Interdiffusion in Mo/Ge and Mo/Si Multilayer Thin Films

Interdiffusion in Mo/Ge and Mo/Si Multilayer Thin Films*

Hideo Nakajima and Hiroyasu Fujimori
Institute for Materials Research
(Received November 1, 1989)

Synopsis

Multilayered Mo/Ge and Mo/Si thin films have been prepared by dual rf-sputtering technique, and the interdiffusion and structural change on annealing have been investigated by X-ray diffraction measurements. X-ray diffractometry shows that for the modulation wavelength λ shorter than 5 nm both Mo and Ge(Si) sublayers are amorphous, while for λ longer than 5 nm crystalline bcc structure appears in Mo sublayers. The interdiffusivities have been determined from the decay rate of satellite peak intensity around (000). The temperature dependence of the effective interdiffusivities in Mo/Ge and Mo/Si multilayer films is, respectively, expressed as

$$\tilde{D}_{\lambda(\mathrm{Mo/Ge})} = 1.3\times10^{-16}\exp[-(115\pm7)\mathrm{kJmol^{-1}/RT}]\ \mathrm{m^2s^{-1}}, \text{ and}$$
$$\tilde{D}_{\lambda(\mathrm{Mo/Si})} = 2.0\times10^{-16}\exp[-(105\pm5)\mathrm{kJmol^{-1}/RT}]\ \mathrm{m^2s^{-1}}.$$

On initial annealing, the satellite peak intensity decreases drastically and the modulation wavelength also decreases, which are interpreted to be due to structural relaxation and interdiffusion. The thermodynamic behaviour of the amorphous Mo-Ge system is discussed on the basis of the dependence of the effective interdiffusivity on λ.

I. Introduction

Properties of artificially multilayered superlattices have been studied extensively because of uniqueness they exhibit. The idea of growing chemically modulated films dates back to the work of DuMond and Youtz[1]. It was, then, followed by the early diffusion studies of Hilliard and his co-workers for metallic multilayer films[2]. Among the properties that have been the focus of attention are the electronic, magnetic, superconducting, interdiffusion and mechanical

---

* The 1846th report of Institute for Materials Research.

properties[3]. Recent impetus has been given by the development of preparation technique with precise control over layer thickness.

The remarkable features of the multilayer films are ascribed to the atomistic and electronic structures of the interfaces as well as the two-dimensional property. Therefore, the knowledge of interdiffusion and interfacial reaction is important for the understanding of various properties of the multilayer films. X-ray diffraction method is one of the most sensitive techniques for diffusivity measurements on the multilayered or compositionally modulated films with a repeat length of a few nanometers. This technique has been developed by Cook and Hilliard[2], and interdiffusivities as low as 10^{-27} m^2s^{-1} can be measured. The method, originally developed for crystalline materials, has been also applied to measure diffusivities in amorphous metals. Previous measurements have been carried out for the crystalline metallic multilayers of Au/Cu[1][4], Pb/Mg[5], Au/Mg[6], Au/Ag[2], Cu/Pd[7], Nb/Ta[8], Cu/Ni[9], Ag/Pd[10], Nb/Zr[11] and Cu/NiFe[12], and for amorphous multilayers of PdSi/FeB[13], PdAuSi/Fe[13], PdSi/FeB[14], FeC/Si[15], $Fe_{60}B_{40}/Fe_{80}B_{20}$[16], Si/Ge[17], Mo/Si[18]-[20],and Mo/Ge[21]. The present authors and co-workers have performed a series of investigations of interdiffusion[19]-[21] and superconducting properties of Mo-base multilayer films[20][22][23]. The superconductivity of Mo/Si multilayers results from amorphous MoSi phase formed by interdiffusion in the interfacial region of the sublayers. The aim of the present paper is to review and summarize the interdiffusion and structural change of sputter-deposited Mo/Ge and Mo/Si multilayer films caused by annealing and discuss the thermodynamic behaviour of Mo-Ge amorphous alloys in relation to the interdiffusion. Furthermore, we add a new result of the cross-sectional transmission electron microscope image of an as-deposited Mo/Si multilayer film.

II. Experimental Procedure

Mo/Ge and Mo/Si multilayer films were prepared by rf-sputtering. The Mo and Ge(or Si) sublayers were alternately deposited onto fused quartz substrates placed on a rotating table cooled by blowing air. Targets of Mo, Ge and Si were 99.9%, 99.999% and 99.999%, respectively. The details of the apparatus were described elsewhere[19][24][25].

The sample chamber was evacuated to a pressure lower than 10^{-5} Pa before deposition. The surface of each substrate was cleaned by sputter-etching. The sputtering was made in an argon atmosphere of

2.7 Pa; the sputtering rates of Mo, Ge and Si were adjusted between 0.098 and 1.17 nms^{-1}. The modulation wavelength λ is the sum of the thickness of individual sublayers; $\lambda = d_{Mo} + d_{Ge(Si)}$. In the present interdiffusion experiments the modulation wavelength was designed to range from 0.3 to 27.9 nm with the equal thickness of the sublayers. The overlayer is Mo of the thickness d_{Mo}. The total thickness of the multilayer films was approximately 500 nm.

For diffusion anneal, the specimen mounted on a sample holder was placed in a vacuum furnace evacuated to $(3\text{-}5)\times10^{-6}$ Pa by a Turbomolecular pump system. The temperature was measured with a thermocouple of Pt/Pt-13%Rh attached to the sample holder. The anneals were carried out at specified temperatures controlled within ±0.6 K. Correction for the diffusion-annealing time was made by taking into account the heat-up and cool-down times.

