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**THE EFFECT OF DIGM AND IRRADIATION-INDUCED GRAIN GROWTH
ON INTERDIFFUSION IN BILAYER ION-BEAM MIXING EXPERIMENTS***

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THE EFFECT OF DIGM AND IRRADIATION-INDUCED GRAIN GROWTH ON INTERDIFFUSION IN BILAYER ION-BEAM MIXING EXPERIMENTS*

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ABSTRACT

Experiments were performed demonstrating that ion irradiation enhances diffusion-induced grain boundary migration (DIGM) in polycrystalline Au/Cu bilayers. Here, a model is presented relating film-averaged Cu composition in Au with treatment time, grain size and film thickness. Application of this model to the experimental results indicates that irradiation enhances DIGM by increasing the grain boundary velocity. The effects of DIGM and irradiation-induced grain growth on the temperature dependence of ion mixing in bilayers are discussed.

INTRODUCTION

Ion-beam mixing experiments employing bilayer geometries are commonly used to study mass transport resulting from irradiation. Typically, RBS profiles are fit to solutions of the diffusion equation to extract an effective diffusion coefficient during irradiation. The dependence of this diffusion coefficient on ion properties (mass, energy, energy deposition) and target properties (density, thermochemistry) has been used to probe the fundamentals of ion-solid interactions.

Bilayer experiments examining the temperature dependence of ion mixing have generally shown the existence of two regimes [1]. In addition to a temperature-independent regime, a temperature-dependent regime typically begins near room temperature. The kinetic processes governing mixing in this thermally assisted regime are not well-understood. Attempts to understand this dependence have invoked some form of radiation-enhanced diffusion [2] or cascade effects [3]. Only limited attention has been paid to the role that the thin film microstructure may have on interdiffusion in this temperature dependent regime [4].

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 [5]. Diffusion of a solute in a grain boundary can induce the boundary to migrate, forming an alloyed zone in its wake. DIGM occurs at relatively low temperatures and may therefore impact on the interpretation of ion-beam mixing in the thermally-assisted regime.

This paper summarizes experiments examining the effect of ion irradiation on DIGM in Au/Cu bilayers. Additionally, the influence of film microstructure on the Arrhenius behavior of ion mixing is addressed.

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EXPERIMENTAL

Bilayers were prepared by e-beam evaporation of Au onto single-crystal MgO substrates followed by an overlayer of Cu. Polycrystalline Au films were produced with a grain size greater than or equal to the film thickness. As demonstrated previously [6], this microstructure is well-suited for analyzing DIGM kinetics. In order to produce the Au films, annealing treatments at temperatures between 675-725 K were performed to facilitate grain growth after room temperature deposition on MgO, and to harden the films against further thermally-driven grain growth at subsequent treatment temperatures (≤ 550 K).

Samples were irradiated with 1.5 MeV Kr ions at temperatures ranging between 300-550 K. Dose rates varied between $(0.5-1.0) \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and doses were typically $1 \times 10^{15} \text{ cm}^{-2}$. However, for one sample, a maximum dose of $6 \times 10^{15} \text{ cm}^{-2}$ was studied. Table I details the experimental parameters examined.

1.5 or 3.0 MeV He Rutherford backscattering spectrometry (RBS) was used to profile the Cu present in the Au films before, and after, irradiation and annealing treatments. Direct evidence of DIGM resulting from ion irradiation was obtained from detection of Cu alloyed zones in Au using small probe X-ray energy dispersive spectroscopy (XEDS) performed on a cross-section TEM sample [7]. A Hitachi 2000 transmission electron microscope with a field emission gun, operated in analytical mode at 200 kV, was used for analysis. Small electron-beam probes, approximately 20 Å in diameter, were employed.

