Ion mixing of metal/Al bilayers near 77 K

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(Received 19 September 1988; accepted for publication 20 November 1988)

The efficiency of interfacial ion mixing is measured for metal/Al (metal = Ti, Cr, Ni, and Mo) thin-film bilayers irradiated with 285 keV Xe^+ ions near 77 K. The results indicate that, as a group, mixing of 3*d*-metal/Al pairs irradiated by Xe can be explained by neither a pure binary collision cascade nor a pure thermal spike model. Such a situation should exist; that it should be found at the average atomic numbers of the present bilayers is consistent with recent theoretical predictions.

Atomic displacements in solids generated by energetic ion irradiation (ion mixing) at low ambient temperatures have been attributed to two distinct mechanisms: binary collision cascades and thermal spikes. Initially, ion mixing was thought to be solely due to energetic binary collisions.[1–3] Quantitative models based on such a mechanism, however, have proven inadequate since they predict mixing efficiencies that do not reflect the magnitude and variations of experimental observations.[4–6] It is now generally agreed that diffusional processes during the thermal spike phase of the cascade evolution contribute significantly to the mixing.[5–8] A phenomenological model derived on the premise of diffusion within a well-developed thermal spike has been established.[7,9] The model has been shown to be successful in quantitatively describing the mixing efficiencies for Xe irradiation near 77 K of a large number of transition-metal bilayers (3*d*-5*d* and 4*d*-5*d* pairs), where dense collision cascades and well-developed thermal spikes dominate.[6,9,10] However, the validity ranges of the current model descriptions, and in turn the dependences of the contributions of different mixing mechanisms on the target system and irradiation conditions, have not been determined.[5,10] Application of the fractal concept to collision cascades has recently yielded new insights into the necessary conditions for the development of spikes.[11–13] In particular, it has been predicted that spikes should not occur in targets with an atomic number $Z < 20$.[13] One then expects that in the absence of thermal spike mixing, the amount of mixing in light targets would tend towards that set by binary collision cascade mixing.

In this letter, we present experimental data of Xe ion mixing in bilayer targets involving Al. The average atomic number of a 3*d*-metal/Al, $\bar{Z}$, is in the vicinity of 20. The results demonstrate that the magnitude of ion mixing indeed varies as would be expected when the underlying mixing mechanism changes in character.

Samples used in this study are bilayers of metal/Al thin films prepared by electron beam evaporation onto SiO_2 or single crystalline Si substrates. Each bilayer is made up of a bottom layer of Al (200–300 nm thick) and a top layer of a transition metal (3*d*-metal Ti, Cr, Ni, and 4*d*-metal Mo). The thickness of the top metal layer, ranging from ~30 nm for Mo to ~60 nm for Ti, was designed to be slightly thinner than the projected range of 285 keV Xe^+ ions in the metal. Evaporations of the bilayers were performed in a vacuum that increased from the base pressure of 5×10^{-8} to $\sim5\times10^{-7}$ Torr during evaporation. Irradiations were carried out with 285 keV Xe^+ ions at a flux of $\sim0.5\,\mu A/cm^2$ to doses ranging from $\sim1\times10^{15}$ to 1×10^{16} ions/cm^2. During irradiation, samples were cooled with liquid nitrogen in a target chamber evacuated to $\sim7\times10^{-7}$ Torr. To guard against possible interferences from sputtering and/or impurity pick-up at the outer sample surface, a thin Si cap or a bottom reference marker layer was adopted.

Following ion irradiation near 77 K, the samples were analyzed at room temperature by 2 MeV $^4He^+$ backscattering spectrometry with the sample normals tilted 55° from the incident beam and a scattering angle of 170°. The amount of the interfacial ion mixing, defined as $4Dt$, is extracted from the high-energy edge of the bottom layer (Al) signal in the backscattering spectra following a routine procedure of numerical data transformation and fitting with an error function.[6,10] Ni/Al samples irradiated to high doses ($\geqslant5.6\times10^{15}$/cm^2) were not used for data collection due to signs of deviation from the assumed error function type profile.

Plots of the amount of mixing, $4Dt$, versus ion dose have been constructed for each bilayer system, as done in our previous papers.[6,10] The data points for each system were least-squares fitted with a straight line. The mixing efficiency of a bilayer system, defined as $d(4Dt)/d\phi$, was obtained from the slope of the linear fit. Table I compiles mixing efficiencies measured in this experiment. Values for Ni/Al and Mo/Al systems are in agreement with those obtained in our previous experiments[14,15] to within error bars. Also included in Table I are two additional values found in the literature for mixing in Cu/Al [500 keV Xe^+, 40 K (Ref. 16)] and Fe/Al [900 keV Xe^{3+}, 77 K (Ref. 17)] bilayers.

