Collective interdiffusion in compositionally modulated multilayers

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Interdiffusion in Fe–Ti, Ag–Bi, Fe–Mo, Ni–Si, Mo–Si, Nb–Si, and Ag–Si multilayers (MLs) was investigated by an *in situ* low-angle x-ray diffraction technique. Temperature-dependent interdiffusivities were obtained which can be described as Arrhenius relations. The interdiffusion characteristics of the MLs were summarized. The extremely small values of the prefactor D_0 and the marked correlation between the D_0 and activation energy H_e for interdiffusion suggest that a collective atomic jumping mechanism involving 8–15 atoms govern the interdiffusion in the MLs. © *1999 American Institute of Physics.* [S0021-8979(99)07220-5]

I. INTRODUCTION

Physical properties and fundamental phenomena in multilayers (MLs), such as interfacial structure, stabilization of nonequilibrium structure and strains, coupling interactions in magnetism, and transport behavior, are of scientific importance as well as potential application in microelectronic technology.[1] Interdiffusion is closely related to these phenomena in the MLs. Thus a knowledge of the interdiffusion data and mechanism is highly desired for understanding the physical properties and phenomena in the MLs. The discovery of solid state reaction in the MLs added to the importance of interdiffusion investigation. However, despite many years of effort, the interdiffusivity in MLs has remained poorly quantified due to the measurement difficulties associated with low diffusivity (less than 10^{-23} m²/s) and complicated interfacial reactions. The difficulties are even higher in the MLs with nanometer scale modulation period, because the measurements must be done at a sufficiently low temperature to avoid the occurrence of interfacial reactions. Rutherford backscattering, Auger electron spectroscopy, and secondary ion mass spectrometry, which are normally used to measure the diffusivity in thin films are difficult to measure diffusivity less than 10^{-23} m²/s which is often the case for the MLs.[2] Therefore, the general diffusion characteristics and mechanism in the MLs are still unclear.

Interdiffusion in MLs can be determined from the rate of homogenization of compositional modulation structure of the MLs according to the theory developed by Cahn.[3] By assuming that the linear decay of the intensity [$I(t)$] of the first-order modulation peak represents the process in the isoconfigurational condition, $I(t)$ is related to the effective interdiffusivity (D_e), and the modulation period (L) in the kinematic diffraction approximation by[2,3]

$$D_e = \frac{-L^2}{8\pi^2} \frac{d}{dt} \ln\left(\frac{I(t)}{I(0)}\right). \tag{1}$$

We developed an *in situ* low-angle x-ray diffraction (XRD) technique based on the linearized diffusion theory[4,5] to study the interdiffusion in Fe–Ti, Ag–Bi, and Fe–Mo metal–metal MLs and Mo–Si, Ni–Si, Nb–Si, and Ag–Si MLs. The interdiffusivity is obtained by carefully *in situ* monitoring the intensity changes of the low-angle XRD modulation peak with annealing time. It is indeed possible for this technique to measure interdiffusivities as low as 10^{-27} m²/s in MLs with L of a few nanometers. The measurement difficulties mentioned above can be overcome, and the interdiffusion process in the MLs can be discriminated from the crystallization, precipitation, and interfacial reactions in the measurement process. The technical details are published elsewhere.[4,5] Our obtained interdiffusion data are in good agreement with those reported in many other MLs measured using various methods and were also verified by a series of other studies.[6–8]

II. EXPERIMENTS

Compositional modulated MLs were prepared by ion beam sputtering with a base pressure of 1×10^{-7} Torr. Single-crystal Si(100) wafers were used as substrates and cooled by water through a substrate holder. The total thickness of the films was about 0.8 μm. The values of L for the MLs ranges from 2 to 10 nm. There are approximately more than 100 modulation periods for the investigated MLs. Details of the sample preparation were described at length in previous publications.[4,5] The MLs were found to pass through two distinct processes depending on the annealing temperature ranges: a pure interdiffusion process and an interfacial reaction process. The pure interdiffusion process precedes the interfacial reaction during the low temperature range.[4,5,7] The high-angle XRD and transmission electron microscope observations show no phase transitions during