RESULTS AND DISCUSSION

Results of RBS analysis showed that nearly uniform distributions of Cu were present in the Au films consistent with DIGM having alloyed a certain volume fraction of the Au layer during irradiation or annealing. Small probe XEDS performed on an irradiated cross-section TEM sample showed these DIGM alloyed zones to have compositions between 14-20 at.% Cu [7], similar to those measured in a thermal study by Pan and Balluffi [6]. Values of film-averaged Cu composition, \bar{C} , obtained from analysis of RBS spectra showed variations between 3-34 at.% Cu in irradiated areas and 2-27 at.% Cu in annealed-only areas. In all cases, irradiation enhanced the amount of DIGM relative to annealed-only areas.

A simple model of DIGM is able to account for the observed variations in film averaged compositions, \bar{C} , extracted from RBS spectra. These compositions may be related to the measured experimental parameters of treatment time, t , film thickness, ℓ , and average grain diameter, L , as follows. In a time, t , a grain boundary perpendicular to the film surface migrates in a direction parallel to the surface with an average velocity, v , forming behind it a substitutionally alloyed zone with Cu composition, C' . In a simple two-dimensional picture of the process, the film-averaged composition is then given by

$$\bar{C} = \frac{2 C' v t}{L}. \quad (1)$$

If the boundary motion is described by the average diffusivity, D_{DIGM} , then the velocity becomes, $v=D_{\text{DIGM}}/\ell$, and eqn.(1) may be expressed as,

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

Note that D_{DIGM} describes boundary migration and represents the average area per unit time swept out by grain boundaries during DIGM.

The functional dependence described by eqn.(2) is displayed in Fig. 1 for the data obtained at 500 K. Remarkable linearity is exhibited by both the irradiated and annealed-only data in support of the simple model of DIGM outlined above. The irradiation enhancement of DIGM is clearly evidenced by the approximately factor of three greater slope in the irradiated versus annealed-only linear-fits. The underlying mechanism for this enhancement is presently uncertain. However, from examination of eqn.(2), the increased slope ($=2C'D_{\text{DIGM}}$) indicates that irradiation may increase the amount of Cu alloyed in the wake of the boundary and/or increase the boundary migration velocity. Plan-view XEDS data combined with cross-section TEM results [7] indicate that the alloyed zone composition is nearly the same for both irradiated and annealed-only treatments ($C' \approx 20$ at.%). Therefore the results indicate that irradiation enhances the grain boundary velocity.