The observed mixing efficiencies are first compared with predictions by the phenomenological model of Johnson and co-workers[7,9,10] for diffusion in a thermal spike, which predicts a mixing efficiency described by

$$\left(\frac{d(4Dt)}{d\phi}\right)_{\rm spk}\frac{\rho^{5/3}(\Delta H_{\rm coh})^2}{\epsilon^2}=K_1+K_1K_2\left(\frac{\Delta H_{\rm mix}}{\Delta H_{\rm coh}}\right), \quad (1)$$

where ϵ is the energy deposited per unit path length at the interface, ρ is the average atomic density, $\Delta H_{\rm mix}$ and $\Delta H_{\rm coh}$ are heat of mixing and cohesive energy, respectively, and K_1 and K_2 are fitting constants with values $K_1 = 0.0035$ nm and $K_2 = 27$ for 22 transition-metal pairs. The values we have used for these parameters to calculate the mixing efficiency

 0003-6951/89/050413-03$01.00

TABLE I. Parameters of mixed systems and comparison between experimental and calculated $[d(4Dt)/d\phi]$.

System (A-B)	$-\Delta H_m$[a] (kJ/g at)	$-\Delta H_{coh}$[b] (eV/particle)	ϵ[c] (eV/Å)	E_d[d] (eV)	$[d(4Dt)/d\phi]_{exp}$[e] (10^4 Å^4)	$[d(4Dt)/d\phi]_{spk}$[f] (10^4 Å^4)	$[d(4Dt)/d\phi]_{col}$[g] (10^4 Å^4)
Ti-Al	61	4.75	262	18	1.19	5.56	0.98
Cr-Al	30	4.06	348	22	0.97	6.38	0.84
Fe-Al	32	4.17	369	17	1.21	6.83	1.13
Ni-Al	48	4.41	390	20	6.02	8.15	0.97
Cu-Al	16	3.61	400	18	9.60	7.65	1.18
Mo-Al	24	5.35	362	26	2.72	3.69	0.74

[a] Heat of mixing for $A_{50}B_{50}$, obtained from A. R. Miedema, Philips Tech. Rev. 36, 217 (1976).
[b] Cohesive energy for $A_{50}B_{50}$ calculated from $\Delta H_{coh} = \frac{1}{2}(\Delta H_A^0 + \Delta H_B^0) + \Delta H_m$, (Ref. 7) where ΔH_A^0 and ΔH_B^0 are the cohesive energies of solids A and B, obtained from C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 74.
[c] Average energy deposited per unit length due to nuclear collisions at the interface of A and B, J. P. Biersack and J. F. Ziegler, in *Ion Implantation Techniques*, edited by H. Ryssel and H. Glawisching (Springer, Berlin, 1982), p. 122.
[d] Average minimum displacement energy for elements A and B, taken from Ref. 2.
[e] Experimentally observed mixing efficiency $d(4Dt)/d\phi$.
[f] Calculated mixing efficiency $d(4Dt)/d\phi$ using Eq. (1) with the least-squares-fitted values $K_1 = 0.035$ Å and $K_2 = 27$.
[g] Calculated mixing efficiency $d(4Dt)/d\phi$ using Eq. (2).

$[d(4Dt)/d\phi]_{spk}$ according to Eq. (1) are listed in Table I. In Fig. 1, we compare our experimental data with those summarized by Cheng *et al.*[9] for transition-metal bilayers irradiated by Xe near 77 K. The dashed lines in the figure mark the boundaries of the range of the data in Ref. 9. The solid line is the linear fit reported for those data points that yields the values of K_1 and K_2 given above for transition-metal bilayers. The experimental data points for metal/Al pairs (Table I) are shown with circles in the figure. It is seen that while some systems (Ni/Al, Cu/Al, Mo/Al) conform reasonably well to the model predictions, other systems (Ti/Al, Cr/Al, Fe/Al) do not at all. We have thus found that if Al is substituted for the 3*d* or 4*d* metals in these bilayers, the description of the phenomenological model is no longer valid in general.

The present data are also compared with predictions

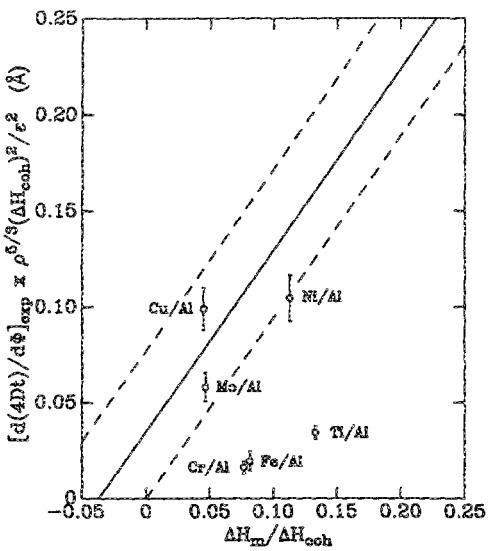

FIG. 1. Normalized mixing efficiency vs $\Delta H_{mix}/\Delta H_{coh}$. A plot with these coordinates was introduced in Ref. 9. The dashed lines bracket the range of data points summarized in Ref. 9 for transition-metal bilayers. The solid line is the linear fit to their data. Our data for metal/Al bilayers (see Table I) are added with circles.