X-ray diffraction measurements were performed by a computer-controlled Rigaku RAD-RC X-ray diffractometer using $CuK\alpha$ radiation. The monochromatic diffraction intensities were obtained by using a singly-bent graphite counter-monochrometer. The diffracted intensities were step-scanned at an interval of $2\theta = 0.002°$. The thickness of the sputter-deposited films was measured by a depth profilometer, Surfcom of Tokyo Seimitsu Keiki, Ltd. Cross-sectional transmission electron microscopic observation was carried out for Mo/Si multilayer thin films on a JEOL TEM-200B microscope.

III. Results and Discussion

1. Structure of as-deposited multilayer films

A low angle part of an X-ray diffraction pattern from the as-deposited Mo/Ge multilayer film with $\lambda = 4.08$ nm is shown in Fig.1. The appearance of the several satellite peaks around the (000) reflection indicates the formation of the multilayer structure with the modulation wave vector perpendicular to the film plane. Higher order reflections up to the fourth-order are observed for this sample. The number of higher order reflections increases with increase of the wavelength λ ; for example, for $\lambda = 27.9$ nm, the satellites up to the 9-th order are observable. The satellite peak width becomes broader for the higher order reflections. The observed peak broadening indicates the fluctuation in modulation wavelength so that the individual Mo and/or Ge layer thicknesses are not perfectly constant throughout the film. Such a fluctuation of the modulation wavelength is attributed to an experimental uncertainty in the layer thickness control during sputter-deposition and also the roughness of

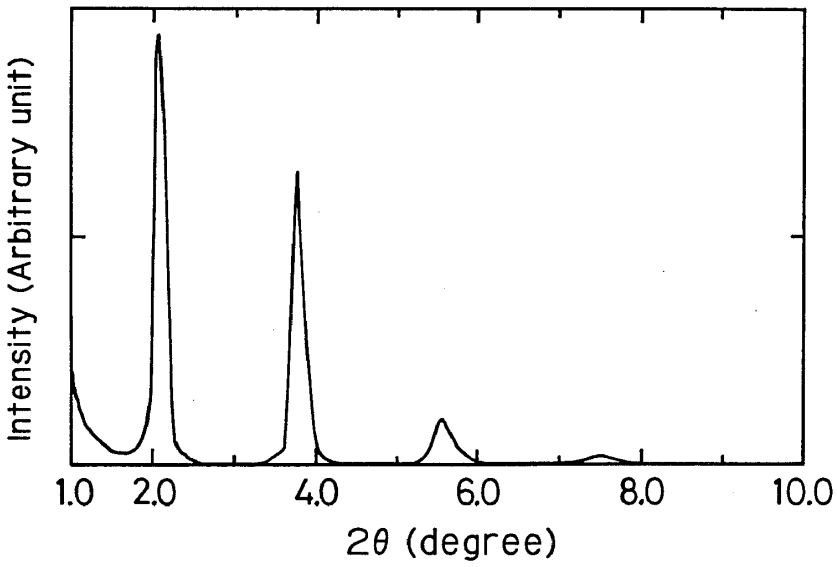

Fig.1 Low angle part of X-ray diffraction pattern from as-deposited Mo/Ge multilayer film with the modulation wavelength, 4.08 nm.

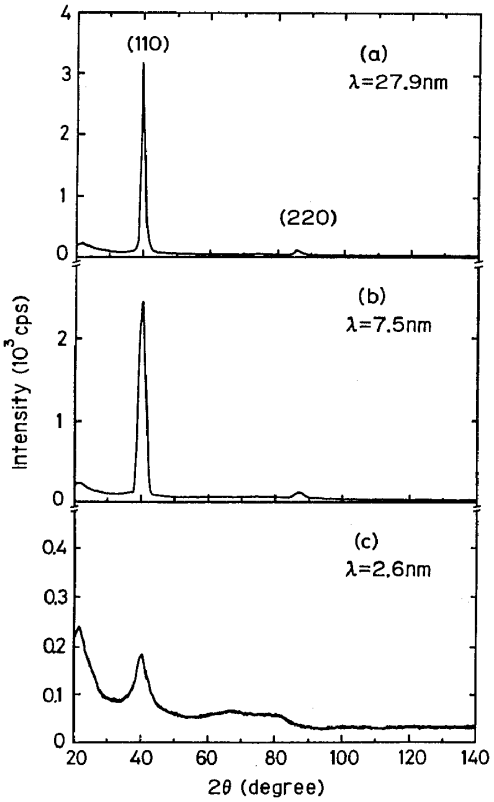

Fig.2 High angle part of X-ray diffraction patterns from as-deposited Mo/Ge multilayer films: (a) λ = 27.9 nm, (b) λ =7.5 nm, (c) λ =2.6 nm.

interfaces[26]. The modulation wavelength λ was determined from the location of the satellites using the following modified Bragg equation,

$$\lambda = \frac{\lambda_x}{2}\sqrt{\frac{(n+1)^2 - n^2}{\sin^2\theta_{n+1} - \sin^2\theta_n}} \qquad (1)$$

where n is the order of satellite, θ_n is the scattering angle of the n-th order satellite peak and λ_x is the X-ray wavelength.

The textile structure was determined by use of a high angle $\theta - 2\theta$ X-ray diffractometer. Figure 2 shows high angle diffraction patterns from as-deposited Mo/Ge multilayer films with three different modulation wavelengths. The high angle diffraction patterns from the multilayer films for λ longer than about 5 nm indicate a texture with the bcc(110) planes parallel to the film plane for the Mo sublayers, while the Ge sublayers are considered to be amorphous because of the absence of the corresponding Bragg peaks. For λ shorter than about 5 nm, both Mo and Ge sublayers are amorphous. Figure 3 shows the FWHM (full-width at half-maximum) of the X-ray peak corresponding to bcc Mo(110) as a function of the modulation wavelength in the multilayers. (For λ shorter than 3.4 nm, the FWHM of the broad peak which may correspond to halo-patterns in an electron diffraction is plotted instead of the Bragg peak.) The value of FWHM is large for the multilayers with λ <5 nm, while for λ >5 nm the value decreases with increasing λ. As shown in the same figure, the size of Mo crystallites,t, is evaluated from the FWHM data of the Bragg peak using the following Scherrer formula[27]

$$t = 0.9\,\lambda_x/(B\cos\theta) \qquad (2)$$

where θ is the scattering angle and B is the FWHM for the (110) peak in radians. The size increases with increasing λ. The variation in FWHM is mainly attributed to the size of the Mo crystallites, and however, other possibilities such as the finite sublayer thickness and/or crystallinity (degree of crystallization) are also conceivable. The λ dependence of FWHM of Mo/Ge multilayer films is very similar to that of Mo/Si multilayer films[23] shown in the same figure.