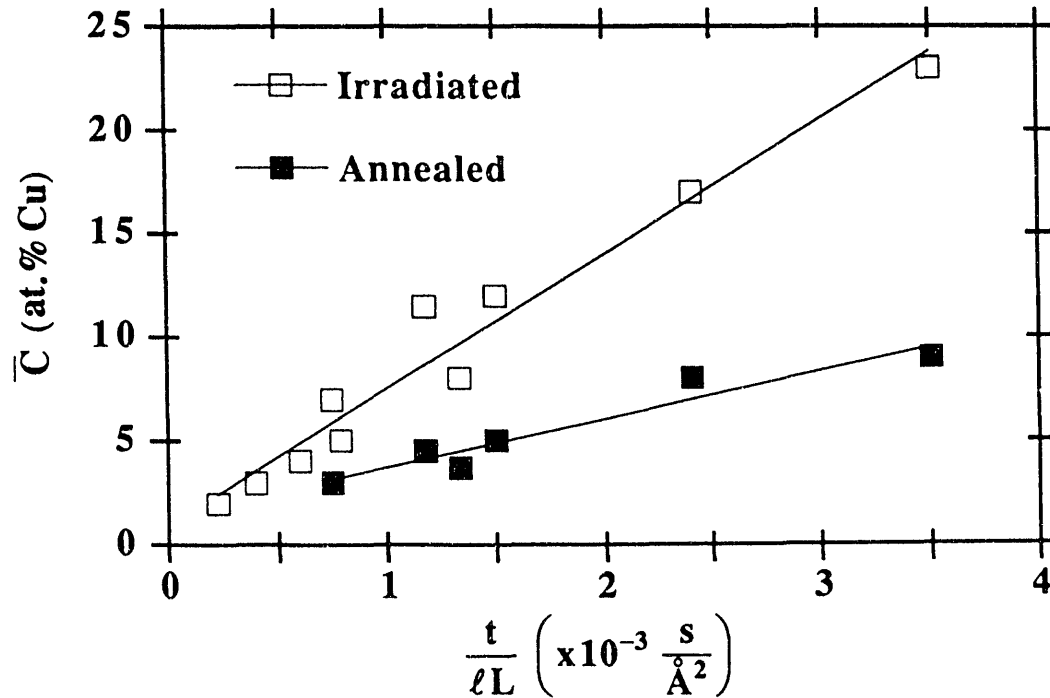


Fig. 1. Variation in RBS measured uniform Cu composition, \bar{C} , in Au at $T=500$ K as a function of treatment time, t , film thickness, ℓ , and Au grain diameter, L , derived using simple description of DIGM [eqn. (2)]. Lines are least-squares linear fits.

Having demonstrated that DIGM can occur during irradiation, it is reasonable to consider its role in ion-beam mixing experiments of the type normally performed on bilayer films. The efficient interdiffusion provided by DIGM at relatively low temperatures can help explain the temperature dependence of ion mixing. Bilayer experiments typically use evaporated films with grain sizes much less than the film thickness. An extrapolation of the DIGM results presented above to small grain sizes is complicated by the fact that irradiation induces grain growth in fine-grained films *independent of DIGM* (i.e. without chemical interdiffusion) [8]. Unlike the thermally-hardened Au films used in the DIGM studies, a strong driving force exists for irradiation-induced grain growth in fine-grained metal and semiconductor films even at LN₂ temperatures. Therefore, an extrapolation from the large grained DIGM results is not straightforward.

In a temperature regime where grain boundary diffusion is operative, the occurrence of irradiation-induced grain growth can be expected to enhance interdiffusion in a manner similar to DIGM. This issue has been previously addressed by those interested in extracting grain boundary diffusion coefficients from annealing experiments in which boundary migration has occurred [9]. Although originally derived for the interpretation of thermal studies, the analysis may be applied to irradiation-induced grain growth. Glaeser and Evans [9] have shown, in the limit that the grain boundary migration distance, vt , is much greater than the boundary width, δ , that the depth dependence of the solute concentration is,

$$\bar{C}(x) = \frac{C_0 vt}{L} \exp\left(-x \sqrt{\frac{v}{\delta D_{gb}}}\right), \quad (3)$$

where δD_{gb} is the grain boundary diffusivity, C_0 is the solute surface concentration and the other parameters are as described previously. Since irradiation-induced grain growth occurs essentially at all temperatures ($v > 0$), eqn.(3) indicates that under the appropriate experimental conditions (dose rate, temperature, etc.) modest amounts of grain boundary diffusion may result in significant increases in mixing between bilayers. Analogous to DIGM this process may help explain observations of enhanced ion mixing at moderate temperatures. Note that eqn.(3) reduces to that derived for DIGM (eqn.(1)) in the limit that grain boundary diffusion is infinitely fast and assuming $C_0 = 2C'$.

As an example, Fig. 2 shows concentration profiles in Ni obtained using eqn.(3) and superimposing interdiffusion anticipated from cascade mixing at the interface (via a complimentary error function profile). For grain boundary diffusion, Ni self-diffusion values were used assuming irradiation temperatures of 450 and 500 K [10]. Grain size was taken as $L = 200 \text{ \AA}$ and the boundary migration velocity was assumed to be 0.1 \AA s^{-1} as determined previously from Ar irradiation studies of Ni films [8]. An irradiation time of 600 s was determined assuming typical experimental parameters of dose (10^{15} cm^{-2}) and dose rate ($1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$). Cascade mixing was simulated using $D_{mix} = 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ [4]. The

resulting solute composition profiles show penetrating tails, which are particularly pronounced for $T=500$ K (see Fig. 2). Attempts to "force fit" simple one-dimensional solutions of the diffusion equation to such profiles are expected to result in erroneously large ion-mixing diffusion coefficients.

