

⁹S. Licht and J. Manassen, *J. Electrochem. Soc.* (in press); Initial results reported by J. Manassen, S. Licht, G. Hodes, and D. Cahen, in *Abstract Presentation, 7th Photoelectrochemical Contractors Review Meeting*, Golden, CO (Dec. 1983), pp. 52–65.
¹⁰H. Flaisher, R. Tenne, and G. Hodes, *J. Phys. D* **17**, 1055 (1984).
¹¹G. Hodes, *Nature (London)* **285**, 29 (1980).
¹²G. Hodes, J. Manassen, and D. Cahen, *J. Amer. Chem. Soc.* **102**, 5962 (1980).
¹³R. Triboulet and Y. Marfaing, *J. Cryst. Growth* **51**, 89 (1981).
¹⁴A. N. Frumkin, *Trans. Faraday Soc.* **55**, 156 (1958).

¹⁵W. Giggenbach, *Inorg. Chem.* **10**, 1333 (1971).
¹⁶B. Meyer, K. Ward, K. Koshlap, and L. Peter, *Proceedings of the 185th ACS National Meeting*, Seattle Washington, March 20–25, 1983, Abstract 9.
¹⁷S. Licht and J. Manassen (unpublished).
¹⁸R. J. Matson, K. A. Emery, and R. E. Bird, *Solar Cells* **11**, 105 (1984).
¹⁹D. Cahen, J. Manassen, and G. Hodes, *Solar Energy Mater.* **1**, 343 (1979); R. Tenne, N. Müller, Y. Mirovsky and D. Lando, *J. Electrochem. Soc.* **130**, 852 (1983).
²⁰A. Heller (private communication).

Correlation between cohesive energy and mixing rate in ion mixing of metallic bilayers

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

(Received 29 October 1984; accepted for publication 4 January 1985)

We have compared the mixing rate of several 5d-4d metal bilayers which form ideal solutions. We observe a strong correlation between the mixing rate and the average cohesive energy of each bilayer. A model based on the thermal spike concept is proposed to explain this behavior. The model leads to a general expression describing mixing rates in metallic bilayers.

In the usual theoretical description of cascade mixing, the mixing rate is assumed to be inversely proportional to the effective displacement energy E_d inside the cascade volume.¹ However, due to the complexity of the ion mixing process, the mixing rate actually depends on many factors. Recently, a relationship between the mixing rate and the heat of mixing ΔH_m was established for a series of transition metal bilayers by the present authors.² By eliminating chemical effects (i.e., taking systems with $\Delta H_m = 0$), we now can investigate the role of E_d directly.

The systems we have chosen to study are metallic 5d-4d bilayers of Au-Ag, Pt-Pd, Hf-Zr, W-Mo, and Ta-Nb. Due to their isoelectronic structure, similar Goldschmidt radii and density, ideal solution behavior, and corresponding near zero heat of mixing,³ these binary systems are well suited for studying those effects which are not related to the chemical effects examined earlier. Furthermore, all 5d and 4d elements have nearly the same atomic number and mass, while the mass difference between the top (5d) and bottom (4d) layer of each couple is sufficient to resolve their signals and study the intermixing process by backscattering spectrometry.

Thin bilayer films were prepared by *e*-gun evaporation in an oil-free vacuum system with a base pressure below 10^{-7} Torr. All bilayers consisted of a layer of the 5d metal on top of a 2000-Å-thick layer of the 4d metal sequentially evaporated on a SiO₂ substrate. The top layer thickness was adjusted to the projected range of 600 keV Xe⁺⁺ ions. To reduce sputtering effects, a thin layer of Si (100 Å) was evaporated on top of the samples. Ion mixing was performed at LN₂ temperature in order to minimize radiation enhanced

diffusion. The vacuum during the irradiation was maintained below 5×10^{-7} Torr. Irradiation doses ranged from 10^{15} to 1.5×10^{16} Xe⁺⁺ ions/cm² at a flux of about 200 nA/cm². Different samples were irradiated simultaneously to a specific dose in order to avoid dose and dose rate variations. Backscattering analysis was performed with 3-MeV He⁺⁺ ions and a target tilted at 60°. Different samples were placed on the same holder to cancel uncertainty in tilt angle.

