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IN SITU STUDIES OF AMORPHIZATION OF THE Ge-Al AND Si-Al SYSTEMS INDUCED BY 1 MeV ELECTRON IRRADIATION*

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October 1990

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*Dr. X. W. Lin received support from the Robert R. McCormick School of Engineering and Applied Science for this research. Additional support was received through the use of the central facilities of Northwestern University's National Science Foundation funded Materials Research Center. Dr. P. R. Okamoto was supported by the U. S. Department of Energy, BES-MS, under contract W-31-109-Eng-38.

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IN SITU STUDIES OF AMORPHIZATION OF THE Ge - Al AND Si - Al SYSTEMS INDUCED BY 1 MeV ELECTRON IRRADIATION

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Abstract

Ge/Al and Si/Al bilayer specimens, as well as Al -2.3 at.% Ge two-phase alloy specimens, were irradiated *in situ* with 1 MeV electrons at temperatures (T's) in the range 10 - 190 K in a high voltage electron microscope. At 10 K it is found that for a Ge/Al bilayer specimen amorphization at the interface occurs only when the Ge layer faces the incident electron beam, while for a Si/Al bilayer specimen amorphization occurs regardless of the direction of the incident beam. In this case, the critical fluence for amorphization (Φ_c) to occur is $\approx 3 \times 10^{23} \text{ cm}^{-2}$ ($\approx 30, 19$ and 18 displacements per atom in Ge, Si and Al respectively). In the case of Al - 2.3 at.% Ge alloy specimens irradiated at 10 and 50 K a crystalline-to-amorphous (c-to-a) transition is observed at $\Phi_c \approx 2.4 \times 10^{23} \text{ cm}^{-2}$ (24 and 14 dpa in Ge and Al respectively). The temperature dependence of Φ_c is also studied for a Ge/Al bilayer specimen. The value of Φ_c is a constant for $T < \approx 160$, and then it increases rapidly with increasing T; Φ_c becomes immeasurably large at a critical temperature of ≈ 190 K. Our results can be understood in terms of an electron-irradiation induced recoil-implantation mechanism.

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1. Introduction

Formation of amorphous phases at the interface region between Si or Ge and pure metals (e.g., Au and Pd) can be observed during a high energy electron beam irradiation (Sumida and Fujita 1985). This phenomenon is of interest because electron irradiation experiments have failed to render elemental crystalline Si or Ge specimens amorphous at temperatures as low as 10 K (Matthews and Ashby 1973, Föll 1974, Seidman, Averbach, Okamoto and Baily 1987), while Si or Ge specimens are readily amorphized when ion-irradiated at room temperature to a fluence of < 1 displacement per atom (dpa) (Vook 1972, Christel, Gibbons and Sigmon 1981). Two phase Al - 0.7 at.% Ge or Al - 0.94 at.% Ge specimens containing plate-shaped Ge precipitates undergo a crystalline-to-amorphous (c-to-a) transition when irradiated with 1 or 2 MeV electrons at 143 or 170 K (Rusbridge 1983, Mori, Nakamura and Fujita 1986). The presence of the interface between the Ge precipitates and the Al matrix plays an essential role in the formation of the amorphous phase. Two mechanisms have been proposed to account for this result. First, the c-to-a transition is attributed to the amorphization of Ge precipitates when the vacancy concentration in Ge exceeds a critical value (Rusbridge 1983). The Ge/Al interface is assumed to act as a biased sink for mobile Ge self-interstitial atoms (SIA's) generated during electron irradiation; this is suggested to lead to a steady-state vacancy concentration significantly greater than the vacancy supersaturation in an electron-irradiated pure Ge specimen. A second set of experiments, however, suggest a different mechanism (Mori, Nakamura and Fujita 1983). In fact, they observed that amorphization occurs initially at the interface farthest from the incident electron beam, when the normal to a plate-shaped Ge precipitate is parallel to the direction of the incident beam. Amorphization should therefore result from atomic mixing at a Ge/Al interface via an irradiation-induced recoil implantation mechanism. Recoiling of Ge atoms into an Al matrix, due to the elastic transfer of energy from the electron beam plays an

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essential role. This mechanism is basically different from the first one.

