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Ion Beam Mixing of Marker Layers into Amorphous Aluminum Oxide

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Thin layers of various marker species embedded in amorphous Al_2O_3 were ion beam mixed with 210 keV Ar in a temperature range of -166°C - 790°C . All of the metal markers (Ag, Fe, and Zr) were found to mix only to a ballistic level. The oxide markers studied were Fe_2O_3 , Cr_2O_3 , Y_2O_3 , and ZrO_2 . Thermally assisted ion mixing was seen, in decreasing amounts, in Fe_2O_3 , Y_2O_3 , and Cr_2O_3 . No thermally assisted ion beam mixing was observed for ZrO_2 or the metal markers.

1. Introduction

Ion mixing has been shown to be a powerful technique for the alloying of two metals or metal-semiconductor systems [1]. Mixing studies for these systems have shown that in many instances a ballistic mixing regime can be followed by a thermally activated mixing regime at high temperatures. The transition between the ballistic and thermally activated regimes typically occurs near 300 K and the effective activation energy for the thermally enhanced mixing in the range 0.1-0.5 eV [2].

In contrast to the extensive work completed in metal and semiconductor system, ion beam mixing in ceramic systems has not been investigated until very recently [3-7]. Early experiments involving metal markers in alumina and silica showed no thermally activated mixing for temperatures up to 500 K [3]. A review of metal-ceramic bilayers by McHargue[4] is primarily limited to mixing at temperatures in the ballistic regime. Temperature dependent bilayer mixing of Cr_2O_3 and ZrO_2 into alumina showed no detectable mixing in either system at 25°C , but a small amount of ballistic mixing in both systems at 860°C . The first indications of thermally assisted ion mixing were recently reported for Fe_2O_3 markers in Al_2O_3 [6-7]. A companion study determined thin iron metal markers mixed only ballistically into the

alumina matrix in the same temperature regime [3], and that doping of the alumina matrix with Fe inhibited the Fe_2O_3 marker mixing [4].

Based on the current ceramic mixing data, it is still unclear what parameters, thermodynamic or kinetic, control the degree of mixing in alumina. In non-ceramic mixing experiments, it has been seen that solubility, heat of mixing, intermetallic phase stability, and cohesive energy all contribute to some degree to the ion mixing behavior. The purpose of the present study is to investigate and isolate factors which might be contributing to the degree of mixing in alumina. Our approach is to extend the number of markers, both oxide and metal, mixed in alumina, choosing markers based on their solubility and potential to form compounds with alumina.

2. Experimental

The thin film marker samples were made by sequential e-beam deposition onto R-cut sapphire substrates. Table 1 lists the composition, layer thicknesses, and stoichiometry of the deposited marker layers. The amorphous alumina was deposited directly from sintered oxide pieces, as was the zirconia, but the other oxide markers were deposited from metals in high oxygen environment (10^{-4} torr). The metal markers were deposited in good starting vacuum (10^{-8} torr) from metal sources. The density of the deposited layers was determined by profilometry (true thickness) and RBS (areal density). The layer thicknesses in the experimental samples were determined by RBS using RUMP [8] to fit the spectra.

Ion irradiation experiments were made using 170 or 210 keV Ar. The projected range of these ions, as calculated by TRIM [9], placed the bulk of the implanted ions well behind the marker layer, and in front of the deep Pt marker. The Pt marker was used to monitor the degree of surface sputtering during the irradiation. The samples were loaded onto a Ni implantation block which was capable of being heated or cooled to the desired irradiation temperature. For the highest temperature experiments, a control sample was mounted on the back side of the Ni block so that the effect of thermal diffusion of the marker

into the alumina matrix could be monitored and the resulting thermal diffusion could be subtracted from the net marker spreading. Most samples were irradiated with a dose of 2.5×10^{16} Ar/cm², but the dose dependency of the mixing was monitored on some samples using a range of $1.25\text{--}5 \times 10^{16}$ Ar/cm².

3. Results

After the ion irradiation, the degree of marker spreading was examined using RBS. A typical RBS spectrum for the Y₂O₃ marker sample before and after an irradiation of 5×10^{16} Ar/cm² at 760°C is shown in Fig. 1. The RBS peak for the marker species was fitted using PeakFit [10] for an appropriate fitting peak shape [11] (generally gaussian-like). The peak variance (Ω^2) was determined for both an unirradiated (Ω_{un}^2) and ion irradiated (Ω_{irr}^2) specimen under identical RBS conditions. The net marker spreading due to the irradiation (or thermal treatment) was determined by subtracting, in quadrature, the unirradiated virgin sample variance from the irradiated sample variance[12]. Thermal effects, if any, were also subtracted in quadrature. Since both spectra were taken under the same RBS conditions, effects due to detector resolution and straggling were removed from the net marker spreading through this subtraction procedure. Examining the before and after spectra, we see that the Pt marker shifts toward the surface following irradiation, indicating a sputter loss of the surface alumina. Simulations of the RBS spectra indicate a loss of 120×10^{15} atoms/cm² for the Ar dose of 5×10^{16} cm⁻² giving a sputtering yield of 2.4 for our alumina films at 760°C.

Fig. 2 plots the results of the ion mixing experiments for all of the markers listed in Table 1 as a function of irradiation temperature. The metal markers did not show any thermally assisted mixing. For the oxide markers, ZrO₂ shows a decrease in the marker width for temperatures greater than 525°C. There are several possible explanations for this trend, one is that the ZrO₂ is being reduced during irradiation, or possibly that the oxide layer is sintering and/or crystallizing during the irradiation at high temperature. Electron microscopy will be necessary to confirm these hypotheses. Some

increased marker mixing can be seen for the Cr_2O_3 and Y_2O_3 at high temperatures, but it is well below that observed for the Fe_2O_3 marker in the same temperature range.

