INVESTIGATION OF ION BEAM MIXING OF IRON MARKER LAYERS IN ALUMINUM OXIDE BY RBS

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ABSTRACT

Thin films made with a thin embedded marker layer of iron or iron oxide in amorphous alumina were ion mixed with 210 keV Ar over a temperature range of RT to 750°C in vacuum. The dose range was 5×10^{15} - 7×10^{16} ions/cm² with an average dose rate of 4.5×10^{12} ions/cm²-sec. The resulting marker distributions were analyzed using RBS. Spreading of the iron RBS peak due to mixing into the alumina matrix was observed in the Fe₂O₃ marker samples and was clearly seen to be a function of temperature (>400°C) and dose, whereas for the Fe marker sample, no such temperature dependence was observed. An activation energy for the thermally assisted ion mixing in the Fe₂O₃ marker sample was determined to be 0.69 eV in comparison to an activation energy of 1.77 eV for samples that underwent only a thermal treatment.

INTRODUCTION

Ion beam mixing as a function of substrate temperature has been extensively studied in metal and semiconductor matrices, with limited work on ceramic systems. Recently, ion mixing in oxide-oxide bilayer films has been investigated [1], but the results are inconclusive. In general, at low temperatures, ion mixing is dominated by ballistic processes, characterized by a temperature independent regime in which all mixing is done by the primary knock-on action and the resulting low energy recoils in cascades. However, above a critical temperature, T_c , a thermally assisted ion mixing process is present for which an activation energy can be extracted.

For example, mixing in a Si/Ge layered structure [2] was observed to have a thermal activated mixing regime with a critical temperature of 150°C and a thermal assisted ion mixing activation energy of 0.16 eV, much lower than the reported thermal intermixing activation energy of 1.55 eV for the systems studied. However, the little data available for metal markers in ceramic matrices indicate that only ballistic ion mixing is in effect for the entire temperature range investigated [3]. In this work, we will investigate the effect of embedding an oxide marker in an oxide matrix and compare the effect of temperature on the ion beam marker spreading in this system to one in which a metal marker is embedded.

EXPERIMENTAL

The two films used for this study were e beam deposited on 2" sapphire wafers. A layer of Pt was deposited on the substrate first to be used as a deep marker to

monitor sputtering. This was followed by alumina, the marker (either Fe metal or Fe_2O_3), and lastly a top layer of alumina. To deposit Fe_2O_3 , an oxygen backpressure of 2×10^{-4} torr was maintained during the iron evaporation. Alumina films deposited on carbon substrates were subjected to profilometry measurements in conjunction with RBS to determine the deposition density of the alumina. The density of the deposited alumina was determined to be 2.55 g/cm^3 which is 64% of ρ_{th} . Based on this density, the thicknesses of each deposited layer could be determined by RBS and are listed in Table I.

Table I. Thickness of deposited layers in marker layer samples (in Å)

sample	Pt	alumina	marker	alumina
Fe	7.5	1450	83	800
Fe_2O_3	8.2	1825	75	1250

The 2" wafers were cleaved into small pieces, approximately 6mm x 6mm, so that sufficient samples would be available to run a range of doses and experimental implantation temperatures. The samples were mounted onto a Ni block for implantation by holding one corner of the substrate with a screw coated with ZrO_2 to avoid seizing of the screws to the block. Samples were similarly attached to the back side of the block, protected from the ion beam, for thermal anneals.

TRIM [4] range calculations were run for Ar in alumina (based on the measured density) to determine the acceleration voltage necessary for a projected range of 2000Å. An implantation energy of 210 keV was selected to place the bulk of the implanted Ar^{++} in the rear alumina layer and in front of the deep Pt marker.

Implantations were made by heating the samples up to temperature using a cartridge heater installed in the center of the Ni block. Ar^{++} implantations were started as soon as the substrates reached the desired temperature. The average dose rate was 4.5×10^{12} ions/ cm^2 /sec, with a variation of $\pm 0.2 \times 10^{12}$ ions/ cm^2 . The vacuum in the chamber before implantation was typically 6×10^{-7} torr. After the implantation was complete, the block was cooled by conduction to a liquid N_2 supply at a initial rate of 35-50°/min. To determine the degree of marker mixing, Rutherford backscattering spectrometry was conducted on each implanted specimen, as well as an as deposited specimen, using 2 MeV He^{++} at a tilt angle of 60° to beam-normal, and a scattering angle of 167°.

RESULTS

Shown in Fig. 1 is a series of RBS spectra. The Al and O elemental surface scattering edges were fitted and used to calibrate the backscattering energy scale and to convert channels to energy for each spectra. Shown are spectra from an as-deposited specimen, a specimen implanted at 407°C, and a specimen held at 407°C for the duration of the implant. The two spectra from the as deposited and thermally annealed control samples overlap completely indicating little or no mixing from thermal processing alone. However, as can be seen, there is clearly a

change in the width of the Fe peak following ion mixing at this temperature.

The change in energy variance of the peak distribution, Ω^2 , relative to the untreated sample is given by:

$$\Omega^2 = \Omega^2_{\text{treated}} - \Omega^2_{\text{untreated}} \quad (1)$$

where both the treated and untreated Ω^2 contain contributions due to detector resolution and ion straggling, and are thereby subtracted out of the final Ω^2 . This can be converted into a depth distribution change by:

$$\sigma^2 = \Omega^2 / (N \cdot [\epsilon]) \quad (2)$$

where σ is the effective mixing distance, N is the atomic density (atoms/cm³), and $[\epsilon]$ the stopping cross-section factor for He scattering from iron in a alumina matrix [5].