The cross-sectional transmission electron micrograph of the as-deposited Mo/Si multilayer thin film is shown in Fig.4. The bright-field micrograph shows that the molybdenum layers (dark colored layers) are polycrystalline and in a form of columnar grains. The light silicon layers have a amorphous appearance. Between the amorphous-Si and the polycrystalline Mo there is an area of gray

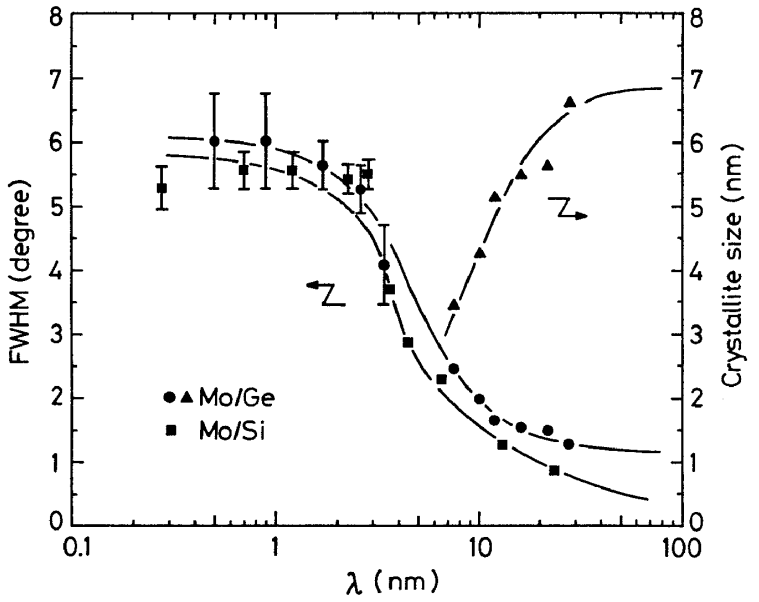

Fig.3 FWHM of X-ray peak corresponding to bcc Mo(110) and size of Mo crystallites as a function of the modulation wavelength.

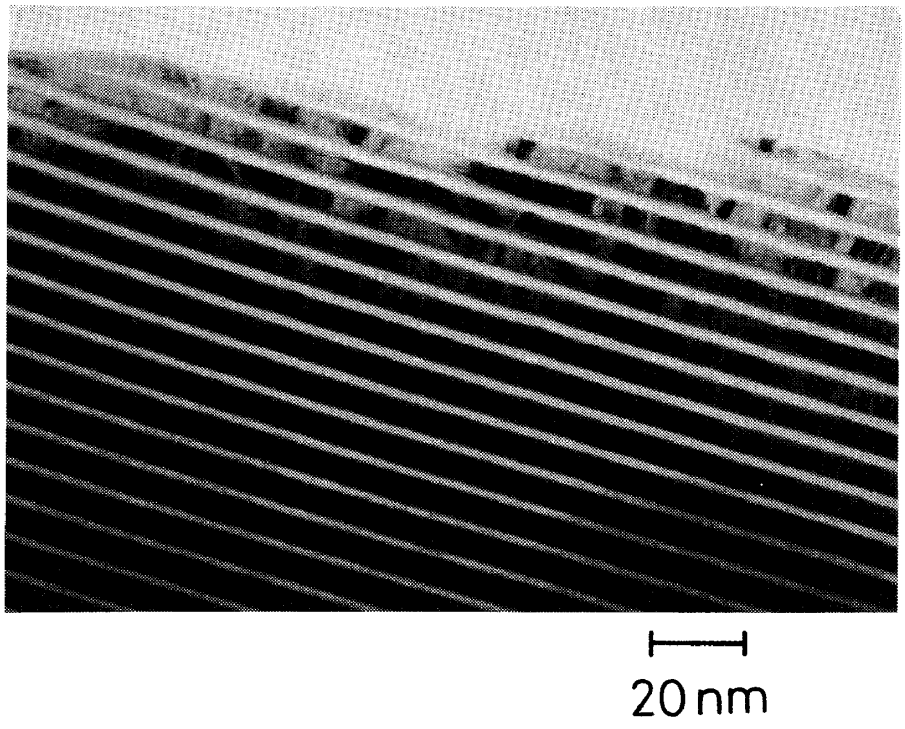

Fig.4 Bright-field cross-sectional transmission electron micrograph of as-deposited Mo/Si multilayer thin film.

contrast which looks like an amorphous-alloy intermixed region. The existence of such amorphous-alloy region was confirmed by the previous study on the superconductivity[20][23]. For the modulation wavelength 8.9 nm, the thickness of each layer is evaluated from the micrograph: 2.7 nm for amorphous Si layer, 0.9 nm for the intermixed region and 4.4 nm for cyrstalline Mo layer. Further TEM investigation will be described elsewhere[28].