given by a binary collision cascade model. The analytical formula used for the calculation is that of Sigmund and Gras-Marti[1] in the form

$$\left(\frac{d(4Dt)}{d\phi}\right)_{col} = \frac{2}{3}\Gamma_0 \xi \frac{\epsilon R_c^2}{\rho E_d}, \tag{2}$$

where $\Gamma = 0.608$, $\xi = [4m_1m_2/(m_1+m_2)^2]^{1/2}$, R_c^2 is the mean-square range of a displaced atom taken to be 1 nm,[2,16] and E_d is the average minimum displacement energy.[2] The calculated mixing efficiency values, $[d(4Dt)/d\phi]_{col}$, are also tabulated in Table I. The experimental mixing rates in the three lightest 3*d*-metal/Al bilayers (Ti/Al, Cr/Al, Fe/Al) are close to the model predictions, whereas those in other systems (Ni/Al, Cu/Al, Mo/Al) are higher by a factor of 4–9.

Neither of the two models alone can explain the wide range of mixing efficiency values observed in this experiment. While the mixing of the lightest 3*d*-metal/Al pairs seems to be largely attributable to binary collisional mixing, diffusional mechanisms must be invoked to account for the large magnitude and variation of mixing observed in the rest of the bilayers.

These observations can be understood by analyzing a collision cascade from the perspective of fractal dimensionality,[11,12] where it is shown that a local spike develops only when the kinetic energy of a displaced particle falls below a critical value E_c. E_c decreases monotonically with decreasing atomic number of the target element, Z. For light elements, E_c can fall below the minimum energy required for an atomic displacement in a binary collision, E_d. In such a case, the collision cascade stops before a spike is initiated. The fractal geometry approach predicts that spikes cannot be expected in a matrix consisting of elements with $Z < 20$ (assuming 30 eV for E_d).[13] Viewed from this perspective, spikes are unlikely to be well developed in our 3*d*-metal/Al pairs, which have a $\bar{Z}$ below 20 and none of the constituents with Z much larger than 20. If the spikes form at all, the low E_c would lead to a late initiation of spikes in the evolution of the cascade, resulting in isolated spikes with low-energy density, small size, and very short duration. In 3*d*-5*d* and 4*d*-5*d*

pairs, on the other hand, well-developed dense local spikes are always expected.[7,10]

Measured against the predictions of the thermal spike model (solid line in Fig. 1), our experimental normalized mixing parameters (ordinate in the figure) are ~20% of the predicted values for Ti/Al ($\bar{Z} = 17.5$), Cr/Al ($\bar{Z} = 18.5$), Fe/Al ($\bar{Z} = 19.5$), ~70% for Ni/Al ($\bar{Z} = 20.5$) and Mo/Al ($\bar{Z} = 27.5$), and ~120% for Cu/Al ($\bar{Z} = 21$). The trend here is consistent with the idea developed from the fractals approach that spikes do not develop well in light targets. The transition seems somewhat abrupt at $\bar{Z} = 20$. Materials-related parameters other than the atomic number evidently also affect the development of spikes. It was recently shown by computer simulation studies using molecular dynamics[18] that the thermal-spike phase in Cu lasts substantially longer and induces much more mixing than in Ni. Since our 3*d*-metal/Al bilayers are borderline cases ($\bar{Z} \sim 20$), it is not surprising to see significant differences between various systems in terms of their thermal spike behavior.

The large variations in mixing observed here for different bilayers could also be attributed to other causes, such as contaminations of the specimens, variation in diffusion properties in the mixed alloys during the spike,[19] or other mechanism(s) such as the electron-phonon coupling that influences the evolution of a spike.[20] To determine the merit of these alternative interpretations requires additional knowledge of these specific subjects. In contrast, our idea of a transition from a well-developed spike towards binary collisions stands as an interpretation that requires no additional information. It is probable that the factors mentioned above become increasingly important as spikes wane.

In the lower limit, the observed mixing efficiencies should be no less than those set by linear binary collision events. Our results for 3*d*-metal/Al pairs (Table I) are consistent with that idea.

In summary, we find that the mixing efficiencies for metal/Al bilayers span a wide range in values as would be expected when the dominant mixing mechanism changes from that of binary collision cascade to that of thermal spike. As a group, 3*d*-metal/Al bilayers are systems that are beyond the validity limits of the established ion mixing models.

The authors thank Dr. R. S. Averback and Dr. Y.-T. Cheng for useful comments and discussions. This work was supported in part by National Science Foundation-Materials Research Group-DMR-8811795.

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