

Effect of thermodynamics on ion mixing

T. W. Workman, Y. T. Cheng,^{a)} W. L. Johnson, and M-A. Nicolet
California Institute of Technology, Pasadena, California 91125

(Received 10 December 1986; accepted for publication 30 March 1987)

Ion mixing of elemental *4d-5d* metallic bilayers at 77 K by 600 keV Xe⁺⁺ ions has been studied to test the validity of the phenomenological model of ion mixing that predicts a dependence on the chemical heats of mixing, ΔH_{mix} , and on the cohesive energies, ΔH_{coh} , of the bilayer elements. A series of samples was chosen to minimize the variation in kinematical properties between samples while maximizing the variation in heats of mixing. The experimental results agree well with the model's predictions, and the experimentally determined constants $K_1 = 0.034 \text{ \AA}$ and $K_2 = 27$ agree with those of previous work.

A number of recent experiments have shown variations in bilayer mixing rates under heavy ion bombardment that cannot be explained by purely collisional models.¹⁻³ Large variations between systems with similar collisional properties (atomic mass and density) have been explained by differences in thermodynamic characteristics (heat of mixing, ΔH_{mix} , and cohesive energy, ΔH_{coh}). In experiments involving both heavy ions and heavy metal matrices ($Z > 20$), where dense collision cascades are most likely, and where radiation-enhanced diffusion has been suppressed by irradiation at liquid-nitrogen temperature, the phenomenological model proposed by Johnson *et al.* has given relatively good predictions of the mixing rates.^{4,5} The model predicts a mixing rate described by

$$\frac{d(4Dt)}{d\phi} = K_1 \frac{\epsilon^2}{\rho^{5/3} (\Delta H_{\text{coh}})^2} \left(1 + K_2 \frac{\Delta H_{\text{mix}}}{\Delta H_{\text{coh}}} \right), \quad (1)$$

where $4Dt$ is the variance of the spreading at the bilayer interface, ϕ is the ion dose, ϵ is the energy deposited per unit path length, ρ is the average atomic density, and K_1 and K_2 are fitting constants. The model assumes mixing by chemically biased diffusional processes within a thermal spike.

In order to further study the effect of thermodynamic factors on ion mixing, we have chosen to examine the mixing of metallic bilayers with widely varying heats of mixing and similar, dense collision cascade behavior. Our study is similar to that of Ref. 1, but with *4d-5d* metal bilayers instead of *3d-5d* metal bilayers. Thus, we endeavor to extend the range of systems in which mixing rates and thermodynamic properties can be correlated in order to better quantify the new model.

The systems chosen for this study are made up of the *5d* metals Hf and Pt as top layers, with a series of *4d* metals as the bottom layers for each system. The Hf series includes the bottom layer metals Zr, Ru, Pd, and Ag. The Pt series includes Zr, Nb, Mo, and Ru. The difference in atomic mass between the top and bottom layers is large enough to allow analysis by backscattering spectrometry.⁶ Pertinent parameters of the systems are listed in Table I.

The bilayer samples were prepared by electron beam evaporation in an oil-free vacuum system. The base pressure was less than 5×10^{-8} Torr, and the pressure remained below 3×10^{-7} Torr during evaporation. Each bilayer consist-

ed of a 600- \AA Hf or 375- \AA Pt layer on top of a 1500- \AA layer of a *4d* metal. The top layer thickness is designed to be 90% of the projected range of 600 keV Xe⁺⁺ ions. A 30- \AA layer of Ti was deposited on the SiO₂ substrate before deposition of the bottom layer to improve adhesion.

Ion mixing was performed with the samples at liquid-nitrogen temperature to minimize the possible effects of radiation-enhanced diffusion. The pressure during irradiation was maintained below 5×10^{-7} Torr. The samples were irradiated with 600 keV Xe⁺⁺ ions to doses of 10^{15} , 3×10^{15} , 5×10^{15} , and 7×10^{15} ions/cm², at a flux of about 200 nA/cm². At each dose, samples of all bilayers were irradiated simultaneously to remove possible variations in dose and dose rate.

After ion mixing, the samples were analyzed by means of 2 MeV He⁺ backscattering with sample normals tilted 50° from the incident beam direction and a scattering angle of 170°. Two series of samples, Hf-Pd and Pt-Zr, exhibited enough mixing that analysis with 3 MeV He⁺⁺ ions and a target tilt of 50° was necessary to resolve top and bottom layer signals. The high-energy edge of the bottom layer signal of each spectrum was numerically transformed from counts versus energy to concentration versus depth. All concentration profiles, except one, were found to be smoothly varying and showed no horizontal steps indicative of compound formation. The one exception, Hf-Pd, showed a kink in its slope, and has been shown to form the compound Pd₃Hf under high-dose ion mixing.² The Hf-Pd spectra were evaluated in the same manner as all the others, but were given larger uncertainties due to this feature.