The effective ion mixing activation energy, E_{irr} , for the temperature dependent spreading of the Fe_2O_3 , Cr_2O_3 , and Y_2O_3 markers was calculated by first subtracting out the ballistic level of mixing and assuming Arrhenius behavior, using the expression

$$E_{\text{irr}} = k_B \frac{d \ln(\Omega_{\text{mix}}^2)}{d(1/T)}$$

where k_B is Boltzmann's constant, and $\Omega_{\text{mix}}^2 = \Omega_{\text{irr}}^2 - \Omega_{\text{un}}^2$ is the squared variance for the net marker spreading. The effective activation energy as a function of irradiation temperature is shown in Fig. 3. The data shows that a thermally activated regime exists for the Fe_2O_3 , Y_2O_3 , and Cr_2O_3 marker samples with a high temperature activation energy for the ion mixing of 0.52, 0.25, and 0.35 eV, respectively. In addition, both Fe_2O_3 and Y_2O_3 possessed activation energies of 0.08 eV at intermediate mixing temperatures.

4. Discussion

Substantial temperature dependent mixing was observed for the Fe_2O_3 marker samples, while only ballistic mixing was observed for the Fe markers. In fact, ballistic mixing was only observed for all of the metal markers. The metal marker (Zr, Ag, and Fe) mixing results are comparable to previous ion mixing results for W and Au in alumina [3]. The difference of ion mixing in the Fe_2O_3 and the Fe marker samples was discussed in previous work [6] and was attributed to the increased solubility of Fe_2O_3 relative to Fe in alumina.

Limited or no thermally ion mixing was observed for the other oxide markers. The mixing results of the Y_2O_3 and ZrO_2 , where there is limited and no solubility in alumina, respectively, are consistent with solid solubility arguments. The lack of thermally assisted mixing in the ZrO_2 markers is consistent with previous bilayer mixing experiments [5]. However, the Cr_2O_3 mixing at elevated temperatures was well

below that for the Fe_2O_3 marker mixing. This was unexpected since Cr_2O_3 has a complete solid solubility in alumina. While there is a partial correlation between solubility and the extent of temperature dependent mixing, these results indicate that solubility is necessary but not sufficient to predict the amount of high temperature ion mixing.

In an attempt to account for our results, we have investigated other correlating factors or properties to give a more consistent explanation. Table 2 lists the marker/alumina solid solution range, possible equilibrium compounds, and liquidus temperatures for the lowest melting temperature component. Phase equilibria information was obtained from Ref. [13]. A comparison of our data with information in Table 2 shows that the largest amount of mixing occurs for Fe_2O_3 and Y_2O_3 where compounds form. Next in the hierarchy of mixing is Cr_2O_3 where no compounds are observed, but complete solubility exists. For the case of ZrO_2 and the metals Zr, Ag, and Fe, where no temperature dependent mixing is observed, solubility is extremely limited and compound formation does not occur. Thus it appears that a measure of the thermodynamic driving force for temperature dependent mixing can be found in the extent of solid solubility and the potential to form compounds.

The effective activation energies shown in Fig. 3 for Fe_2O_3 , Cr_2O_3 , and Y_2O_3 span a range of 0.08 to 0.52 eV. The low activation values observed for these ceramic marker mixing systems are similar to what is observed in non-ceramic systems. A recent analysis of non-ceramic material mixing has attributed these low activation energies to mixing in the melt [2]. TRIM calculations for the damage energy deposited in the vicinity of the marker by 210 keV Ar give a local energy density of approximately 2 eV/atom. Converting this energy into temperature, using the approximation $E=3k_B T/2$ gives an instantaneous temperature in excess of 10,000 K, sufficient to induce cascade melting for alumina and all the components listed in Table 2. It should be noted that liquid-like diffusion will only occur in systems where thermodynamic driving forces exist.

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Table 1. Summary of Sample Compositions

marker	marker composition	alumina top layer (nm)	marker thickness (nm)	alumina bottom layer (nm)	Pt thickness (nm)
Fe ₂ O ₃	Fe ₂ O _{2.88}	125	7.5	180.0	0.82
Cr ₂ O ₃	Cr _{1.8} O ₃	90	12.0	150.0	0.68
Y ₂ O ₃	Y _{1.62} O ₃	90	7.5	220.0	0.70
ZrO ₂	ZrO _{1.86}	88	14.0	247.5	0.68
Fe	Fe	80	8.0	145.0	0.75
Ag	Ag	100	2.0	250.0	0.60
Zr	Zr	80	4.5	187.5	0.75

Table 2. Summary of Alumina-Marker Systems for this Study

marker	solid solution range in alumina	Lowest Liquid T_m	compounds
Fe_2O_3	4.4% (800°C)	1600°C	spinel
ZrO_2	<5% (1900°C)	1870°C	none
Y_2O_3	10% (1800°C)	1780°C	YAG, etc.
Cr_2O_3	complete	2045°C	none
Zr (metal)	?	1852°C	no
Ag (metal)	?	960°C	no
Fe (metal)	0	1536°C	no

Figure Captions

Figure 1. RBS for an unirradiated Y_2O_3 sample, and RBS for a sample irradiated with 210 keV Ar at 760°C. Both plots show the fitted Ω values for the Y peak.

Figure 2. Marker spreading as a function of inverse temperature for the oxide and metal markers normalized to a dose of 1×10^{16} Ar/cm².

Figure 3. Activation energy calculations for the thermally assisted ion beam mixing of Cr_2O_3 , Y_2O_3 , and Fe_2O_3 marker samples.

Y_2O_3 marker

Fig 3

Fig 3, cont

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