2. Structure of annealed films

Figure 5 shows high angle diffraction patterns from annealed Mo/Ge multilayer films at two different temperatures. Since the satellite peaks disappear in the low angle diffraction pattern after the anneals, any compositional modulation is considered to be lost due to interdiffusion and/or reactive-diffusion to form uniform monolayer films. After annealing at temperatures of 873 and 1073 K several different peaks appear in the higher angle region, which are identified as those coming from the mixture of intermetallic compounds $Mo_{13}Ge_{23}$ and Mo_3Ge; no obvious Mo(110) peaks are observed. After annealing at 1273 K, the observed Bragg peaks are identified as those from a compound Mo_3Ge with A15-type structure. Table 1 summarizes the result on the structures of the as-deposited and annealed Mo/Ge multilayer films. As for 773 K anneal, the crystalline phases $Mo_{13}Ge_{23}$ and Mo_3Ge are observed, which are formed due to interdiffusion. However, several satellite peaks in the low-angle diffraction pattern are still clearly visible so that composition modulation is considered to be maintained to some degree; the compositionally modulated films involve the intermetallic compound layers.

3. Change in modulation amplitude and wavelength on initial annealing

The variation of the first-order satellite peak intensity on isothermal annealing was investigated at various temperatures. Figure 6 shows low angle part of X-ray diffraction patterns from the as-deposited Mo/Ge multilayer films and the film annealed at 689 K for different periods. The intensity of the satellite peaks decreases on a series of annealing. Figure 7 shows the decay of the first-order satellite peak intensity as a function of the diffusion-annealing time. The decay of the intensity shows decrease of the compositional modulation amplitude. After initial annealings, the intensity decreases drastically to 15-40% of the original intensity I(0) for amorphous multilayer films, while it decreases only to 80% for the intermetallic compound multilayer films (773K diffusion).

Table 1 Structure of Mo/Ge multilayer films

Temperature (K)	Annealing time (s)	Modulation wavelength (nm)†	Structure
as-deposited		<5	amorphous Mo/Ge multilayer film
		>5	Mo(110)/amorphous Ge multilayer film
773	3.4×10^3	3.98	$Mo_{13}Ge_{23}/Mo_3Ge$ multilayer film
873	3.6×10^3	3.71	monolayer film with mixture of $Mo_{13}Ge_{23}$ and Mo_3Ge
1073	3.6×10^3	3.71	
1273	3.3×10^3	3.71	Mo_3Ge monolayer film

† Modulation wavelength for multilayer films before anneals.

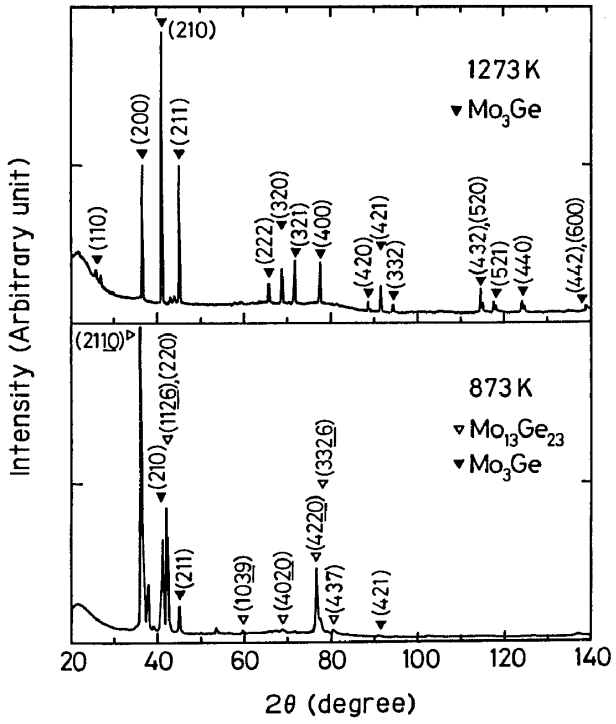

Fig.5 High angle X-ray diffraction patterns from Mo/Ge multilayer films annealed at two different temperatures: 1273K and 873K.

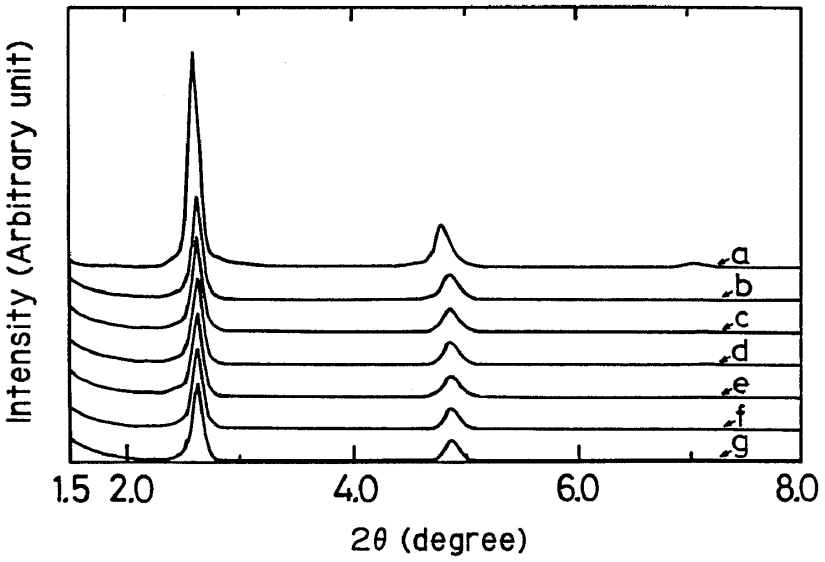

Fig.6 Low angle X-ray diffraction patterns from as-deposited Mo/Ge multilayer film and the film annealed at 689K for different periods: (a) as-deposited, (b)1.76×10^{3}s, (c)4.63×10^{3}s, (d)1.18×10^{4}s, (e)3.31×10^{4}s, (f)6.87×10^{4}s and (g)1.01×10^{5}s.