To understand the mechanism of amorphization process occurring at Ge/Al or Si/Al interfaces during an electron irradiation, we performed *in situ* 1 MeV electron irradiation studies on Ge/Al and Si/Al bilayer specimens at temperatures (T's) in the range 10 - 190 K in the high voltage electron microscope (HVEM) at the Argonne National Laboratory. The specimens were prepared by vapor deposition of an Al layer onto a prethinned Ge or Si disk. For an irradiation at 10 K, it was found that for Ge/Al bilayer specimens amorphization occurs only when the Ge side of a bilayer specimen faces the incident beam, while for Si/Al specimens amorphization occurs regardless of the direction of the incident beam; critical irradiation fluences (Φ_c 's) for a c-to-a transition to occur were obtained. We also studied the temperature dependence of Φ_c for amorphization of a Ge/Al bilayer specimen. We found that a critical temperature exists above which no amorphization is observed. Also, Al - 2.3 at.% Ge two-phase alloy specimens containing Ge precipitates were irradiated at 10 or 50 K with 1 MeV electrons. Amorphization of the precipitates was observed to occur at $\Phi_c \approx 24$ dpa, as in the case of Ge/Al bilayer specimens. Our results are explained in terms of recoil implantation-mechanism.

2. Experimental

We prepared: (a) Ge/Al and Si/Al bilayer specimens; and (b) Al-2.3 at.% Ge alloy specimens containing pure Ge precipitates in an Al matrix.

(a) Ge/Al or Si/Al bilayer specimens were prepared by vapor deposition of Al onto 3 mm diam Ge or Si discs which were cut from Ge wafers with a [110] normal or Si wafers with a [111] normal. The Ge or Si discs were thinned by grinding followed by dimpling, and finally chemically etching with a solution of HF:H₂O₂:H₂O = 2:1:30 (by volume) for Ge discs and a solution of HF:HNO₃ = 1:9 (by volume) for Si discs. The thinned discs were

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rinsed in deionized water before they were inserted into a vacuum evaporator. A 40 nm thick Al layer was vapor deposited onto the Ge or Si discs at room temperature at a pressure of $\approx 10^{-6}$ Torr; the deposition rate was 1 nm s^{-1} . The vapor-deposited Al layers are polycrystalline with a grain diameter of $\approx 100 \text{ nm}$.

(b) Specimens with pure Ge precipitates were obtained in an Al-2.3 at.% Ge alloy, in the form of a foil, which had been heat treated by a combined quenching and aging procedure; i.e., a foil was solution treated at 770 K and then quenched into an iced-brine solution; it was then annealed immediately at 430 K for 10 h to grow the Ge precipitates. After this heat treatment HVEM specimens were prepared by electrolytically jet-polishing 3 mm diam discs employing a solution of 20% perchloric acid and 80% ethyl alcohol; the discs were directly cut from the foil. We observed the specimens initially by conventional transmission electron microscopy (TEM). Figure 1 is a bright-field micrograph of a specimen showing plate-shaped Ge precipitates in an Al matrix; the inset is the corresponding selected-area diffraction pattern (SADP). The Ge precipitates are single crystals and their orientation relationship with the Al matrix is $[110]_{\text{Al}}//[110]_{\text{Ge}}$ and $\{111\}_{\text{Al}}//\{111\}_{\text{Ge}}$; this is consistent with other results (Köster 1969/70, Hugo and Muddle 1990).

In situ 1 MeV electron irradiation experiments were performed in a 1 MeV TEM equipped with a specially fabricated liquid-helium cooled double-tilt stage (Haga, King, Merkle and Meshii 1986). This stage allowed us to maintain a specimen at any T between ≈ 10 and 300 K during an irradiation.

Two types of irradiation experiments were performed on Ge/Al or Si/Al bilayer specimens at 10 K: (a) the Ge or Si layer of a Ge/Al or Si/Al bilayer specimen faces the direction of the incident electron beam (Fig. 2a); and (b) the Al side of the same bilayer specimen faces the incident beam (Fig. 2b). The latter experiment is performed by simply inverting the same specimen. The same flux ($\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$), specimen temperature ($T = 10 \text{ K}$), and total fluence ($\Phi_{\text{total}} \approx 5.3 \times 10^{23}$ or $6.7 \times 10^{23} \text{ cm}^{-2}$ for Ge/Al or Si/Al bilayer

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specimens, respectively) were used for both experiments.

