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Ion Beam Mixing of Au/Cu Bilayers***

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ABSTRACT

Experiments were performed to evaluate the effect of 1.5 MeV Kr irradiation on diffusion-induced grain boundary migration (DIGM) in Au/Cu bilayers in the temperature range of $300 \leq T \leq 550\text{K}$. The experimental results were consistent with DIGM occurring in bilayers both during irradiation and during annealing treatments. Rutherford backscattering spectrometry showed a nearly uniform distribution of Cu present through the entire thickness of appropriately prepared polycrystalline Au films irradiated or annealed at temperatures $\geq 400\text{K}$. No parallel effect was seen in similarly treated single-crystal films. In each polycrystalline sample studied, irradiation resulted in greater amounts of Cu present uniformly in the Au compared to annealing-only. The magnitudes of measured Cu compositions were substantially greater than that expected solely from grain boundary diffusion. A simple analysis of the process indicated that ion irradiation affects DIGM by increasing the composition of Cu present in alloyed zones and/or by increasing the grain boundary velocity in the Au.

1. Introduction

Diffusion-induced grain boundary migration (DIGM) is a well-documented, highly efficient mode of interdiffusion observed during thermal annealing of a variety of polycrystalline diffusion couples [1]. However its role during ion beam mixing is not well understood. DIGM may be key to explaining the relatively low onset in the temperature dependence of the mixing rate typically observed in ion beam mixing experiments [2]. Furthermore, should DIGM during irradiation prove to be pervasive in many alloy systems, it would impact substantially on our understanding and modeling of mass transport during ion mixing. DIGM might also account for the variations observed in grain growth behavior between multilayer and coevaporated alloy films during ion irradiation [3].

The DIGM process is schematically illustrated in fig. 1 for a Au/Cu bilayer. Diffusion of Cu solute into the Au grain boundary induces the boundary to migrate, creating an alloyed zone in its wake. This process commonly occurs at temperatures for which lattice diffusion and normal grain growth are negligible. Despite considerable empirical evidence that DIGM occurs in a variety of binary alloy systems [1], the driving force and mechanism responsible for the phenomenon remain the subject of debate [4].

In this work we evaluate the role that ion irradiation has on DIGM in Au/Cu bilayers. Extensive studies on thermal DIGM in this system were previously performed by Pan and Balluffi [5], and by Grovenor [6]. Thus Au/Cu provides a good basis against which to compare the irradiation effects. This work supplements our earlier study [7] by examining the effect of different temperatures, Au film thicknesses, Au grain sizes and treatment times.

2. Experimental

Bilayer films of Au and Cu were prepared by e-beam deposition onto MgO or NaCl single-crystal substrates. Au films were first evaporated onto substrates in both polycrystalline and single-crystal form with film thicknesses ranging between 340-2170Å. Polycrystalline Au was prepared by different techniques, producing grain boundaries extending through the entire thickness of the films. As demonstrated previously, this type of microstructure permits quantitative analysis of DIGM [5]. All samples, except two (Samples 1 and 3), were prepared by room temperature deposition followed by a post evaporation anneal at ~725K for up to 1 hr. Sample 1 was prepared by deposition at ~550K. Sample 3 was prepared by deposition at ~575K plus a post evaporation anneal at ~725K for up to 1 hr. The annealing effectively hardened the Au films against any thermally-induced grain boundary migration in the temperature range used for the subsequent DIGM experiments ($\leq 550\text{K}$). Without breaking vacuum, a Cu overlayer

ranging in thickness from 115-225Å was deposited on the Au at room temperature to serve as a source of solute. Average grain size in the Au films was characterized by a linear intercept technique performed on plan-view transmission electron microscopy (TEM) micrographs of the Au films after they were etched and detached from their substrates.

Single-crystal Au films were prepared by deposition onto NaCl substrates held at ~490K. Difficulties were encountered in fabricating single-crystal films free of holes. Such defects were believed to contribute to anomalies in measured composition profiles as mentioned below. As with the polycrystalline films, an overlayer of Cu was deposited on top of the Au film.