The observed diffusion profiles were smooth and showed no steps that would indicate the presence of a layered compound. The high-energy backscattering edge of each bottom layer was transformed numerically to concentration versus depth profiles, assuming lateral uniformity over the mixed interface. The transformed profiles were least squares fitted to complementary error functions, using the expression

$$Y = a(3) \operatorname{erfc}[(x - a(1))/a(2)] + a(4), \quad (1)$$

where $a(1)$, $a(2)$, $a(3)$, and $a(4)$ are fitting variables. The good quality of the erfc fits to all intermixing profiles is a direct indication of an unbiased random walk process, as would be expected for systems with nearly zero heat of mixing. The result of such an analysis of the experimental data is shown in Fig. 1. A linear relationship between $[a(2)]^2 = 4Dt$ and dose (ϕ) is observed in all cases. The straight lines in Fig. 1 are fits obtained by linear regression analysis. The slope of each line $d(4Dt)/d\phi$ characterizes the mixing rate of the corresponding bilayer. The nonzero value of $4Dt$ at $\phi = 0$ is due to the finite extension of the interface of the as-deposited samples and the limited instrumental resolution.

A theoretical estimate of the mixing rate for the systems under consideration can be derived from the well-known formula for cascade mixing in the binary collision approxima-

^{a)} Present address: BTMC, Gasmeterlaan 106, B-9000 Gent, Belgium.

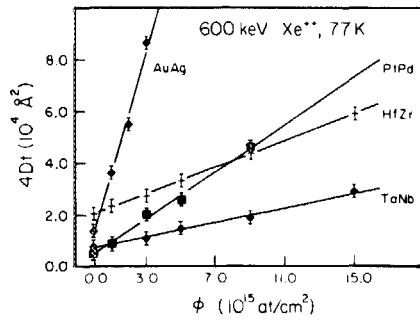


FIG. 1. Mixing rates ($4Dt$ vs dose) of various $5d-4d$ metallic bilayers.

tion⁴:

$$\frac{4Dt}{\phi} = \frac{2}{3} \Gamma_0 \frac{\epsilon_D(x)}{N} \xi_{21} \frac{\langle R_c \rangle^2}{E_d}, \quad (2)$$

where ϵ_D is the energy deposited per unit path length, N is the atomic density of the material, E_d the effective displacement energy, $\langle R_c \rangle^2$ is the mean square range of a displaced atom, $\Gamma_0 = 0.608$, and $\xi_{21} = [4m_1 m_2 / (m_1 + m_2)^2]^{1/2}$. Little difference in mixing rate would be expected for the various bilayers involved if conventional values for R_c (10 Å) and E_d (~30–40 eV)⁵ were used, whereas the experimental values vary by an order of magnitude.

In an effort to understand the origin of this discrepancy, we have plotted $[d(4Dt)/d\phi]^{-1}$ versus the average cohesive energy of each bilayer (Fig. 2). The latter was estimated from the heat of sublimation of the pure elements.⁶ A striking correlation suggests that values of E_d and/or R_c deduced from binary collision experiments are inappropriate for ion mixing under the present conditions. To understand why we need to examine the physical basis of E_d in the case of ion mixing experiments, the displacement energy may be considered to consist of two major contributions. The first is the minimum energy required to remove an atom from its site and is therefore close to the formation energy of a vacancy

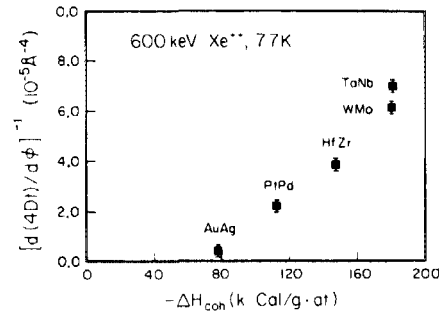


FIG. 2. Correlation between mixing rate and average cohesive energy of each bilayer.