We also studied the temperature dependence of Φ_c in an electron-irradiated Ge/Al bilayer specimen. For six different temperatures in the range of 10 to 190 K we used six different areas of the same specimen; i.e., for each T an area free of radiation damage was utilized. The geometry of Fig. 2a was employed for this experiment, as irradiation-induced amorphization occurs only for this configuration (section 3.1.1); $\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ was used for all T's. At each temperature SADP's were recorded after an increment of fluence $\Delta\Phi \approx 5 \times 10^{22} \text{ cm}^{-2}$. The value of Φ_c was determined as the Φ value at which diffuse scattering rings first appeared on negatives. Since SADP's were not recorded unless $\Delta\Phi$ was achieved, the appearance of diffuse scattering rings during an increment of $\Delta\Phi$ were not observed. Therefore, the uncertainty in determining Φ_c is about 20%.

For Al - 2.3 at.% Ge alloy specimens *in situ* irradiation experiments were performed at T = 10 and 50 K with $\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, and a Φ_{total} as large as $4.4 \times 10^{23} \text{ cm}^{-2}$.

The fluence (cm^{-2}) is converted to the number of displacements per atom (dpa) using tabulated cross-sections (Oen 1973) and displacement threshold energies (T_d) equal to 15, 17, and 16 eV for Ge (Ferreira-Lima and Howie 1976), Si (Loferski and Rappaport 1959, Novak 1963), and Al (Vajda 1977), respectively. The value $\Phi = 10^{23} \text{ cm}^{-2}$ corresponds to 10, 6.4, and 6.1 dpa for Ge, Si, and Al, respectively.

3. Results

3.1 Irradiation at low temperatures

3.1.1 Al - 2.3 at.% Ge alloy specimens at 10 or 50 K

Al- 2.3 at.% Ge alloy specimens with irradiated at T = 10 or 50 K, with 1 MeV electrons and $\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$. The dark-field electron micrographs exhibited in Fig. 3

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illustrate typical results of our observations for specimens which had been irradiated at 50 K. The dark-field images in Fig. 3 were recorded employing the $(220)_{\text{Ge}}$ reflection from Ge precipitates, as shown in the accompanying SADP's; therefore each bright spot indicates Ge precipitate. Figure 3a was taken before irradiation, and Figs. 3b, 3c, and 3d were recorded after an irradiation to 5.9×10^{22} , 1.8×10^{23} , and $2.4 \times 10^{23} \text{ cm}^{-2}$, respectively. Qualitatively the number density and the mean diameter of Ge precipitates decrease gradually, while the intensity of the $(220)_{\text{Ge}}$ reflection decreases gradually with increasing Φ . For comparison, arrows indicating two Ge precipitates are given in Figs. 3b and 3c, respectively. The Ge precipitates disappear almost completely from the irradiated zone at $\Phi = 2.4 \times 10^{23} \text{ cm}^{-2}$ (24 dpa in Ge and 14 dpa in Al). The Ge reflections become very weak at this value; they do not, however, completely disappear from the SADP's for $\Phi_{\text{total}} = 4.4 \times 10^{23} \text{ cm}^{-2}$ (44 dpa in Ge and 27 dpa in Al). Our results are similar to the ones reported previously (Rusbridge 1983). Since no diffuse scattering rings are observed in our experiments, we cannot determine, from this type of experiments, whether the disappearance of Ge precipitates from the dark-field images is due to amorphization of Ge precipitates or their dissolution induced by electron irradiation. The answer is provided from the experiments on Ge/Al bilayer specimens, which demonstrate that a c-to-a transition indeed takes place at the Ge/Al interface region when a bilayer specimen was irradiated at $T = 10$ and 50 K with 1 MeV electrons (section 3.1.2 and 3.2). Therefore, the absence of diffuse scattering rings of an electron-irradiated two-phase alloy specimen is attributed to the fact that the volume fraction of amorphous phase is not large enough to give rise a strong diffraction to be observed using HVEM.