Irradiations were conducted at temperatures ranging from 300 to 550K using 1.5 MeV Kr to doses $\leq 6 \times 10^{15} \text{ cm}^{-2}$. Dose rates varied between $(0.5-1.0) \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$. Only a portion (3 mm diameter spot) of each sample was irradiated. This provided regions on each sample which could be subsequently analyzed for irradiated and for annealed-only effects.

In most thermal annealing experiments, DIGM is readily identified using analytical TEM, which combines observation of boundary migration with identification of alloyed zones (see for e.g. Ref.[5]). However, in irradiation experiments, ion-induced damage and interfacial mixing obscure the grain boundaries in plan-view, thereby precluding the typical analytical TEM analysis. Instead, to provide evidence for DIGM we relied on 1.5 and 3.0 MeV He Rutherford backscattering spectrometry (RBS) to profile the Cu in appropriately prepared bilayers. Analysis of the RBS spectra was performed using the RUMP code [8].

3. Results and Discussion

Fig. 2 shows the typical Cu portion of the RBS signal obtained after irradiation and after annealing in polycrystalline (a,b) and single-crystal (c) bilayer samples. In the polycrystalline samples, both treatments resulted in a nearly uniform distribution of Cu in the Au films, with film-averaged Cu compositions, $\bar{C}$, of 5 and 12 at.% for annealed-only and for irradiated areas, respectively. Also note that interfacial mixing is seen in both the polycrystalline and single-crystal bilayers, as evidenced by the decreased slope at the back edge of the Cu layers. The importance of grain boundaries to the transport process during mixing is obvious from fig. 2(c). The absence of boundaries in the single-crystal sample correlates with the absence of a uniform composition of Cu in Au. The small Cu "bump" apparent at the back surface of the single crystal Au sample in fig. 2(c) is believed to be an artifact of the film morphology. Holes present in the Au films of these samples likely provide pathways for Cu to diffuse to the NaCl substrates. Such Cu bumps were not observed in spectra obtained from thicker (1550Å) single-crystal Au samples.

Table 1 summarizes the RBS measured values of $\bar{C}$ obtained for the variety of polycrystalline Au samples and temperatures studied. Confirming our previous observations [7], irradiation enhanced the amount of Cu present uniformly through the thickness of the Au films for all polycrystalline samples studied at temperatures $\geq 400\text{K}$. No DIGM alloyed layer was observed for Sample 3 upon annealing-only at 450K, although it was present at the same temperature following irradiation. In Sample 5 (500K), the thick Au film sample, Cu was detected in the Au layer, but did not show the uniform depth dependence expected for DIGM.

A possible explanation other than DIGM for the observed enhancement of Cu interdiffusion during irradiation is that ion-induced damage (e.g. dislocation networks, etc.) may provide additional pathways for diffusion into Au. In order to evaluate this possibility, an experiment was performed in which a portion of a polycrystalline bilayer was initially irradiated at room temperature to produce a suitably damaged microstructure. This sample was then annealed at 500K for 1025 s. RBS subsequent to annealing showed no enhancement in Cu transport within the pre-irradiated area relative to that in an unirradiated area of the same sample. Therefore the contribution of the ion-induced damage structure to the transport of Cu in Au appears to be negligible at this temperature.