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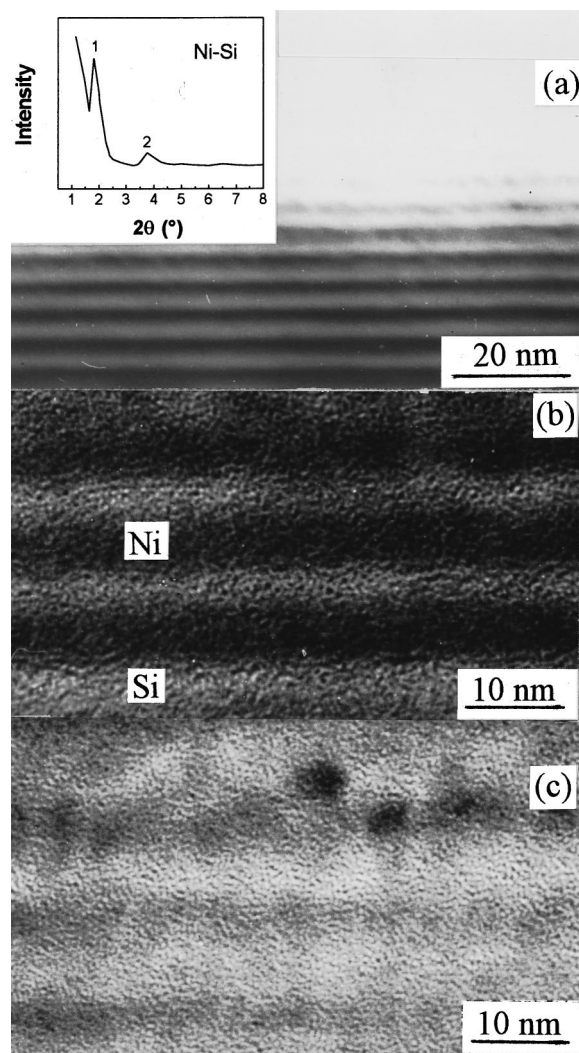[a)]Corresponding author; electronic mail: whw@aphy.iphy.ac.cn

FIG. 1. (a) Cross-sectional TEM image of the as-deposited Ni–Si ML. (b) Cross-sectional high-resolution TEM picture of the as-deposited Ni–Si ML. (c) Cross-sectional HRTEM picture of the Ni–Si ML after annealing at 613 K. The inset is the low-angle XRD pattern (Cu $K\alpha$ radiation) of the as-sputtered Ni–Si ML with $L=4.80$ nm.

TABLE I. Modulated structural and compositional data for the investigated MLs. N is the number of the XRD modulation peaks. The total thickness of the MLs is about 0.8 μm. There are approximately more than 100 modulation periods for each investigated ML.

System	L(nm)	Composition (at. %)	N
Fe–Ti	2.0	50.0 Fe	2
Ag–Bi	9.0	45.0 Ag	4
Fe–Mo	2.74	50.0 Fe	2
Mo–Si	2.6	35.0 Mo	2
Ni–Si	4.8	49.2 Ni	2
Nb–Si	3.2	50.0 Nb	2
Ag–Si	6.7	43.0 Ag	4

a result of intermixing in the deposition process, the ML evolves into two alternative amorphous sublayers with composition gradient. However, the ML still has a compositionally modulated structure as shown in Fig. 1(b). The x-ray modulation peaks induced from the compositionally modulated structure are shown in the inset of Fig. 1. The Ni–Si ML has a sharp modulation peak at $2\theta=1.80°$ and a weak peak at $2\theta=3.75°$ which means that a good composition modulation along the film growth direction is maintained in the MLs despite considerable intermixing at the interfaces. The modulation period L derived from the modulated peaks by a modified Bragg law[9] is 4.8 nm; the value agrees well with that obtained from the cross-sectional HRTEM picture. The cross-sectional HRTEM image for the Ni–Si ML after 613 K annealing is shown in Fig. 1(c). The picture shows that no crystalline phase forms in the annealing temperature range of 423–613 K. The result confirms that the effect of the annealing is to homogenize the composition gradient of the ML. The modulated structural and compositional data for these investigated MLs are presented in Table I.