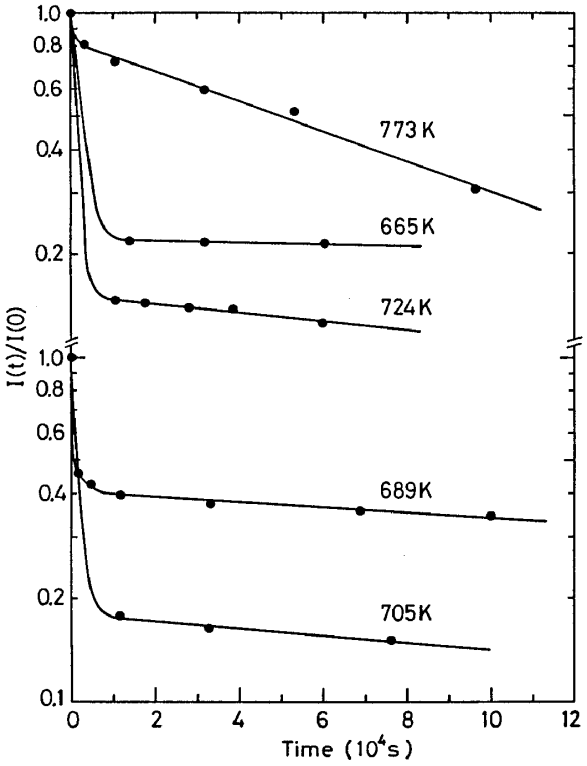

Fig.7 Decay of the first-order satellite peak intensity as a function of the annealing time for Mo/Ge multilayer films with the modulation wavelength 3.4-4.2 nm.

Furthermore, the satellite peak shifts are found in the multilayer films on annealing. The peak shift to higher angle indicates the decrease in the modulation wavelength of the multilayer films. Such the peak shift is interpreted as an evidence for densification of the multilayer films, which is given by[29]

$$d\theta/\tan\theta = -dV/V \qquad (3)$$

where V is the average atomic volume. The estimated volume change due to anneals are compiled in Table 2 of Ref.(21). The volume decreases by about 1-2% for Mo/Ge and by 8-12% for Mo/Si multilayer films. Such densification may be attributed to

(a) structural relaxation of the amorphous sublayers
(b) interdiffusion through the interfacial regions so as to improve the lattice mismatching, and/or
(c) formation of nanocrystalline intermetallic compounds.

These three possibilities are briefly discussed as described below.

(a) Structural relaxation of amorphous ribbons or thin films is known to occur during annealing. The relaxation is accompanied with volume change; the volume usually decreases by an amount less than 1%[30]. If such structural relaxation takes place in each sublayer of amorphous Mo and Ge (Si), the volume decrease may be observed in the annealed multilayer films.

(b) In the interfacial regions between Mo and Ge (Si) sublayers, packing is relatively loose, because the atomic sizes of the constituents are different. After annealing, interdiffusion takes place so that the porous interfacial regions change to densely packed Mo-Ge (Mo-Si) alloy structure so as to improve the lattice mismatching.

(c) If some intermetallic compounds are formed in the multilayer films, volume reduction should be observed. Actually $Mo_{13}Ge_{23}$(773-1073 K) and Mo_3Ge(773-1273 K) phases are observed by X-ray diffraction after anneals. It seems also possible that not only structural relaxation and/or simple alloying of MoGe (MoSi) but formation of such compounds occurs even at lower temperature annealing, although the diffraction pattern from the compounds could not be observed probably because of too thin layers. This possibility may be related to a recent study by Clevenger et al[31]. They observed explosive silicidation in Ni/amorphous-Si and V/amorphous-Si multilayer films due to annealing. Volume change with shrinkage results from the silicidation. Detailed investigations of the structural change due to annealing are required for a better understanding of Mo-base multilayer films.

The difference in volume change between Mo/Ge and Mo/Si may be attributed to difference in lattice mismatching; the atomic-size ratios of Ge and Si to Mo is 0.985 and 0.949, respectively. The effect of the lattice mismatching should be by far more pronounced in Mo/Si multilayer films.

4. Interdiffusion

Interdiffusion can be determined from the rate of homogenization of compositionally modulated multilayer films. The amplitude of the composition modulation can be described with the linearized diffusion equation derived by Cahn[32]. In X-ray diffraction pattern, a composition modulation gives rise to satellites around the (000) reflection. The intensity of the first-order satellite is proportional to the square of the amplitude of the first Fourier component of the modulation. The effective interdiffusivity $\tilde{D}_\lambda$ is given by the relative decrease in the first-order satellite intensity I(t):

$$\tilde{D}_\lambda = -\frac{\lambda^2}{8\pi^2}\frac{d}{dt}\ln\{I(t)/I(0)\} \qquad (4)$$

where I(0) is the initial intensity, and t is the annealing time. As shown in Fig.7, after a rapid initial drop, $\ln\{I(t)/I(0)\}$ falls linearly with the annealing time. By assuming that the linear decay at a later stage in Fig.7 represents the interdiffusion process in the isoconfigurational condition, the effective interdiffusivity is calculated using eq.(4). Temperature dependence of the effective interdiffusivities in Mo/Ge and Mo/Si multilayer films is shown in Fig.8. The temperature dependence of the effective interdiffusivities is expressed as follows:

For amorphous Mo/amorphous Ge multilayer films with λ =3.4-4.2 nm,

$$\tilde{D}_{\lambda(Mo/Ge)} = 1.3\times10^{-16}\ \exp[-(115\pm7)kJmol^{-1}/RT]\ m^2s^{-1}.$$

For crystalline Mo/amorphous Si multilayer films with λ =3.8-7.6 nm,

$$\tilde{D}_{\lambda(Mo/Si)} = 2.0\times10^{-16}\ \exp[-(105\pm5)kJmol^{-1}/RT]\ m^2s^{-1}.$$

The effective interdiffusivities of Mo/Ge multilayer films are about one order of magnitude smaller than those of Mo/Si multilayer films. The pre-exponential factor is smaller by a factor of 2, while the activation energy is in good agreement with that for Mo/Si multilayer films.