It is clear from the experimental results described above that grain boundaries play a critical role in the observed interdiffusion. It is well known that grain boundary diffusion permits deep penetration of solute into Au. However, it can be shown that such a process is insufficient to account for the amount of Cu interdiffusion measured. According to Fisher's grain boundary diffusion model [9], the composition of Cu present at any lateral position, x , in the film at a given depth $y = \ell$ (back surface of the Au film) is,

$$C(x, \ell, t) = \begin{cases} C_0 \exp \left[- \left(\frac{\sqrt{4D_1}}{\delta D_b \sqrt{\pi t}} \right)^{1/2} \ell \right], & 0 \leq x \leq \frac{\delta}{2} \\ C_0 \exp \left[- \left(\frac{\sqrt{4D_1}}{\delta D_b \sqrt{\pi t}} \right)^{1/2} \ell \right] \operatorname{erfc} \left(\frac{x}{\sqrt{4D_1 t}} \right), & \frac{\delta}{2} < x \leq \frac{L}{2} \end{cases} \quad (1)$$

where ℓ is the film thickness, L is the average grain diameter, t is the time of treatment (irradiation and/or annealing), δ is the grain boundary thickness ($\delta = 5\text{\AA}$), δD_b is the boundary diffusivity parameter, D_1 is the lattice diffusivity and C_0 is the Cu surface

concentration ($C_0=100$ at.%). The film-averaged composition expected at the back surface of the Au film, $\bar{C}(\ell, t)$, can then be determined according to,

$$\bar{C}(\ell, t) = \frac{2}{L} \int_0^{L/2} C(x, \ell, t) dx . \quad (2)$$

In order to apply this analysis, it is necessary to specify δD_b and D_l . The grain boundary diffusivity parameter is readily obtained from the literature [10]. Values of D_l were obtained by fitting a complementary error function diffusion profile to the back edge of the Cu peak in the RBS spectrum obtained from annealed-only, and from irradiated portions of a single-crystal bilayer sample. The results of this calculation for $T=500K$ are provided in table 1 in columns adjacent to the measured values of $\bar{C}$. In all cases, the measured value of $\bar{C}$ is substantially (by almost an order of magnitude) greater than that estimated from the grain boundary diffusion analysis. Clearly, grain boundary diffusion alone cannot account for the magnitude of Cu present in the Au films. It is interesting to note that, many years ago, Borders [11] came to the identical conclusion, after observing the same thermal interdiffusion of Cu into polycrystalline Au. Such results appeared puzzling at the time, which was before DIGM had been discovered.

The RBS results indicate that DIGM occurs both during irradiation and during annealing treatments. The variations in the values of $\bar{C}$ (table 1) may be interpreted using a relatively simple model. Referring to fig. 1, the film averaged composition of Cu in Au, $\bar{C}$, is expressed as,

$$\bar{C} = \frac{2C'd}{L} , \quad (3)$$

where d is the average width of the DIGM alloyed zone. It is assumed that boundary migration during DIGM is characterized by an average velocity, $v=D_{DIGM}/\ell$, where D_{DIGM} is the boundary migration diffusivity. The alloyed zone width may then be expressed as $d=D_{DIGM}t/\ell$, and eq. (3) becomes,

$$\bar{C} = 2C' D_{DIGM} \frac{t}{\ell L} . \quad (4)$$

Note that D_{DIGM} describes grain boundary migration and should not be confused with the diffusion parameters (δD_b and D_l) introduced earlier. D_{DIGM} simply represents the area per unit time swept out by grain boundaries undergoing DIGM.

Fig. 3 depicts graphically the functional dependence described by eq. (4) for the data obtained at $T=500\text{K}$. The linearity is remarkable in light of the variety of experimental parameters involved. The factor of three increase in slope observed for the irradiated samples demonstrates clearly that ion irradiation enhances DIGM. While the underlying mechanism for this enhancement is presently unclear, three possibilities may be postulated upon examination of eq. (4) (slope= $2C'D_{\text{DIGM}}$): (1) irradiation may increase the amount of Cu, C' , alloyed in the wake of the boundary, (2) irradiation may increase the boundary migration velocity ($v=D_{\text{DIGM}}/\ell$) or (3) a combination of both (1) and (2) may occur. Limited data [7] indicates that the alloyed zone composition is nearly the same for both irradiated and annealed-only treatments ($C'=20$ at.%) and is of the same magnitude as that measured previously by Pan and Balluffi [5] ($C'=15\text{-}35$ at.%). This would suggest that irradiation enhances the boundary velocity.