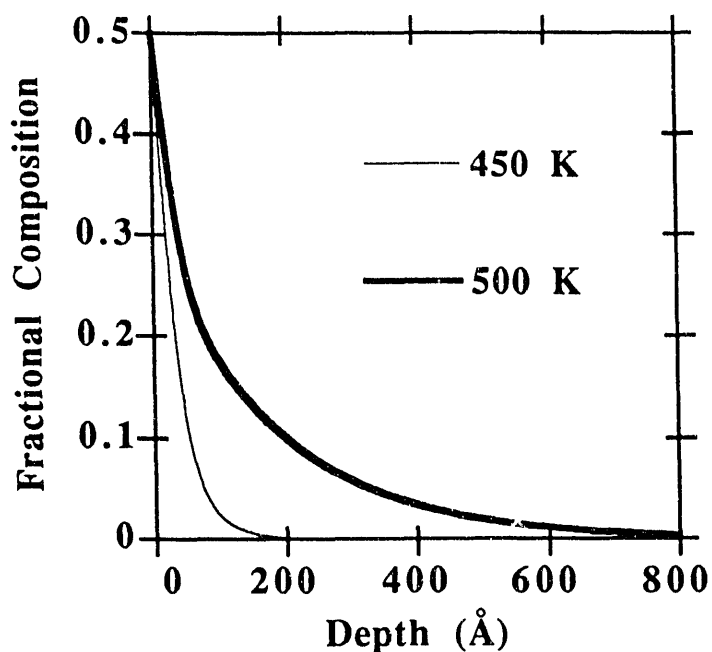


Fig. 2. Calculated solute profiles in Ni resulting from combined ion-induced grain growth and grain boundary diffusion. Dose = 10^{15} cm $^{-2}$ and $t=600$ s.

Supporting evidence of the influence of film microstructure on ion mixing is found in comparison of two experiments investigating the temperature dependence of mass transport during ion irradiation in Ni. Akano et al. [4] studied Ar ion-mixing of Pd into fine-grained (~ 100 Å diameter) Ni. Muller et al. [11] examined the broadening of an isotopic marker in single-crystal nickel resulting from 300 keV Ni irradiation. Both experiments employed nearly the same damage rate ($\sim 10^{-2}$ dpa s $^{-1}$). The Arrhenius behavior of the ion irradiation diffusion coefficient obtained from these experiments is shown in Fig. 3. Both sets of data exhibit two temperature regimes of mixing with each having about the same magnitude of mixing in the temperature-independent regime. However, in the fine-grained films, the enhancement in diffusivity occurs at a noticeably lower temperature than in the single-crystal Ni. Substantial grain growth from 100-600 Å was also observed. Although Akano et al. [4] attribute this enhancement to grain boundary diffusion it appears that the Glaeser and Evans description (eqn.(3)) would be more appropriate for understanding the observed interdiffusion behavior in these fine-grained films. In the single-crystal Ni, an enhancement of diffusion is not observed until substantially higher temperatures, at which point conventional radiation-enhanced diffusion begins.