Figure 2 represents a typical result we obtained by *in situ* low-angle XRD method, which shows the logarithm of the normalized intensity of the first modulation peak versus time at various annealing temperatures for Fe–Ti ML. The intensity exhibits a more rapid nonexponential decay in the early stage of the annealing (0–1.0 h). The enhancement in intensity decay is attributed to the presence of a large number of nonequilibrium defects in the as-deposited ML.[2] These data points were not taken into account. A relative steady exponential decay state was obtained after 1.0 h annealing. D_e was determined by linear fit from the linear part of the intensity curves in Fig. 2. The temperature dependence of D_e for Fe–Ti ML is shown in the inset of Fig. 2. The data can be fitted by a straight line over the whole measuremental temperature range yielding an activation energy $H_e=0.29$ eV and a pre-exponential factor $D_0=1.50\times10^{-22}$ m^2/s. The temperature dependence of the effective interdiffusivities for Fe–Ti, Fe–Mo, Ag–Bi, Ni–Si, Mo–Si, Nb–Si, and Ag–Si MLs obtained using the same method is summarized in Arrhenius plot in Fig. 3. The interdiffusion data display excellent Arrhenius behavior as shown in the figure. The H_e, D_0, and the bulk interdiffusivities D_v (at 458 K) derived from Cahn's theory[3] for the MLs, are presented in Table II. The important interdiffusion characteristics are summarized in the following:

the interdiffusion measuremental processes. This indicates the interdiffusion investigations were made without the influences of the interfacial reactions. The modulated structure of the MLs was examined by low-angle XRD and cross-sectional high-resolution transmission electron microscope (HRTEM). The cross-sectional HRTEM specimens were prepared by mechanical grinding, polishing and finally, argon ion milling in liquid nitrogen cooling stages with a power of less than 4 keV. The HRTEM image was carried out in a JEM-200CX operating at 200 kV.

III. RESULTS AND DISCUSSION

The modulation structure of the MLs was examined using the low-angle XRD and HRTEM. All of the investigated as-deposited MLs have good modulation structure.[4,5] As a representative example, the cross-sectional TEM image of the as-deposited Ni–Si ML is shown in Fig. 1(a). It can be seen that the ML consists of clearly layer structure. Figure 1(b) exhibits the HRTEM picture of the as-deposited ML. As
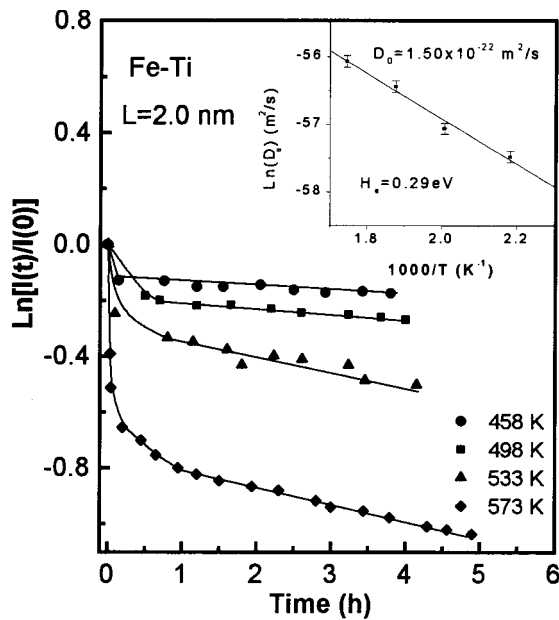
FIG. 2. Typical decay of the intensity of the first-order modulation peak of Fe–Ti multilayer ($L=2.0$ nm) with annealing time at various annealing temperatures. The inset is the temperature dependence of the interdiffusivity D_e for the Fe–Ti ML.