3.1.2 Ge/Al and Si/Al bilayer specimens at 10 K

Irradiation of a Ge/Al bilayer specimen with 1 MeV electrons, at 10 K , is found to induce a c-to-a transition only if the Ge side of the bilayer specimen faces the direction of

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the incident beam -- we call this effect *selective amorphization*. Figure 4a is a bright-field image of a Ge/Al bilayer specimen before irradiation; crystalline Al grains (≈ 100 nm diam) in dark contrast can be seen. Figure 4b is the corresponding SADP; the strong diffraction spots in the SADP are reflections from the Ge single crystal layer, while the weak ones, forming concentric rings, are due to the vapor-deposited polycrystalline Al layer. For a Si/Al specimen similar micrographs are obtained. Figure 5 exhibits SADP's of the same Ge/Al bilayer specimen irradiated at 10 K with $\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ to $\Phi_{total} = 5.3 \times 10^{23} \text{ cm}^{-2}$ (53 dpa in Ge and 32 dpa in Al). Figure 5a is for the Ge layer facing the direction of the incident beam. In this case the appearance of diffuse rings, in comparison with Fig. 4b, indicates the formation of an amorphous phase in the Ge/Al bilayer. These diffuse rings first appear at $\Phi_c = 2.5 \times 10^{23} \text{ cm}^{-2}$ (25 dpa in Ge and 15 dpa in Al) and their intensity increases with increasing fluence. We reported previously a value of $\Phi_c \approx 3 \times 10^{23} \text{ cm}^{-2}$ (Lin, Koike, Seidman and Okamoto 1989); the difference between these two values is due to the uncertainty in determining the value of Φ_c . In the case when the Al layer faces the direction of the incident beam (Fig. 5b), no diffuse rings are observed for $\Phi_{total} = 5.3 \times 10^{23} \text{ cm}^{-2}$. We observed that diffraction spots from the Al layer, as well as the Ge layer, become diffuse as a result of irradiation-induced secondary defects -- i.e., a high density of dislocations.

A Si/Al bilayer specimen, irradiated at 10 K, exhibits a different behavior. Irradiation-induced amorphization occurs in a Si/Al bilayer specimen regardless of the direction of incident beam with respect to the specimen. The diffuse rings observed when the Si side of a Si/Al bilayer specimen faces the incident beam (Fig. 6a), or *vice versa* (Fig. 6b), indicate an amorphous phase. They first appear at $\Phi_c = 3 \times 10^{23} \text{ cm}^{-2}$ (19 dpa in Si and 18 dpa in Al), and their intensity increases with increasing Φ ; we achieved $\Phi_{total} = 6.3 \times 10^{23} \text{ cm}^{-2}$ (40 dpa in Si and 38 dpa in Al).

The center of the first diffuse ring in the SADP of an electron-irradiated Ge/Al (Fig. 5a) or Si/Al (Fig. 6a and 6b) bilayer specimen is located at a Bragg angle corresponding

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to the (111) reflection from a crystalline Ge or Si, and the center of the second diffuse ring has a spacing between those of the (220) and (311) reflections from crystalline Ge or Si. In fact the diffuse rings in Fig. 5a, Fig. 6a, or Fig. 6b constitute a diffraction pattern almost identical to those observed for pure amorphous Ge (Köster 1972) or Si (Köster and Weiss 1975) thin films. An important question is whether the composition of an irradiation-induced amorphous phase in Ge/Al or Si/Al bilayer specimens can be deduced from the difference in the spacings of diffuse rings of an observed amorphous phase and pure amorphous Ge or Si. It was reported previously that amorphous thin films of $\text{Ge}_x\text{Al}_{1-x}$ ($x \geq 0.5$) (Köster 1972) and $\text{Si}_x\text{Al}_{1-x}$ ($x \geq 0.6$) (Köster and Weiss 1975) can be made by a vapor co-evaporation technique; the substrate temperature was maintained at room temperature or 77 K during deposition. TEM studies on these amorphous thin films showed that the diffuse scattering rings in SADP's change with the composition of a thin film. The change in the diffuse scattering ring spacings relative to that of a pure Ge or Si amorphous thin film ($x=1.0$) is, however, small; i.e., $<5\%$ in $\text{Ge}_x\text{Al}_{1-x}$ for $0.5 < x \leq 1.0$, and $<3\%$ in $\text{Si}_x\text{Al}_{1-x}$ for $0.6 < x < 1.0$. This small effect therefore makes it difficult to deduce the composition of the irradiation-induced amorphous phases by measuring the diameters of diffuse scattering rings in SADP's.