The transformed profiles were least-squares fitted to complementary error functions with a four-parameter fit of the form

$$C(x) = A(3) \operatorname{erfc} \left(\frac{[x - A(1)]}{A(2)} \right) + A(4), \quad (2)$$

where $C(x)$ is the atomic concentration at depth x , $A(3)$ is the height, $A(1)$ is the center point, $A(2)$ is the spreading and is defined as $(4Dt)^{1/2}$, and $A(4)$ is the background. A linear relationship between $[A(2)]^2 = 4Dt$ and the ion dose, ϕ , is indicated by previous experimental evidence and current ion mixing models.^{7,8} For the present data, a linear least-squares fit of $4Dt$ versus ion dose gives a good fit for most of the systems studied (Fig. 1). The nonzero value of $4Dt$ for the as-deposited samples ($\phi = 0$) is due to an initial-

^{a)} Present address: Physical Chemistry Department, General Motors Research, Warren, MI 48090-9055.

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)	ρ^d (10^{-2}Å^{-3})	$[d(4Dt)/d\phi]_{exp}^e$ (10^5Å^4)	$[d(4Dt)/d\phi]_{cal}^f$ (10^5Å^4)
Pt-Zr	151	7.61	480	5.46	1.21	1.13
Hf-Pd	122	6.43	440	5.66	1.17	1.20
Pt-Nb	104	7.78	515	6.09	0.79	0.75
Hf-Ru	77	7.39	450	5.94	0.50	0.55
Pt-Mo	42	6.77	540	6.52	0.37	0.56
Hf-Ag	31	5.02	415	5.19	0.41	0.88
Pt-Ru	2	6.31	570	6.99	0.27	0.25
Hf-Zr	0	6.35	355	4.41	0.23	0.19

^a Heat of mixing for $A_{50}B_{50}$, obtained from A. R. Miedema, Phil. Tech. Rev. 36, No. 8, 217 (1976).

^b Cohesive energy for $A_{50}B_{50}$ calculated from $\Delta H_{coh} = \frac{1}{2}(\Delta H_A^0 + \Delta H_B^0) + \Delta H_m$,² where ΔH_A^0 and ΔH_B^0 are the cohesive energies of the corresponding solids A and B, obtained from C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, NY, 1976) and from R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, eds., *Selected Values of the Thermodynamical Properties of the Elements* (ASMT, Metal Parks, Ohio, 1973).

^c Average energy deposited per unit length due to nuclear collisions at the interface of A and B, J. P. Biersach and J. F. Ziegler, in *Ion Implantation Techniques*, edited by H. Ryssel and H. Glawisching (Springer, Berlin, 1982).

^d Average atomic density for $A_{50}B_{50}$ obtained from averaging the atomic densities of the pure elements A and B.

^e Experimentally observed mixing rate $d(4Dt)/d\phi$.

^f Calculated mixing rate $d(4Dt)/d\phi$ using Eq. (1) with the least-squares fitted values $K_1 = 0.034 \text{Å}$ and $K_2 = 27$.

ly blurred interface and the limited instrumental resolution. The slope of each line, $d(4Dt)/d\phi$, characterizes the rate of ion mixing for the corresponding bilayer.

The observed variation in mixing rates (slopes) between systems cannot be explained by differences in collisional properties. A purely collisional model, such as that given by Sigmund,⁷ predicts a variation in mixing rates of less than 35% over the entire range of these systems, while the actual values vary by more than a factor of 5. However, there is a good correlation between the mixing rate and the heat of mixing (see Table I). The relationship between mixing rate and heat of mixing is roughly linear, as is predicted by the

phenomenological model. To better compare the experimental results to the model, we rewrite Eq. (1) in the form

$$\frac{d(4Dt)}{d\phi} \frac{\rho^{5/3} (\Delta H_{coh})^2}{\epsilon^2} = K_1 + K_2 \left(\frac{\Delta H_{mix}}{\Delta H_{coh}} \right). \quad (3)$$

The left-hand side of Eq. (3) is the mixing rate normalized to a common atomic density ρ , cohesive energy ΔH_{coh} , and energy deposited per unit path length between bilayers ϵ , and can be referred to as the normalized mixing parameter. The experimental values of this parameter are plotted against $\Delta H_{mix}/\Delta H_{coh}$ in Fig. 2. The solid line is obtained with the least-squares fitted constants $K_1 = 0.034 \text{Å}$ and $K_2 = 27$.

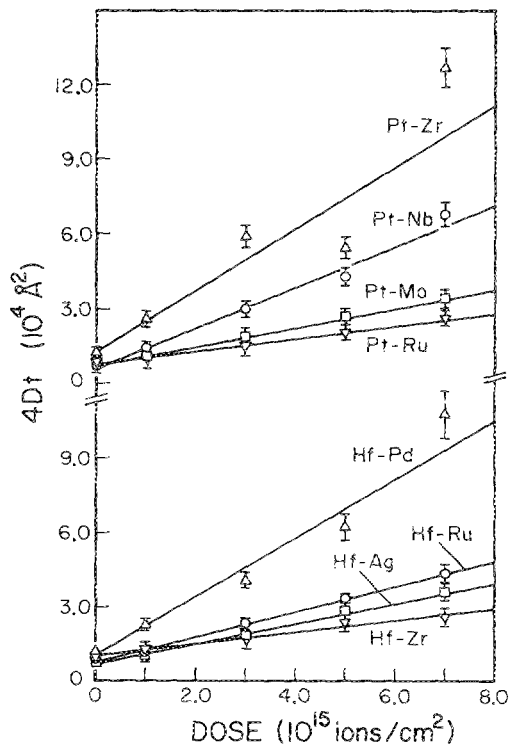


FIG. 1. Variance of the interface vs dose for each of the bilayers studied.

