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Amorphization of Sapphire During Ion Beam Mixing

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ABSTRACT

Earlier studies indicated that implantation of zirconium into sapphire at room temperature produced an amorphous layer at a critical composition of approximately 6.5 % (cation).

Further insight into the amorphization of sapphire has been provided by ion beam mixing studies. Bi-layer couples of ~80 nm thick polycrystalline ZrO₂ films deposited on the (0001) face of α -Al₂O₃ single crystals were irradiated to 4×10^{16} ions/cm² with Kr (475 keV, 20°C) or Cr (340 keV, 20°C or ~900°C).

Transmission electron microscopy showed the unirradiated couples to have sharp, planar interfaces between the films and substrates. Recoil mixing by both ion species gave Zr concentrations greater than 10% (cation) to depths of 10-20 nm. An amorphous layer containing Zr was present at the interface for samples irradiated at room temperature. The sample mixed at the elevated temperature contained a sharp interface similar to the as-deposited sample.

The present results suggest that both irradiation-produced damage (defects) and certain chemical species are required to amorphize sapphire.

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INTRODUCTION

The amorphization of sapphire (α -Al₂O₃) induced by ion implantation has been studied for several years. It has been known for some time that the amorphous state can be produced in Al₂O₃ by ion beam induced displacements alone at -196°C, where dynamic recovery is suppressed [1]. At room temperature, the combination of displacements and chemical effects can induce amorphization, while displacements alone cannot. This is illustrated by studies in which sapphire substrates were implanted with either Zr or Nb, at nearly the same energy and fluence [2]. Here, the Zr produced an amorphous layer, while the Nb did not. Since the masses of the two species differ by only 3 atomic mass units, the cascade dynamics should be similar. The differences in the resulting disorder must be due to some chemical effect occurring after the cascade [2].

For an Al₂O₃ substrate implanted at room temperature with 175 keV Zr to a fluence of 4×10^{16} ions/cm², McHargue et al. [3] reported that a critical composition for amorphization appeared to exist. Examination of the sample by analytical electron microscopy (AEM) showed that a subsurface amorphous layer was formed with a minimum measured value of Zr/Al being 0.065.

EXPERIMENTAL PROCEDURE

Zirconia films (~50 - 80 nm thick) were deposited on sapphire by rf sputter deposition, and subsequently annealed in 96% Ar + 4% H₂ for 2 h at 500°C to remove excess oxygen. Samples were bombarded with either 160 or 340 keV Cr⁺ or 475 keV Kr⁺ to a fluence of 4×10^{16} ions/cm². An area of each specimen was masked during implantation to allow analysis of unimplanted interfaces. The Cr⁺ implantations were performed at either 20°C or at temperatures near 900°C. The calculated projected ranges of the implanted ions in such couples are listed in Table 1 [4]. The ions' projected ranges are greater than the films' thicknesses.

Specimens for the analytical electron microscopy were prepared by mounting in cross section, mechanical grinding and dimpling to a thickness of ~20 μ m, and ion milling to electron transparency with Ar⁺. The samples were carbon coated (< 10 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.

The chemical states of the components of selected samples were determined via X-ray photoelectron spectroscopy (XPS). The analyses were performed in a V.G. ESCALAB II system operating with a base pressure of approximately 1×10^{-7} Pa. The analyzing radiation was Mg K_{α} x-rays (1253.6 eV); the analyzer pass energy was 100 eV for all analyses; 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.

RESULTS AND DISCUSSION

A micrograph of the unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couple is shown in Fig. 1. The film/substrate interface, marked with an arrow, is discrete. Figure 2 is a micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature with 340 keV Cr^+ to a fluence of 4×10^{16} ions/ cm^2 . Region A is the ZrO_2 film; regions B and C are in the sapphire substrate. The film/substrate interface is marked by an arrow. 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 in the amorphous region. No Zr is present in region C. These results are in agreement with the amount of recoil mixing predicted by TRIM [4].

Figure 3 is a micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couple implanted at room temperature with 4×10^{16} Kr^+/cm^2 at 475 keV. Four distinct regions are present: A is the ZrO_2 film; B is an amorphous layer in the Al_2O_3 substrate; C is a heavily damaged layer in the substrate; and D is undamaged sapphire. The EDS analysis shows that, again, some Zr is present in the amorphous layer.

A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 900°C with 4×10^{16} Cr^+/cm^2 at 340 keV is shown in Fig. 4. The film/substrate interface, marked with an arrow, is well-defined. Defects in $\alpha\text{-Al}_2\text{O}_3$ are known to be mobile at temperatures near 900°C [5]. These results imply that demixing occurs during the elevated temperature implants: Zr diffuses back toward the interface during these implants as a result of the mobility of the defects in $\alpha\text{-Al}_2\text{O}_3$ at these temperatures, and the fact that the solubility of impurities in $\alpha\text{-Al}_2\text{O}_3$ is small [6].

Profiles of Zr and Al concentration vs. depth from $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couples implanted with 4×10^{16} Cr^+/cm^2 at 160 keV at either 20 or 860°C, obtained by x-ray photoelectron spectroscopy (XPS) are shown in Fig. 5. The concentrations presented here are not absolute, because only the species of interest (zirconium, aluminum, and oxygen) were monitored. Noticeably larger amounts of Zr are found in the substrate in the sample implanted at room temperature than for the sample implanted at 860°C.

CONCLUSIONS

Bombardment of $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couples by Cr^+ or Kr^+ at room temperature can result in the formation of an amorphous layer in the Al_2O_3 due to the presence of Zr recoiled into the substrate from the film. During implantation at elevated temperatures, dynamic recovery in the sapphire leads to partial demixing of the ballistically mixed couples. It appears that both the impurity Zr and irradiation-produced defects are necessary to produce the amorphous phase. The role of the impurity may be the stabilization of defects at relatively low temperatures.

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Fig. 1. A micrograph obtained from an unimplanted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couple. The film/substrate interface is marked with an arrow.

Fig. 2. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at room temperature 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. 3. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couple implanted at room temperature with 4×10^{16} Kr^+/cm^2 at 475 keV. Four distinct regions are present: A is the ZrO_2 film; B is an amorphous layer in the Al_2O_3 substrate; C is a heavily damaged layer in the substrate; and D is undamaged sapphire.

Fig. 4. A micrograph of a $\text{ZrO}_2/\text{Al}_2\text{O}_3$ sample implanted at 900°C with 4×10^{16} Cr^+/cm^2 at 340 keV. The film/substrate interface is denoted with an arrow.

Fig. 5. Profiles of concentration vs. depth from $\text{ZrO}_2/\text{Al}_2\text{O}_3$ couples implanted with 4×10^{16} Cr^+/cm^2 at 340 keV at either 20 or 900°C, obtained by x-ray photoelectron spectroscopy.

Table 1. ion Ranges in $\text{ZrO}_2/\text{Al}_2\text{O}_3$ Specimens Calculated from TRIM [4].

Film thickness (nm)	Ion, Energy (keV)	Range, R_p (nm)
50	Cr, 160	78 ± 30
80	Cr, 340	166 ± 49
80	Kr, 475	155 ± 52

Fig 1

Fig 2

Fig 3

Fig 4

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