3.2. Temperature Dependence of Φ_c in Ge/Al bilayer specimens

A value of Φ_c exists at which an electron irradiation-induced c-to-a transition is observed in Ge/Al or Si/Al bilayer specimens. To understand this result we studied the temperature dependence of Φ_c for Ge/Al bilayer specimens. In this case the Ge side of a bilayer specimen faced the incident beam (Fig. 2a); $\phi = 3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ was used in the range 10 - 190 K. The results are presented in Fig. 7. The measurement error in the value of Φ_c is $\approx 20\%$. Note that the value of Φ_c is approximately constant at $\approx 2.5 \times 10^{23} \text{ cm}^{-2}$ (25 dpa in Ge and 15 dpa in Al), for $T \leq 160 \text{ K}$, and then it increases rapidly in the range 160-190 K. The value of Φ_c becomes immeasurably large at a critical temperature $T_c \approx 190 \text{ K}$, as no

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sign of amorphization can be detected at $T \approx 190$ K at $\Phi_{total} = 7 \times 10^{23} \text{ cm}^{-2}$ (70 dpa in Ge and 43 dpa in Al), this is represented in Fig. 7 by an arrow with its origin at $T = 190$ K and $7 \times 10^{23} \text{ cm}^{-2}$.

4. Discussion

We discuss the amorphization of Ge/Al and Si/Al bilayer specimens, induced by electron irradiation at 10 K, in terms of the elastic collision processes which occur when energetic electrons encounter atoms of a bilayer specimen. During an electron irradiation a fraction of the kinetic energy of the incident electrons is transferred to atoms of the layer facing the incident beam, layer A. The atoms A in the interface region recoil into the bottom layer, layer B, if the transferred energy of an atom is greater than the minimum energy required to displace an atom from its lattice site (T_d). Thus the atoms A are implanted into layer B via a recoil mechanism. The total displacement cross-section for an atom A, σ_A , is a function of T_d , the kinetic energy of the electrons E , and the atomic number Z and the atomic mass M of the recoiling atoms A. For $E \gg mc^2 = 0.511 \text{ MeV}$ (the energy of an electron associated with its mass at rest) σ_A is given by

$$\sigma_A \sim \frac{2\pi}{T_d} \frac{Z^2 e^4}{Mc^2} = (1.4 \times 10^{-22}) \frac{Z^2}{T_d N} \text{ (cm}^2\text{)}, \quad (1)$$

where m is the mass of an electron, e the charge on an electron, c the speed of light, and N the atomic mass number. (Corbett 1966) If we take $N \approx 2Z$, then σ_A is proportional to Z . In the case of an 1 MeV electron irradiation, Eq. (1) gives a rough estimate of σ_A , though E (1 MeV) is not much greater than mc^2 . With $Z = 32, 14$, and 13 ; $N = 72.6, 28$, and 27 ; $T_d = 15, 17$, and 16 eV for Ge, Si, and Al, respectively, we obtain the ratios $\sigma_{Ge}/\sigma_{Al} \approx 2$ and $\sigma_{Si}/\sigma_{Al} \approx 1$. If we take the flux of atoms A recoiling into the layer B, $J_{A/B}$, to be proportional to σ_A , it follows that $J_{Ge/Al} \approx 2J_{Al/Ge}$ and $J_{Si/Al} \approx J_{Al/Si}$. Hence, in the case of Ge/Al bilayer specimens

the flux of recoiling atoms is different by a factor of two when the direction of the incident electron beam is inverted with respect to a specimen, while the flux is independent of orientation for Si/Al bilayer specimens.

Recoil implantation of atoms A into the layer B leads to the formation of a supersaturated solid-solution for both Ge/Al and Si/Al bilayer specimens, as the solid solubility of Ge or Si in Al and *vice versa* is extremely small ($\ll 0.01$ at.%) for $T < 300$ K (McAlister and Murray 1984). The concentration of atoms A in the supersaturated solid-solution, c_A , is proportional to $J_{A/B}$. If we therefore assume that a c-to-a transition takes place when c_A exceeds a critical value $c_{A/B}^{crit}$, which is related to Φ_C at T, our experimental results may be accounted for in terms of the difference between $J_{A/B}$ and $J_{B/A}$. For Ge/Al bilayer specimens the value of Φ_C when Ge layer faces the incident beam (Fig. 2a) is smaller than in the inverse case (Fig. 2b), since $J_{Ge/Al}$ is twice $J_{Al/Ge}$. Furthermore, the absence of amorphization when Al layer faces the electron beam may be attributed to a rather small value of $J_{Al/Ge}$, i.e., $c_{Al/Ge}^{crit}$ can not be reached for the value of Φ_{total} achieved. For Si/Al bilayer specimens the value of Φ_C is independent of the direction of the incident beam, as $J_{Si/Al} \approx J_{Al/Si}$.