(a) The interdiffusion data for various systems display excellent Arrhenius behavior. This is a key test by which to determine whether a method can be used to correctly measure the interdiffusivity in solids as a function of temperature.[10] The Arrhenius behavior of D_e for these MLs suggests that the *in situ* low-angle XRD is the most sensitive method available to probe the interdiffusion in MLs with shorter L.

(b) The obtained values of D_e for the MLs are quite low (10^{-23}–10^{-25} m^2/s) compared with extrapolation of the published high temperature diffusion data in bulk alloys,

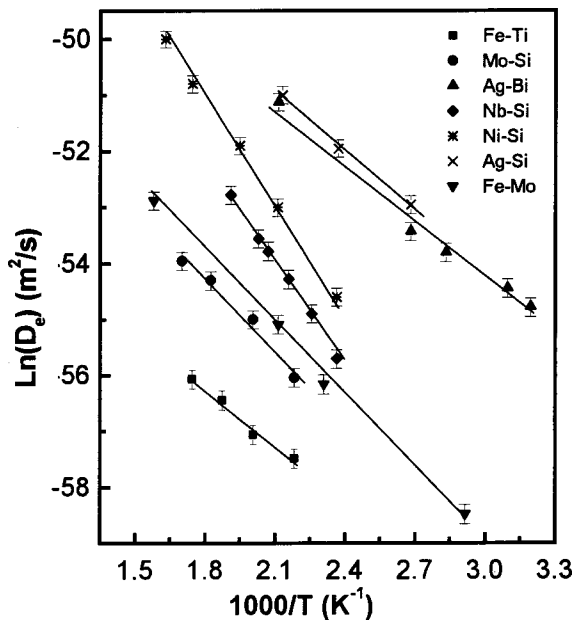FIG. 3. Arrhennius plots of the interdiffusivity D_e of the various MLs.

TABLE II. Bulk interdiffusivities D_v and interdiffusion parameters D_0 and H_e of the MLs.

System	D_v(458 K) (m^2/s)	H_e (eV)	D_0 (m^2/s)
Ag–Bi	2.0×10^{-23}	0.21	4.30×10^{-21}
Fe–Ti	1.75×10^{-24}	0.29	1.50×10^{-22}
Fe–Mo	4.1×10^{-25}	0.33	2.13×10^{-21}
Mo–Si	5.2×10^{-25}	0.37	6.20×10^{-21}
Ni–Si	4.12×10^{-24}	0.69	2.13×10^{-17}
Ag–Si	8.22×10^{-24}	0.24	2.02×10^{-20}
Nb–Si	2.68×10^{-24}	0.55	2.20×10^{-18}

metals,[11] and crystalline silicon (c-Si).[12] However, they are similar to those reported in many other MLs[8,9] and amorphous alloys (a-alloy).[13,14] The reduction of the interdiffusivity was attributed to the defects in the MLs, which act as trapping centers which trap the diffusion atoms temporarily and make the atoms undergo a trap-retarded diffusion, and then reduce the interdiffusivity by[15]

$$D_e = D_f/[1 + C_t \exp(H_t/kT)], \qquad (2)$$

where D_f is the diffusivity in a hypothetical trapping-free MLs. C_t and H_t are the atomic fraction of traps and the binding enthalpy, respectively. The small D_e in MLs may result from the atoms having to pass through large number of the trapping centers in MLs.