The effective interdiffusivities for shorter modulation wavelength, 1.66 nm, are smaller than those for λ = 3.4-4.2 nm as shown in Fig.9. Such a trend can be explained on the basis of the

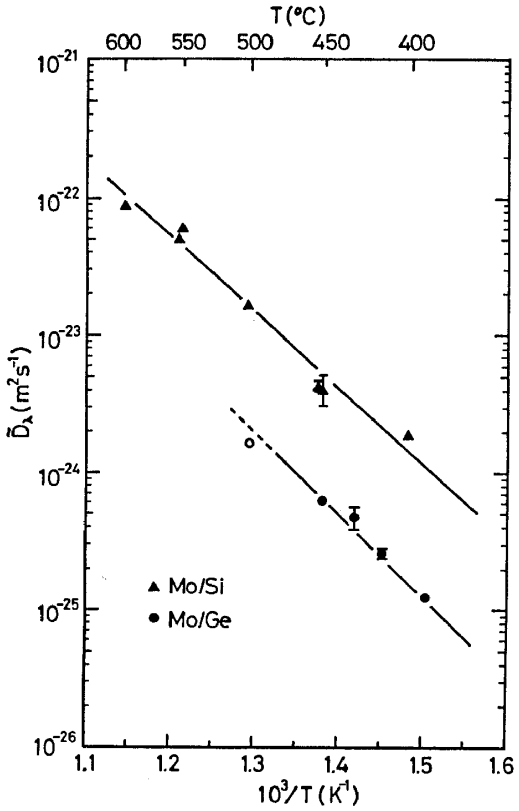

Fig.8 Temperature dependence of the effective interdiffusivities in Mo/Ge and Mo/Si multilayer films.

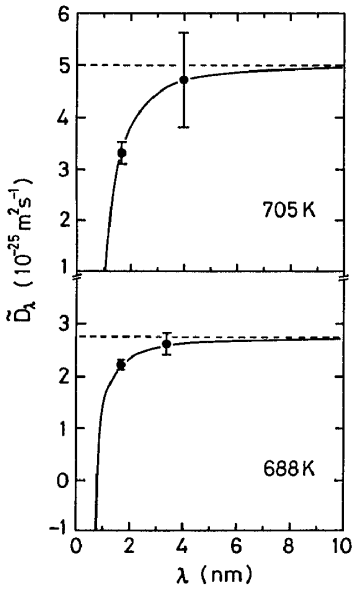

Fig.9 Measured effective interdiffusivities at 705K and 688K as a function of the modulation wavelength. Mo/Ge multilayer film

theories developed by Cahn and Hilliard[33], Hillert[34], and Cook, de Fontaine and Hilliard[35]. According to their theories of compositionally inhomogeneous systems, a correction must be applied to Fick's laws for chemical diffusion if the penetration distances are small. This correction comes from the effect of steep composition gradients on the thermodynamic driving force. From the theory[32] the following linearized diffusion equation is given by

$$\frac{\partial C}{\partial t} = \tilde{D}\frac{\partial^2 C}{\partial x^2} - \frac{2\tilde{D}}{f_o''} K\frac{\partial^4 C}{\partial x^4} \qquad (5)$$

where $\tilde{D}$ is the bulk($\lambda \rightarrow \infty$) interdiffusivity, c is the atomic fraction of a component in a position x at time t, f_o'' is the second derivative, with respect to composition, of the Helmholtz free energy of a homogeneous phase per unit volume and K is the so-called gradient energy coefficient. The second term of eq.(5) cannot be neglected when the variation of composition on distance contains Fourier components with wavelengths less than about 10 nm. For composition modulations of small amplitude, it is reasonable to assume that $\tilde{D}$, f_o'' and K are independent of composition. Under these conditions a particular solution to eq.(5) is

$$C = \exp(-\tilde{D}_\lambda \beta^2 t)\cos\beta x \qquad (6)$$

where $\beta = 2\pi/\lambda$ is the wave number of the composition wave, and the effective interdiffusivity is given by

$$\tilde{D}_\lambda = \tilde{D}\,[\,1 + 2K\beta^2/f_o''\,]. \qquad (7)$$

The quantities, f_o'' and K, can be evaluated for a regular solution model[33]:

$$\left.\begin{aligned} f_o'' &= 4[\,RT - 2\Delta H_m\,]/v \\ K &= 2\Delta H_m r^2/3v, \end{aligned}\right\} \qquad (8)$$

where ΔH_m is the energy of mixing per mole of equiatomic solution, v is the molar volume and r is the nearest neighbour distance. Depending on the sign of f_o'' and K, various dependence of $\tilde{D}_\lambda$ on λ can be conceived[3][32]-[36], as shown schematically in Fig.10.

(a) In the case where K>0 and $f_o''<0$, the homogeneous system is unstable to arbitrarily small composition fluctuations; i.e. spinodal decomposition can occur.

(b) The conditions that K>0 and $f_o''>0$ describe a metastable phase separating system outside the spinodal. The chemical spinodal is

defined by the locus of temperatures on the phase diagram at which $f_o''=0$. Inside the spinodal f_o'' is negative ((a) case), while outside it is positive ((b) case).

(c) The conditions that $K<0$ and $f_o''>0$ describe an ordering system.

(In the regular solution model, K and f_o'' cannot be negative simultaneously.)

Thus, the thermodynamic behaviour of the homogeneous system can be understood from measurements of the dependence of $\tilde{D}_\lambda$ on λ in multilayer films. Since thermodynamic information on amorphous alloys is scarce and difficult to determine by conventional means at high undercooling, the modulated thin film technique is expected to be very useful for characterization of the thermodynamic behaviour of amorphous alloys.