We have assumed that $c_{Al/Ge}^{crit} \approx c_{Ge/Al}^{crit}$ and $c_{Al/Si}^{crit} \approx c_{Si/Al}^{crit}$, i.e., the critical concentration of Al in Ge or Si is equal to that of Ge or Si in Al. In fact, $c_{A/B}^{crit}$ does not have to be equal to $c_{B/A}^{crit}$. In the case of Ge/Al bilayer specimens, the selective amorphization effect is favored if $c_{Al/Ge}^{crit} > c_{Ge/Al}^{crit}$. As mentioned earlier, for amorphous thin films of Ge_xAl_{1-x} (Köster 1972) and Si_xAl_{1-x} (Köster and Weiss 1975) alloys prepared by vapor co-deposition the value of $c_{A/B}^{crit}$ was deduced from TEM observations. It was found that $c_{Al/Ge}^{crit} \approx 0$ and $c_{Ge/Al}^{crit} \approx 0.5$ at.% for Ge_xAl_{1-x} alloys; and $c_{Al/Si}^{crit} \approx 0$ and $c_{Si/Al}^{crit} \approx 0.6$ at.% for Si_xAl_{1-x} alloys. Thus Ge or Si can be vapor deposited in an amorphous state without Al, while a significant amount of Ge or Si is required to render Al amorphous. We argue, however, that the value of $c_{Ge/Al}^{crit}$ or $c_{Si/Al}^{crit}$ should depend very much on the conditions under which a thin film is prepared, such as

the substrate temperature and the deposition rate.

Based on the atomic size effect an empirical model has been proposed to calculate $c_{A/B}^{Cr#}$ for metal-metal and metal-metalloid systems. (Egami and Waseda 1984) Taking the atomic radii of Ge, Si, and Al to be 0.122, 0.118, and 0.143 nm, respectively, this model yields $c_{Al/Ge}^{Cr#} = 0.16$ at.% and $c_{Ge/Al}^{Cr#} = 0.26$ at.% for the Ge-Al system; and $c_{Al/Si}^{Cr#} = 0.13$ at.% and $c_{Si/Al}^{Cr#} = 0.23$ at.% for the Si-Al system. These values are quite different from the experimental values obtained for vapor-deposited thin films of the Ge-Al and Si-Al systems. According to this model (Egami and Waseda 1984), the value of $c_{A/B}^{Cr#}$ is sensitive to the atomic size ratio between atoms A and B. Since the atomic size depends upon the composition and the structure of alloys, the determination of the size factor of an element is ambiguous and sometimes misleading, in particular, when a metalloid element is involved. At the present we are not able to make a conclusive estimation of $c_{A/B}^{Cr#}$ for the Ge-Al or Si-Al bilayer systems.

The recoil-implantation mechanism is further supported by the fact that a large value of Φ_C (≈ 25 dpa in Ge and ≈ 20 dpa in Si) is required to observe a c-to-a transition in Ge/Al and Si/Al bilayer specimens, as well as in Al - 2.3 at.% Ge two-phase alloy specimens; this value is too high to be consistent with a vacancy accumulation mechanism (Rusbridge 1983).