(few eV); the second contribution is the extra energy needed to move the atom some specific distance away from the vacancy and avoid spontaneous recombination. In a low-density cascade with only one type of atoms present (such as in electron or proton bombardment of pure elements) E_d is normally derived from the resulting concentration of stable radiation-produced vacancy-interstitial pairs.⁷ Each such pair has to be separated by a minimum distance (about 10 Å) below which vacancies and interstitials would mutually annihilate each other. To move an atom this distance, an energy of some tens of eV is needed. Therefore, E_d in low-density cascades is dominated by the second part of the contribution to the displacement energy and the defect production is well described by a Kinchin–Pease type model.⁸ In ion mixing with heavy projectiles, the situation is different. Because of the high density of the cascade, correlated motions of neighboring atoms are possible and the medium becomes liquid-like. Therefore, the second contribution to E_d is reduced. Furthermore, an atom ejected from its site and displaced by one or more atomic distances may contribute to ion mixing whereas in a one-component system, an atom must be sufficiently displaced to make a stable vacancy-interstitial pair. These differences between the two types of experiments sug-

TABLE I. Comparison between calculated values of $d(4Dt)/d\phi$ from Eq. (4) and experimental observations.

System (A-B)	$-\Delta H_{\text{mix}}^a$ (kJ/g at)	$-\Delta H_{\text{coh}}^b$ (eV/particle)	ϵ_D^c (10^2 eV/Å)	ρ^d (10^{-2} Å ⁻³)	$d(4Dt)/d\phi_{\text{exp}}^e$ (10^5 Å ⁴)	$d(4Dt)/d\phi_{\text{cal}}^f$ (10^5 Å ⁴)
Pt-Ti	122	6.60	4.45	6.14	1.28	1.07
Pt-V	68	6.27	4.91	6.92	0.68	0.78
Pt-Mn	43	4.82	5.31	7.40	0.73	1.19
Pt-Cr	36	5.34	5.30	7.47	0.45	0.78
Pt-Ni	7	5.21	5.82	7.88	0.45	0.44
Au-Ti	84	5.20	4.14	5.78	1.63	1.48
Au-Cr	0	3.96	4.98	7.12	0.78	0.48
Au-Co	-11	3.99	5.39	7.43	0.45	0.12
Pt-Pd	0	4.87	5.54	6.71	0.45	0.43
Hf-Zr	0	6.34	3.55	4.40	0.26	0.22
W-Mo	0	7.86	5.19	6.36	0.16	0.16
Ta-Nb	0	7.84	4.45	5.56	0.14	0.15
Au-Ag ^g	0	3.38	4.80	5.88	2.37	0.84

^aHeats of mixing of $A_{50}B_{50}$, A. R. Miedema, Phil. Techn. Rev. 36, No. 8, 217 (1976).

^bCohesive energy of $A_{50}B_{50}$ calculated from $\Delta H_{\text{coh}} = \frac{1}{2}(\Delta H_A^0 + \Delta H_B^0) + \Delta H_{\text{mix}}$, ΔH_A^0 and ΔH_B^0 are obtained from C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, NY, 1976), and Ref. 6.

^cAverage energy deposited per unit length due to nuclear collision 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, Heidelberg, New York, 1982), p. 122.

^dAverage atomic density of $A_{50}B_{50}$.

^eExperimental observations of $d(4Dt)/d\phi$ in Ref. 2 and present work.

^fCalculated values of $d(4Dt)/d\phi$ from Eq. (4) with least-square fitted value of $K_1 = 0.037$ Å and $K_2 = 27$.

^gThis data point was not used in determining K_1 and K_2 since it would contribute badly to the quality of the least-square fit.

gest an alternative approach to describe the mixing process. Our previous experiments have shown that most of the mixing takes place when the energy of the particles is in the 1-eV range.² Such energy densities are achieved in the thermalizing regime of the cascade, as described by various authors.^{9,10} Assuming that the particle energy distribution has reached a state of local quasi-equilibrium, we can adopt a thermal spike picture as proposed, e.g., by Vineyard.¹¹ Within this model, ion mixing is a thermally activated diffusion process with jump rate $R = A \exp(-Q/T)$. For a cylindrical spike, Vineyard obtains for the total number of jumps per unit distance induced by one spike

$$\xi = A (\epsilon_D^2 / \kappa C Q^2), \quad (3)$$

where ϵ_D is the energy deposited per unit path length, while κ and C are the (temperature independent) thermal conductivity and specific heat of the lattice. A , κ , and C are roughly constant for the metal pairs in our bilayer experiments. It can be argued that the activation energy Q should scale with the cohesive energy of the lattice, since the latter is a measure of the interatomic binding forces¹²; hence $Dt/\phi \propto (\Delta H_{\text{coh}})^{-2}$. The results reported in Fig. 2 are in good accord with such a dependence.