(c) The obtained D_0 (10^{-17}–10^{-22} m^2/s order) is much smaller than the typical values of those in crystalline materials (10^{-5}–10^{-7} m^2/s order). The differences are found to be more than ten orders of magnitude. This feature is similar to that of liquid metals and a-alloys which is normally much smaller than that of corresponding crystalline materials.[2]

(d) The values of activation energy in the MLs are less than 1.0 eV and similar to that of the interstitial diffusions and/or interstitial-like diffusions in other solids, e.g., transition metals diffusion in α-Zr,[16] c-Si,[12] a-Si, and a-alloys.[13,14] Strains in the MLs may result in the small value of the H_e. Strain frequently exists in the MLs with high-density interface because of the thermal expansion mismatch with the substrate and coherency strains between the sublayers. Even if the strains can be relaxed by annealing, they were found to remain, at least partially, throughout the whole interdiffusion.[8] The strains may cause easier passage of the interstitial diffusers through another sublayer and reduce H_e.

(e) The interdiffusion parameters D_0 and H_e for the MLs and Zr-based a-alloys[11] correlated as shown in Fig. 4. In spite of the relative large scatter, the diffusion parameters are obviously correlated according to the relation

$$\ln D_0 = \ln A + H_e/B, \qquad (3)$$

where A and B are 9.85×10^{-21} m^2/s and 0.053 eV, respectively. A similar correlation has also been observed for diffusion parameters of crystalline α-Zr,[16] α-Ti,[17] and c-Si[12] with A and B as 1.6×10^{-7} m^2/s and 0.37 eV, respectively. Diffusivities, if they are based on a common diffusion mechanism, are expected to satisfy Eq. (2) with the same specific parameters A and B.[18] The parameters A and B are almost the same within experimental error to those reported
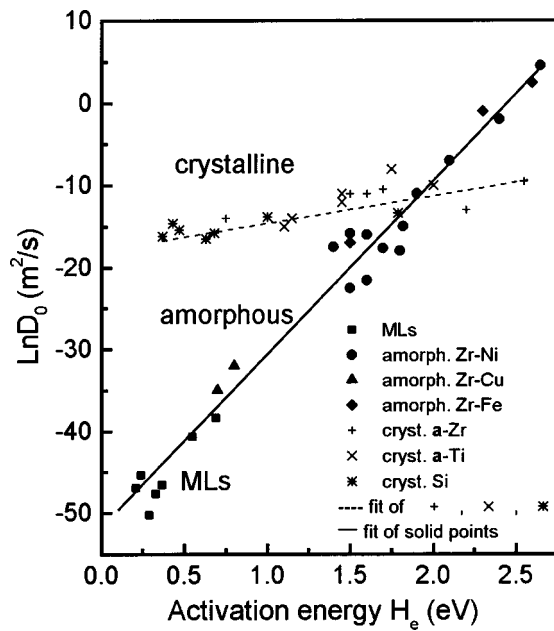
FIG. 4. Plot of $\ln D_0$ and H_e for the MLs, Zr-based amorphous alloys (see Ref. 14), and crystalline α-Zr (see Ref. 16), α-Ti (see Ref. 17), and Si (see Ref. 12).

for other a-alloys.[18,19] The value of A and B in crystalline α-Zr, α-Ti, and Si are quite different from the values of a-alloys and MLs, which means that completely different diffusion mechanisms dominate. The observed relation between a-alloys and MLs indicates that a similar diffusion mechanism is operating in MLs and a-alloys.

From Fig. 3, one can see that the values of D_0 in the MLs are several orders of magnitude smaller than in the a-alloys, even though they correlate according to Eq. (3). This characteristic is generally believed to result from the pre-existing nonequilibrium defects in the MLs.[2,8] D_0 is related to defect concentration by $D_0 = D_0^f / C_t \alpha$,[15] where D_0^f is the pre-exponential factor in a hypothetical defect-free ML, α the parameter related to the binding entropy, the attempt frequency for a diffuser atom, and the number of defect sites available around a defect. The difference of concentration of the defects, C_t, between crystal Si (0.1 ppm%) and amorphous Si ($<1\%$)[15] formed by deposition was found to be less than the order of 10^7. So, the difference of C_t between a hypothetical defect-free ML and the studied ML should be roughly in the same order of 10^7. Therefore, the significant difference in D_0 cannot be totally attributed to the fraction of the defect in MLs, it supports peculiar diffusion mechanism in the MLs. It is known that D_0 can be written as