The channel variance and position of the Fe peak was determined by fitting the spectra in the vicinity of the Fe peak. For each experimental temperature, the σ^2 was plotted against dose, Φ , and linearly fitted to obtain a slope representing σ^2/Φ , the dose independent mixing coefficient. σ^2/Φ was plotted as a function of temperature and is shown in Fig. 2 for both the Fe and Fe₂O₃ marker samples.

Figure 1 RBS spectra for Fe₂O₃ marker sample

Figure 2 Marker spreading as a function of inverse temperature

DISCUSSION

An observation from Fig. 2 is the dramatic difference in temperature dependence on σ^2 between the Fe and Fe_2O_3 markers. As had been previously observed by others for pure metal markers in Al_2O_3 , there is only ballistic mixing for all temperatures for the Fe metal marker. However, the oxide marker, clearly shows two mixing regimes, with a transition between the temperature independent and the temperature dependent regime occurring at approximately 450°C.

One possible explanation for the difference in the marker mixing is based on the low temperature thermochemistry of the alumina-iron-oxygen system. Oxygen pressure dependent experiments show [6] that alumina exists in equilibrium with the oxides of iron, with a region of Fe-O solubility extending to a maximum fraction of 0.042 Fe component. However, no such solubility region exists for Fe metal in alumina. This indicates that a thermodynamic barrier may exist for Fe metal to enter the alumina lattice, consistent with our experimental results for the Fe metal marker.

The data in Fig. 3 for the marker spreading is plotted as an Arrhenius relation, $\ln(\sigma^2)$ vs. $1000/T$ to extract the activation energy for these processes. Both the thermal diffusion and ballistic mixing components have been subtracted from the ion beam mixing results. The activation energy for the thermal assisted ion mixing, Q_{IM} , is 0.69 eV, and that for the thermal intermixing (diffusion), Q_{TH} , is 1.77 eV. The Q_{IM} value obtained is high relative to activation energies for thermally assisted ion mixing experiments in semiconductor materials [2,7], and the temperature onset of the thermally assisted regime is also high, 400-500°C relative to the semiconductor results. The high value for Q_{IM} suggests traditional radiation enhanced diffusion (RED) may be operative in these samples. However, application of the RED model may not be verified until the dose rate dependency of the thermally assisted mixing regime is further investigated.

The mixing parameter can be converted into a mixing rate by using an analogy to diffusivity:

$$D = \frac{1}{2} \sigma^2 / t \quad (4)$$

where t is the dose rate. Shown in Fig. 4 is the σ^2 data converted to $\ln(\text{mixing rate})$. Also plotted in Fig. 4 is some available diffusion data for ^{59}Fe tracer diffusion in alumina in air [8] at high temperature. The activation energy for Fe diffusion in dense, polycrystalline alumina was reported to be 3.09 eV (Q_{bulk}). This is approximately twice that determined for our thermal only Fe diffusivity in amorphous alumina. The difference in activation energies indicates a change in the mechanism for the diffusing Fe species. It is not unusual to find a difference in activation energy for the diffusion of the same species in an amorphous matrix relative to a crystalline one. For example, in a study of the diffusion of Au in a-Si (amorphous Si) and c-Si (crystalline Si) [9], it was found that the activation

Figure 3. Arrhenius plot showing activation energies for experimental data

Figure 4. Mixing rate for ion mixed marker compared to thermal diffusivity and literature values for Fe tracer diffusivity in bulk alumina.

energy was 1.55 eV in a Si and 2.8 eV in c Si, the discrepancy explained by differences in migration mechanisms. In an independent study, it was found that the degree of mixing for a Au layer in a Si had a temperature dependency with an activation energy of 0.37 eV [7]. The results of this study share the same trends in changes in activation energy seen with our current work with a trend in activation energies of $Q_{\text{c(bulk)}} > Q_{\text{act(H)}} > Q_{\text{IM}}$. However, it must be pointed out that diffusivity in amorphous matrices is not fully understood, except that a change in mechanism is certainly possible leading to a change in activation energy. This change in mechanism need not lower the activation energy for the transport of the diffusing species, and thus higher Q values have been observed for diffusivities in amorphous vs. crystalline states [9]. It would appear, however, that in the case of Fe diffusivity in alumina, a lower energy diffusion path has become available in the amorphous state that is not present in the bulk material, and that during the time scale of the Ar¹⁹ implantation, the energy is even further lowered for Fe

migration probably due to a damage induced change in the defect concentration in the local environment of the diffusing species.

CONCLUSIONS

We have found that only temperature independent mixing occurs for the Fe metal marker in alumina. However, the spreading of the Fe_2O_3 marker was observed to be strongly temperature dependent, with an ion mixing activation energy of 0.69 eV at temperatures above 450°C. Thermal control samples examined over the same temperature range exhibited an activation energy of 1.77 eV. The differences observed in the mixing behavior of the two marker materials is consistent with the equilibrium solubility limits for iron metal and Fe_2O_3 in alumina. The value we obtained for the thermal diffusivity for the Fe_2O_3 marker is lower than the literature value of 3.09 eV for Fe tracer diffusivity in crystalline alumina, consistent the higher intrinsic defect concentration of our amorphous material.

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