We have extended this model of ion mixing by dense energy spikes to the case when chemical driving forces are present and derived the following equation for the mixing rate¹²:

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

where ρ is the average atomic density, ΔH_m is the heat of mixing parameter calculated by Miedema.³ $K_1 = 0.037 \text{ \AA}$ and $K_2 = 27$ are two least-square fitted constants.

In Table I we compare experimental and calculated mixing rate for various metallic systems. The proposed expression clearly reproduces the experimental trend. In addition to the data listed in Table I, it has also been observed that several systems with $\Delta H_m \gg 0$ show very low mixing rates (e.g., Cu-W,¹³ Cu-Bi,¹⁴ Ta-Y¹⁵), as expected from Eq. (4).

In summary, we have established a direct correlation between the mixing rate of metallic bilayers and the cohesive energy of the corresponding elements. The experiments were designed to isolate this effect from the chemical effect established earlier. We offer an explanation for this correlation

based on the nature of the microscopic atomic displacement process which leads to the mixing of atoms. An expression is proposed which predicts the mixing rate of transition metal bilayers and includes the chemical enhancement effect. This expression should be appropriate in the case of high-density cascades, where the Kinchin-Pease model based on the binary collision approximation is no longer applicable. More generally, our results illustrate the usefulness of a thermodynamic description of the ion mixing phenomenon. It would be desirable to extend this description to the final stage of the cascade, where intermetallic phase formation is taking place. One might then hope to be able to predict the phases which are produced by cascade mixing.¹²

The authors would like to thank A. Ghaffari (Caltech) for sample preparation, and Dr. S. S. Lau and Dr. D. M. Scott (University of California at San Diego) for use of their RBS equipment. The authors would like to thank the Department of Energy for partial support under Project Agreement No. DE-AT03-81ER10870 under contract No. DE-AM03-76F00767 and the Office of Naval Research for partial support under contract No. N00014-84-K-0275. One of the authors (MVR) also acknowledges the IBM Corporation for support.

¹P. Sigmund and A. Gras-Marti, Nucl. Instrum. Methods. **182/183**, 25 (1981).

²Y.-T. Cheng, M. Van Rossum, M.-A. Nicolet, and W. L. Johnson, Appl. Phys. Lett. **45**, 185 (1984).

³A. R. Miedema, Philips Tech. Rev. **8**, 36 (1976).

⁴F. Besenbacher, J. Böttiger, S. K. Nielsen, and H. J. Whitlow, Appl. Phys. A **29**, 141 (1982).

⁵H. H. Andersen, Appl. Phys. A **18**, 131 (1979).

⁶R. 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).

⁷M. W. Thompson, *Defects and Radiation Damage in Metals* (Cambridge University, Cambridge, 1969), p. 263.

⁸G. H. Kinchin and R. S. Pease, Rep. Prog. Phys. **18**, 1 (1955).

⁹M. W. Guinan and J. H. Kinney, J. Nucl. Mater. **103/104**, 1319 (1981).

¹⁰R. A. Weller, Nucl. Instrum. Methods **194**, 573 (1982).

¹¹G. H. Vineyard, Radiat. Eff. **29**, 245 (1976).

¹²W. L. Johnson, Y.-T. Cheng, M. Van Rossum, and M.-A. Nicolet, presented at the International Conference on Ion Beam Modification of Materials (IBMM-84), Ithaca, New York, July 1984; to be published in Nucl. Instrum. Methods B.

¹³Z. L. Wang, J. F. M. Westendorp, and F. W. Saris, Nucl. Instrum. Methods **209/210**, 115 (1983).

¹⁴R. S. Averbach (private communication).

¹⁵Y.-T. Cheng and M. Van Rossum (unpublished).