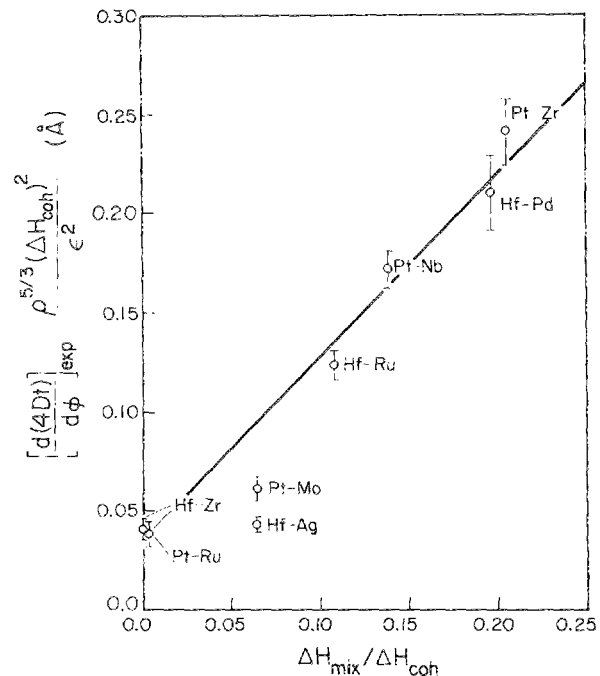


FIG. 2. Correlation between the normalized mixing parameter and $\Delta H_{mix}/\Delta H_{coh}$ for bilayers irradiated with 600 keV Xe^{+} . The fit is obtained with $K_1 = 0.034 \text{Å}$ and $K_2 = 27$.

The calculated mixing rates using these values are shown in Table I. The values of the two constants are in good agreement with those attained in Ref. 4, $K_1 = 0.037 \text{ \AA}$ and $K_2 = 27$, for 3d-5d bilayers mixed with 600 keV Xe^{++} ions.

The picture of the ion mixing process that this model suggests is one in which mixing takes place via a chemically biased diffusional process within individual cascades. In order for chemical driving forces, such as $\Delta H_{\text{mix}} \sim 1 \text{ eV/atom}$, to significantly bias the diffusion, atomic rearrangement within a cascade must continue down to interaction energies on the order of 1 eV. This value is much lower than the minimum displacement energies assumed in binary collision models.⁹ Thus, the thermal spike model appears appropriate in describing the evolution of the cascade. Within a thermal spike region, the energy density is high enough to excite a majority of atoms, causing a disordered state in which diffusion can proceed down to average kinetic energies per atom on the order of 1 eV.

The chemical biasing of the random walk diffusion can be described by Darken's analysis,^{2,10} using the regular solution approximation. Darken's analysis assumes that diffusion is driven by a chemical potential gradient (i.e., ΔH_{mix}), which modifies the diffusion coefficient for pure random walk diffusion by a term $(1 - 2\Delta H_{\text{mix}}/k_B T)$. The characteristic energy of the diffusion process, $k_B T$, can be shown to be proportional to $-\Delta H_{\text{coh}}$, leading to the term in Eq. (1). This analysis predicts a concentration profile that differs slightly from the complementary error function assumed in our data analysis, due to variations in ΔH_{mix} with composition. However, to the first-order approximation, the erfc fit gives an acceptable estimate of the interfacial spreading.

From the phenomenological model, we can assume the series of events that occur within a collision cascade involving heavy atoms. A dense cascade begins with a collision with an energy in the range of about 1000 eV. The energy is transferred to a rapidly increasing number of atoms within a localized volume. As the collision energies decrease, the density of moving atoms increases to a point where "a majority" of atoms within the cascade volume are moving¹¹ (thermal spike condition). The transition from cascade to thermal

spike occurs when the characteristic kinetic energy of the atoms is in the eV range, and can be analyzed using the notion of fractal dimensionality.¹² Within the spike region, random walk diffusion persists down to energies where the chemical bias effect becomes significant. From experimental results, it appears that a dominant part of the mixing occurs at energies where the chemical bias is significant.

Our experimental results are consistent with the notion of chemically biased atomic displacements generated by a thermal spike. A phenomenological model which includes the effects of chemical heats of mixing and cohesive energies of the bilayer gives a good, quantitative description of the behavior of heavy metal bilayers under heavy ion irradiation. It would be interesting to study systems of lighter metal bilayers or use light ion irradiation to find the lower limit of atomic mass where the model still gives an accurate description. This should help to determine the necessary conditions for thermal spike behavior.

We thank R. Gorris and D. Groseth for technical assistance. Financial support by the Office of Naval Research under contract N00014-84-K-0275 is gratefully acknowledged.

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