$$D_0 = a^2 c f \nu_0 \exp\left(\frac{\Delta S}{k}\right), \tag{4}$$

where a is the mean jump distance, c the geometric factor, f the correlation factor, ν_0 the jump attempt frequency, and ΔS the change in the activation entropy during the jump process. D_0 is determined by the five terms. The significant D_0 differences more than ten orders of magnitude between crystalline solids and MLs must result from the large changes in these terms. Since the local microstructures of the

crystalline solids and MLs are similar, c and a could not significantly differ between them. For any reasonable diffusion mechanism and structure, f would vary between 5 and 10 at most. The small changes of the three terms cannot account for the extremely large D_0 differences between crystalline solids and MLs. ν_0, usually taken to be the order of the Debye frequency in crystal, is 10^{13}/s. In a-alloy, ν_0 was observed to be in the order of 10^9/s.[20] The values of ν_0 for the MLs should be roughly the same order of magnitude as those of the a-alloys, which is only about 10^4/s in magnitude. Thus, the large D_0 differences would be attributed to the entropy term $\exp(\Delta S/k)$, e.g., ΔS have to be large and negative. For diffusion in crystalline solids, ΔS is of $(3-5)k$ which corresponds to the single atom diffuse with interstitialcy or monovacancy mechanism. In the MLs, ΔS is estimated to be $-(8-15)k$. The large and negative value of ΔS indicates that the basic diffusion step in the MLs is not a single atom jumping into a vacancy or replacing an interstitial site in the case of diffusion in crystalline solids, but the collective motion of a group of atoms. The entropy of $-(8-15)k$ roughly corresponds to a 8–15 atoms cluster. The cluster may move in a complicated way through the nonequilibrium extended defects in the MLs. The extended defect in MLs involves a large number of neighboring atoms, rather than an interstitial site or mono-vacancy which has been shown to govern the diffusion in crystalline materials. This suggestion is also consistent with the smaller H_e and the marked correlation between the D_0 and H_e found for interdiffusion in these MLs. The extremely small values of D_0 and H_e, displaying an good $D_0 - H_e$ correlation according to Eq. (3), are generally taken as evidence for a collective atomic mechanism.[18] The jumps of clusters of atoms have been observed in the molecular dynamics studied of model glasses and a binary soft sphere mixture near the glass transition. During these jumps, groups of atoms are found to move in a caterpillar-like motion between two nearby equilibrium positions corresponding to a small activation energy.[21] Highly collective diffusion has also been suggested in a-alloys;[22] there are several reasons to support the proposal for a-alloys. The MLs with a high density of interface and large number of nonequilibrium defects are in the metastable state, its local microstructure is close to that of a-alloys. The interdiffusion is known to be governed largely by the local microstructure and defects in solid. Therefore, the similarity in diffusion behavior and mechanism between the MLs and a-alloys is reasonable.

IV. CONCLUSIONS

Interdiffusion in the MLs was studied by an *in situ* low-angle XRD method taking advantage of the compositionally modulated structure of the MLs. The obtained interdiffusivities can be described well by Arrhenius relations. The diffusion characteristics of the MLs are analogous to those in the amorphous alloys. The extremely small values of the diffusion prefactor D_0 and the marked correlation between the D_0 and the activation enthalpy H_e for interdiffusion in the MLs indicate that a collective atomic diffusion mechanism governs the interdiffusion. The atomic jump is a highly coopera-

tive process involving about 8–15 atoms. These atoms collectively move in liquid-like fashion in the MLs.

ACKNOWLEDGMENTS

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