; the film is denoted by the arrow. The film/substrate interface is sharp. A ZrO_2/Al_2O_3 sample implanted at 20°C with 340 keV Cr to a fluence of $4 \times 10^{16} \text{ ions/cm}^2$ is shown in Fig. 4. Region A is the ZrO_2 film; regions B and C are in the sapphire substrate. Region B is an amorphous layer about 30 nm thick; its diffraction pattern is shown in the figure. From EDS line scans, Zr is present to depths of 20 nm into the substrate. No Zr is present in region C. Figure 5 is a micrograph of a ZrO_2/Al_2O_3 sample implanted at 900°C with $4 \times 10^{16} \text{ Cr}^+/\text{cm}^2$ at 340 keV. The film/substrate interface, marked with an arrow, is well-defined.

From the XPS results, it appears that reduction of the oxides occurs during room temperature implantations, probably due to the differences in recoil ranges of the metal and oxygen species. For example, in a Cr_2O_3/Al_2O_3 sample implanted with 160 keV Cr, the recoil range of a Cr atom near the film/substrate interface is about 55 nm into the substrate, whereas the recoil range of the oxygen is about 100 nm. During the elevated temperature implantations, where irradiation-induced defects in Al_2O_3 are known to be mobile [17], the oxygen diffuses back into the interface, and thus the metal species are "re-oxidized." The solubility of impurities in $\alpha\text{-}Al_2O_3$ is small [18], which explains the XPS and TEM results which imply that the film's metal species also diffuses back toward the interface during the elevated temperature implants.

CONCLUSIONS

In the oxide-sapphire systems investigated, no long-range mixing was detected under any condition studied; the width of the "mixed" region in each case was consistent with recoil mixing. Because of the differences in the recoil ranges of the metal ions and the oxygen ions, there is little chance for the ZrO_2 or Cr_2O_3 to form in the sapphire substrate during the room temperature implantations, and the oxide-oxide phase diagrams are of little use in predicting the ion-induced mixing behavior. At the elevated temperatures, the foreign species recoiled into the sapphire diffuse out, and are "re-oxidized."

ACKNOWLEDGEMENTS

Research sponsored in part by the U.S. Department of Energy, Division of Materials Sciences and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Ceramic Technology Project of the Materials Development Program, under contract DE-AC-84OR21400 with Martin Marietta Energy Systems, Inc., and through the SHaRE Program at Oak Ridge National Laboratory under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

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Fig. 1. X-ray photoelectron spectroscopy depth profiles from the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples implanted at room temperature and at elevated temperature with 160 keV Cr to a fluence of 4×10^{16} ions/cm².

Fig. 2. Depth profiles from the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ samples implanted at 20°C and at 860°C with 4×10^{16} Cr⁺/cm² at 160 keV.

Fig. 3. A micrograph of an unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couple is shown in Fig. 7; the film is denoted by the arrow.

Fig. 4. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 20°C with 340 keV Cr to a fluence of 4×10^{16} ions/cm². Region A is the ZrO_2 film; regions B and C are in the sapphire substrate. Region B is an amorphous layer about 30 nm thick; its diffraction pattern is shown.

Fig. 5. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 900°C with 4×10^{16} Cr⁺/cm² at 340 keV. The film/substrate interface, marked with an arrow, is well-defined.

Table 1. Chemical States Determined by XPS.

Film	Implantation	Chemical States	
		In Film	At Interface
Cr_2O_3	160 keV Cr 20°C	Implanted: Cr^0 , Cr^{3+} , Cr^{6+}	Implanted: Cr^0 , Cr^{3+} , Cr^{6+} Al^0 , Al^{3+}
Cr_2O_3	160 keV Cr 860°C	Implanted: Cr^0 , Cr^{3+} , Cr^{6+} (relative amounts different from 20°C)	Implanted: Cr^0 , Cr^{3+} , Cr^{6+} Al^{3+}
Cr_2O_3	475 keV Kr 20°C	Unimplanted: Cr^0 , Cr^{3+} , Cr^{6+}	Unimplanted: Cr^0 , Cr^{3+} , Cr^{6+} Al^{3+}
		Implanted: Cr^0 , Cr^{3+} , Cr^{6+}	Implanted: Cr^0 , Cr^{3+} , Cr^{6+} Al^0 , Al^{3+}
ZrO_2	160 keV Cr 20°C	Implanted: Zr^0 , Zr^{4+}	Implanted: Zr^0 , Zr^{4+} Al^0 , Al^{3+}
ZrO_2	160 keV Cr 860°C	Implanted: Zr^{2+} , Zr^{4+}	Implanted: Zr^{2+} , Zr^{4+} Al^{3+}
ZrO_x (nonstoich.)	475 keV Kr 20°C	Unimplanted mixed Zr oxides	Unimplanted mixed Zr oxides Al^{3+}
		Implanted: mixed Zr oxides	Implanted: mixed Zr oxides Al^0 , Al^{3+}
ZrO_x (nonstoich.)	475 keV Kr 825°C	Unimplanted mixed Zr oxides	Unimplanted mixed Zr oxides Al^{3+}
		Implanted: mixed Zr oxides	Implanted: mixed Zr oxides Al^{3+}

Fig 1

Fig 2.

Fig 3

Fig 4

Fig 5

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