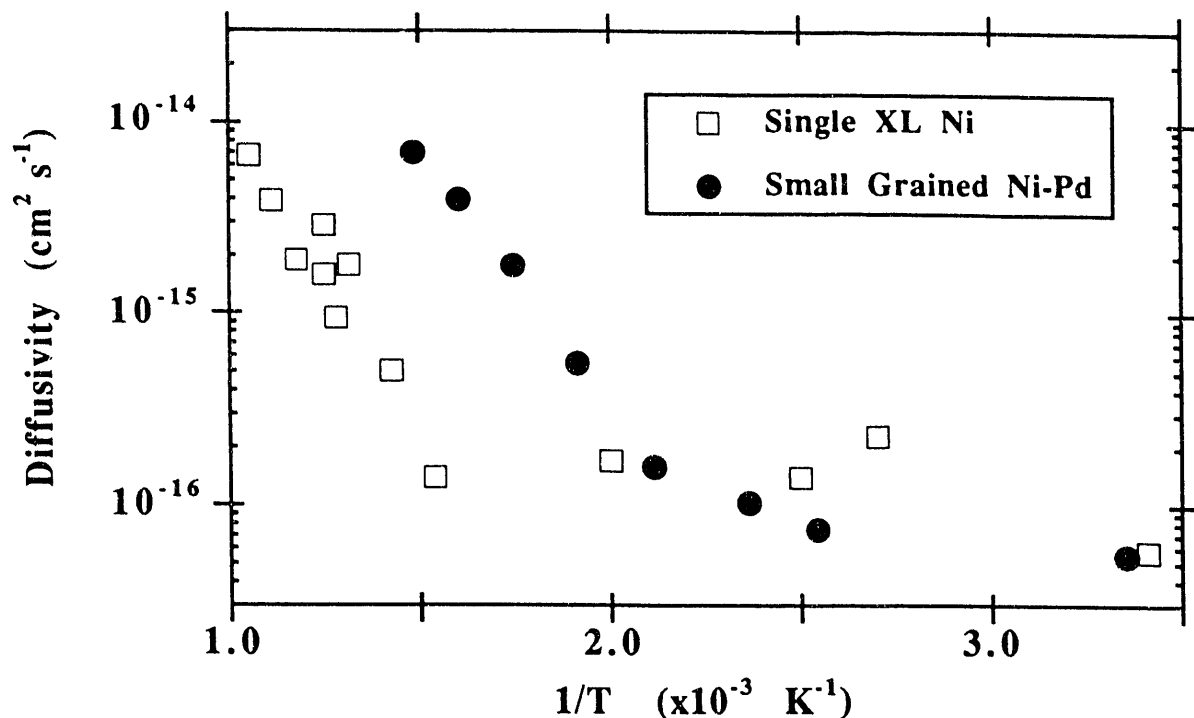


Fig. 3. Comparison of measured diffusion coefficients resulting from irradiation in single-crystal Ni [11] and fine-grained Ni-Pd [4].

CONCLUSIONS

Experiments have demonstrated that DIGM occurs during ion-mixing of polycrystalline Au/Cu bilayers. DIGM, and more generally irradiation-induced grain growth coupled with boundary diffusion, can substantially enhance interdiffusion during irradiation. These microstructural phenomena in polycrystalline films may provide a key to understanding ion-mixing in the thermally-assisted regime.

REFERENCES

- [1] L. E. Rehn and P.R. Okamoto, Nucl. Instrum. Methods **B39**, 104-113 (1989).
- [2] Y. -T Cheng, Phys. Rev. B **40**, 7403-7405 (1989).
- [3] F. Rossi and M. Nastasi, J. Appl. Phys. **69**, 1310-1319 (1991).
- [4] U. G. Akano, D.A. Thompson, W.W. Smeltzer and J.A. Davies, J. Mater. Res. **3**, 1063-1071 (1988).
- [5] C.A. Handwerker in *Diffusion Phenomena in Thin Films and Microelectronic Materials* edited by D. Gupta and P.S. Ho (Noyes Publications, Park Ridge, NJ, 1988).
- [6] J. D. Pan and R.W. Balluffi, Acta. Metall. **30**, 861-870 (1982).
- [7] Y. Gao, D.E. Alexander and L.E. Rehn in these proceedings.
- [8] J.C. Liu and J.W. Mayer, Nucl. Instrum. Methods **B19/20**, 538-542 (1987).
- [9] A. M. Glaeser and J.W. Evans, Acta. Metall. **34**, 1545-1552 (1986).
- [10] I. Kaur and W. Gust, *Handbook of Grain and Interphase Boundary Diffusion Data* (Ziegler Press, Stuttgart, Germany, 1989).
- [11] A. Muller, V. Naundorf and M.-P. Macht, J. Appl. Phys. **64**, 3445-3455 (1988).

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