4. Summary

RBS results showing a nearly uniform composition of Cu through the thickness of polycrystalline Au films were consistent with DIGM occurring during irradiation and/or annealing of Au/Cu bilayers. The importance of grain boundaries to Cu interdiffusion was demonstrated by the absence of a uniform distribution of Cu in irradiated or annealed single-crystal Au samples. It was shown that grain boundary diffusion alone was inadequate to account for the observed magnitude of Cu present in the polycrystalline Au films. A simple description of DIGM was developed to describe variations in measured Cu composition with key sample parameters. The analysis indicated that ion irradiation affects DIGM by increasing the composition of Cu present in alloyed zones and/or by increasing the grain boundary velocity in the Au.

This study has demonstrated the importance of thin film microstructure to interdiffusion during ion mixing. The occurrence of DIGM may well impact on interpretations of previous ion beam mixing experiments. Unlike the present study, ion beam mixing experiments commonly use evaporated thin films with fine-grained microstructures ($L \ll \ell$), in which the effects of DIGM cannot be easily identified. It is unknown whether, or to what degree, DIGM during irradiation occurs in fine-grained films.

Acknowledgments

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Table 1

Summary of sample parameters, experimental conditions and results for the DIGM experiments. $\bar{C}$ are values of film-averaged Cu composition in Au measured via RBS. $\bar{C}(\ell, t)$ are values of film-averaged Cu composition calculated at the back surface of Au assuming grain boundary diffusion.

Sample Number	Au Film Thickness ℓ (Å)	Au Average Grain Size L (Å)	Temperature T (K)	Time t (s)	Ion Dose ($\times 10^{15} \text{ cm}^{-2}$)	Annealed (at.% Cu)		Irradiated (at.% Cu)	
						$\bar{C}$	$\bar{C}(\ell, t)$	$\bar{C}$	$\bar{C}(\ell, t)$
1	700	1950	500	1025	0.5	3.0	0.7	7.0	0.6
				2261	1.0	5.0	1.4	12.0	1.4
2	570	1850	500	1242	0.5	4.5	1.2	11.5	1.2
				2542	1.0	8.0	2.2	17.0	2.5
3	890	2100	450	1200	1.0	0.0	-	1.5	-
			500	1200	1.0	3.8	0.4	7.8	0.3
4	340	1200	400	1410	1.0	1.8	-	3.0	-
			450	1452	1.0	2.5	-	7.7	-
			500	1426	1.0	9.0	3.8	23.0	5.2
			550	1350	1.0	27.0	-	34.0	-
5	2170	3000	500	1447	1.0	-	~0.0	2.0	~0.0
				2607	2.0	-	~0.0	3.0	~0.0
				3910	4.0	-	0.1	4.0	~0.0
				5155	6.0	-	0.1	5.0	~0.0

Fig. 1. Cross section view illustrating DIGM in a Au/Cu bilayer. L is the average Au grain diameter and C' is the Cu composition of the DIGM alloyed zone. Boundary migration characterized by velocity, v , and migration diffusivity, D_{DIGM} .

Fig. 2. 1.5 MeV He RBS signals from Cu in bilayer samples after the various treatments at $T=500\text{K}$. (a) polycrystalline Au/Cu bilayer irradiated with 1.5 MeV Kr to 10^{15} cm^{-2} . (b) same sample as in (a) annealed-only for 2260 s. (c) single-crystal Au/Cu bilayer irradiated with 1.5 MeV Kr to 10^{15} cm^{-2} . $\bar{C}$ is the film-averaged composition of Cu present uniformly through the Au as extracted from the RUMP analysis.

Fig. 3. Variation in RBS measured uniform Cu composition, $\bar{C}$, in Au at T=500 K as a function of treatment time, t, film thickness, ℓ , and Au grain diameter, L, derived using simple description of DIGM (eq. (4)). Lines are least-squares linear fits.

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