The experimental result shown in Fig.9 has the same tendency as the case (c) where amorphous Mo-Ge behaves as an ordering system. In such a system, the enthalpy of mixing is expected to be negative. No data on ΔH_m in amorphous Mo-Ge alloy are available, but in crystalline Mo-Ge alloy the data exist. ΔH_m is given by Niessen, deBoer, Boom, deChatel, Mattens and Miedema[37], which is negative value as large as - 1 $kJmol^{-1}$. It is, therefore, suggested that Mo-Ge in the crystalline state is the ordering system. This is also speculated from two points;(1) the solid solubilities of both constituents are very low, and (2) there are several stable intermetallic compounds in the binary phase diagram. It seems reasonable that both amorphous and crystalline Mo-Ge similarly belong to the ordering system.

For given sets of $\tilde{D}_\lambda$ and λ, one can calculate theoretical curves from eq.(7) which are shown in Fig.9. The value of $\tilde{D}_\lambda$ converges to that of $\tilde{D}$ with increasing λ. In the limit of $\lambda \to \infty$, the bulk interdiffusivity $\tilde{D}$ is determined as follows:

at 705 K $\quad \tilde{D} = 5.0\times10^{-25}\ m^2s^{-1}$

at 688 K $\quad \tilde{D} = 2.7\times10^{-25}\ m^2s^{-1}$.

Temperature dependence of the effective interdiffusivities in Mo/Ge and Mo/Si multilayer films is shown in Fig.11 together with that of self-diffusivities in crystalline bulk Mo[38], Ge[39] and Si[40]. The interdiffusivities in those multilayer films are much larger than that extrapolated from higher temperatures for the self-diffusivities in Mo, Ge and Si. In general, the pre-exponential factor D_o in the amorphous materials is much smaller than typical values for crystalline materials (10^{-3}-10^{-4} m^2s^{-1} order) and is more

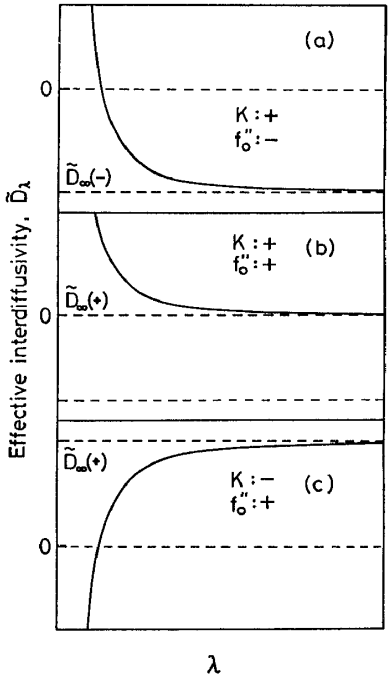

Fig.10 Schematic behaviour of the effective interdiffusivity as a function of the modulation wavelength for three possible thermodynamic conditions.

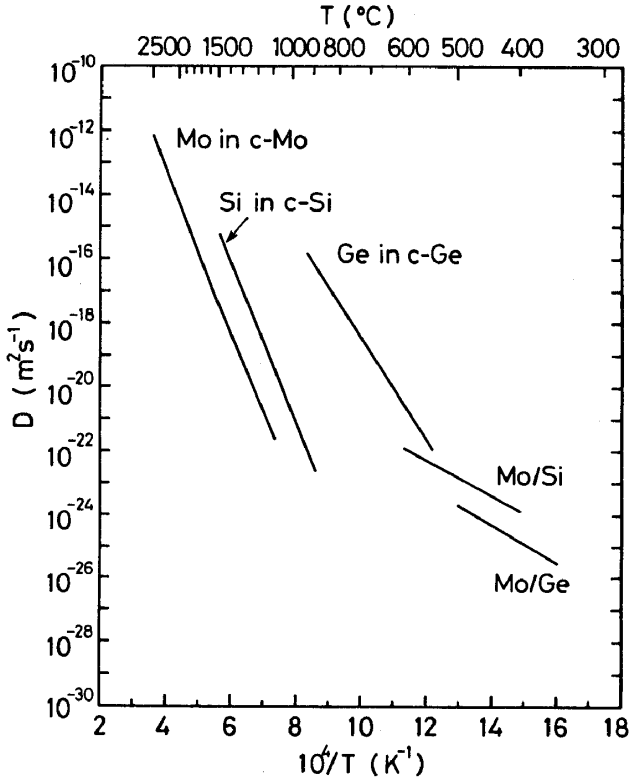

Fig.11 Temperature dependence of self-diffusivities in crystalline Mo, Ge and Si, and effective interdiffusivities in Mo/Ge and Mo/Si multilayer films.

or less characteristic of liquid metal systems[41]. The present value of D_o in the multilayer films is fit to such tendency.

IV. Summary and Conclusions

The salient points of the present investigation of the interdiffusion and structural change on annealing in the sputter-deposited Mo/Ge and Mo/Si multilayer films are summarized as follows.
(1) Both Mo and Ge (Si) sublayers are amorphous for the modulation wavelength λ shorter than 5 nm, while for λ longer than 5 nm crystalline bcc structure appears in Mo sublayers.
(2) The temperature dependence of the effective interdiffusivities in Mo/Ge and Mo/Si multilayer films is, respectively, determined as

$$\tilde{D}_{\lambda(Mo/Ge)} = 1.3\times10^{-16} \exp[-(115\pm7)\ kJmol^{-1}/RT]\ m^2s^{-1}, \text{ and}$$
$$\tilde{D}_{\lambda(Mo/Si)} = 2.0\times10^{-16} \exp[-(105\pm5)\ kJmol^{-1}/RT]\ m^2s^{-1}.$$

The small pre-exponential factor is characteristic of amorphous materials.
(3) The decrease in the satellite peak intensity and the modulation wavelength is interpreted to be due to structural relaxation and interdiffusion.
(4) The result on dependence of the effective interdiffusivities on the modulation wavelength shows that amorphous Mo/Ge alloy is an ordering system.

Acknowledgements

The present work is supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The authors wish to express their appreciation to Prof.T.Masumoto and Mr.K.Saito for use of the X-ray diffractometer. They also would like to express their gratitude to Mr.E.Aoyagi for the TEM analysis.

References

(1) J.DuMond and J.P.Youtz, J.Appl.Phys., 11 (1940),357.
(2) H.E.Cook and J.E.Hilliard, J.Appl.Phys., 40 (1969),2191.
(3) L.L.Chang and B.C.Giessen, Synthetic Modulated Structures, Academic Press, Inc., New York (1985).
(4) W.M.Paulson and J.E.Hilliard, J.Appl.Phys., 48 (1977), 2117.
(5) J.Dinklage and R.Frerichs, J.Appl.Phys.,34 (1963), 2633.
(6) J.B.Dinklage, J.Appl.Phys., 38 (1967), 3781.
(7) E.M.Philofsky and J.E.Hilliard, J.Appl.Phys., 40 (1969),2198.
(8) R.E.Somekh, Z.H.Barber, C.S.Baxter, P.E.Donoven and J.E.

Evetts, J.Mat.Sci.Lett., 3 (1984),217.
(9) T.Tsakalakos and J.E.Hilliard, J.Appl.Phys.,55 (1984), 2885.
(10) G.E.Henein and J.E.Hilliard, J.Appl.Phys., 55 (1984), 2895.
(11) T.Claeson, J.B.Boyce, W.P.Lowe and T.H.Geballe, Phys.Rev., B29 (1984), 4969.
(12) J.Chaudhuri and T.Tsakalakos, Acta Met., 33 (1985),1939.
(13) M.P.Rosenblum, F.Spaepen and D.Turnbull, Appl.Phys.Lett., 37 (1980), 184.
(14) A.L.Greer, C.J.Lin and F.Spaepen, Proc.4th Int.Conf.on Rapidly Quenched Metals, Ed. by T. Masumoto and K. Suzuki, Japan Inst. Metals, Sendai, Japan (1982),p.567.
(15) N.S.Kazama and H.Fujimori, J.Magn.Magn.Mat., 35 (1983), 86.
(16) W.Reill and H.Hoffmann, J.Mat.Sci.Lett., 4 (1985), 359.
(17) S.M.Prokes and F.Spaepen, Appl.Phys.Lett., 47 (1985), 234.
(18) W.G.Sloof, O.B.Loopstra, Th.H.Dekeijser and E.J.Mittemeijer, Scripta Met., 20 (1986), 1683.
(19) H.Nakajima, H.Fujimori and M.Koiwa, J. Appl. Phys., 63 (1988), 1046.
(20) H.Nakajima, M.Ikebe, Y.Muto, S.Yamaguchi and H.Fujimori, MRS International Meeting on Advanced Materials, Vol.10, Ed. by M.Doyama, S.Somiya and R.P.H.Chang, Materials Research Society, Pittsburgh, (1989), p.405.
(21) H.Nakajima, Mat.Trans.,JIM, 30 (1989), 242.
(22) H.Nakajima, H.Fujimori, M.Ikebe and Y.Muto, Jpn.J.Appl.Phys., 26, Supplement 26-3 (1987), 1449.
(23) H.Nakajima, M.Ikebe, Y.Muto and H. Fujimori, J.Appl.Phys.,65 (1989),1637.
(24) N.S.Kazama, H.Fujimori, I.Yuito and H.Kronmuller, Sci. Rep. Tohoku University, (A) 32 (1985), 141.
(25) H.Nakajima, Y.Obi, Y.Fukumoto and H.Fujimori, J.Phys.Soc. Japan, 56 (1987), 295.
(26) N.Nakayama, I.Moritani, T.Shinjo, Y.Fujii and S.Sasaki, J. Phys.F: Met.Phys., 18 (1988), 429.
(27) B.D.Cullity, Elements of X-ray Diffraction, Addison-Wesley Publ. Company, Inc., Reading, (1978), p.102.
(28) H.Nakajima, E.Aoyagi and H.Fujimori, to be published.
(29) E.H.Chason and T.Mizoguchi, Science and Technology of Rapidly Quenched Alloys, Ed. by M.Tenhoever, W.L.Johnson and L.E.Tanner, Materials Research Society, Pittsburgh, (1987), p.61.
(30) A.I.Taub and F.Spaepen, Acta Met., 28 (1980), 1781.
(31) L.A.Clevenger, C.V.Thompson, A.J.Judas and K.N.Tu, MRS

International Meeting on Advanced Materials, Vol.10, Ed.by M.Doyama, S.Somiya and R.P.H.Chang, Materials Research Society, Pittsburgh, (1989), p.431.

(32) J.W.Cahn, Acta Met., 9 (1961), 795.

(33) J.W.Cahn and J.E.Hilliard, J. Chem. Phys., 28 (1958), 258.

(34) M.Hillert, Acta Met., 9 (1961), 525.

(35) H.E.Cook, D.de Fontaine and J.E.Hilliard, Acta Met.,17 (1969), 765.

(36) R.C.Cammarata and A.L.Greer, J.Non-Cryst.Solids, 61&62 (1984), 889.

(37) A.K.Niessen, F.R.de Boer, R.Boom, P.F.de Chatel, W.C.M.Mattens and A.R.Miedema, CALPHAD, 7 (1983), 51.

(38) K.Maier, H.Mehrer and G.Rein, Z.Metallkde., 70 (1979), 271.

(39) G.Vogel, G.Hettich and H.Mehrer, J.Phys.C: Solid State Phys., 16 (1983), 6197.

(40) H.J.Mayer, H.Mehrer and K.Maier, Radiation Effects in Semiconductors 1976 (Inst.Phys.Conf.Ser.,No.31), (1977), p.186.

(41) H.S.Chen, Rep.Prog.Phys., 43 (1980), 353.