In the following discussion we are concerned with the temperature dependence of Φ_C for the Ge/Al bilayer specimens (Fig. 7). Our results may be accounted for in terms of the mobility of the recoil-implanted Ge atoms in an Al matrix. During an electron irradiation with a flux ϕ , the accumulation rate of Ge atoms at a given depth in the Al layer is determined by two factors. The first is due to the recoil implantation of the Ge atoms. It gives rise to an accumulation of Ge atoms at a rate P which is a constant for a given ϕ . The second is due to the temperature dependent mobility of Ge atoms. This factor results in a decrease in the accumulation rate of Ge atoms. The steady state value of c_{Ge} results from the competition of these two factors; amorphization occurs when the resultant c_{Ge} exceeds $c_{Ge/Al}^{Cr#}$. If we ignore the effect of the concentration gradient of the Ge atoms in the Al matrix, a rate equation for

c_{Ge} may be written as

$$\frac{dc_{Ge}}{dt} = P - \nu c_{Ge}, \quad (2)$$

where ν is the temperature dependent jump frequency of a Ge atom. If ν obeys an Arrhenius law, we may write

$$\nu = \nu_0 e^{-E_{Ge}/kT}, \quad (3)$$

where ν_0 is Ge atom attempt jump frequency of an order of magnitude of Debye frequency in Al, E_{Ge} is the activation energy for the migration of the Ge atoms, and k is Boltzmann's constant. With the initial condition that $c_{Ge} = 0$ when $t = 0$, the solution of Eq. (2) may be written as

$$c_{Ge}(t) = \frac{P}{\nu} (1 - e^{-\nu t}). \quad (4)$$

For $t \rightarrow \infty$, we obtain the steady state concentration

$$c_{Ge}(\infty) = \frac{P}{\nu} = \frac{P}{\nu_0} e^{E_{Ge}/kT}. \quad (5)$$

This shows that $c_{Ge}(\infty)$ decreases as T increases and as the mobility of the Ge atoms increases. An equation for the irradiation fluence Φ may be derived by replacing t with Φ and ϕ according to

$$\Phi = \phi t. \quad (6)$$

The critical fluence Φ_c follows from $c_{Ge}(t) = c_{Ge/Al}^{crit}$, that is,

$$\Phi_c = -\frac{\phi}{\nu} \ln(1 - c_{Ge/Al}^{crit} \frac{\nu}{P}). \quad (7)$$

Inserting Eq. (3) into Eq. (7) yields Φ_c as a function of T . The results of the numerical calculations on Φ_c versus T is shown in Fig. 7 (dashed curve); the parameters used in the computations will be given later. At low temperatures, $\nu/P \ll 1$, Eq. (7) becomes

$$\Phi_c \approx \frac{\phi}{P} c_{Ge/Al}^{crit}. \quad (8)$$

In the low temperature range, therefore, Φ_c is independent of the temperature, as observed experimentally. In our experiments $\Phi_c = 2.5 \times 10^{23} \text{ cm}^{-2}$ for $T < 160 \text{ K}$ and $\phi = 3 \times 10^{19} \text{ cm}^{-2}$

s^{-1} , we then obtain, from Eq. (8),

$$c_{Ge/Al}^{crit} / P = \Phi_c / \phi = 8.3 \times 10^3 \text{ s}. \quad (9)$$

According to Eq. (3) and Eq. (7), there exists a temperature T_c at which

$$(c_{Ge/Al}^{crit} / P) v_0 e^{-E_{Ge}/kT_c} = 1, \quad (10)$$

leading to $\Phi_c \rightarrow \infty$. In fact, T_c is the critical temperature above which the steady state concentration, $c_{Ge}(\infty)$, cannot reach $c_{Ge/Al}^{crit}$ and, consequently, for $T \geq T_c$ no c-to-a transition can be observed during an irradiation. From our experiments, we find $T_c = 190 \text{ K}$. Using Eq. (9) and (10), and $v_0 \approx 10^{13} \text{ s}^{-1}$, the value of the activation energy for the migration of Ge atoms may be obtained from Eq. (10); i.e., $E_{Ge} \approx 0.64 \text{ eV}$. This value is about the migration energy of an Al monovacancy, $E_{1v}^m = 0.65 \text{ eV}$ (Levy, Lanore and Hillairet 1973).

The parameters in Eq. (3) and Eq. (7) are listed in Table 1. Using these parameters, we may make numerical calculations for $\Phi_c(T)$; the results are shown in Fig. 7 (the dashed curve). We note that $\Phi_c(T)$ remains constant for a wide temperature range 0 to $\approx 180 \text{ K}$, and then abruptly increases with increasing T . $\Phi_c(T)$ tends to infinity at $T = 190 \text{ K}$. Therefore, our model is in very good agreement with the experimental results. Note that the predicted change in $\Phi_c(T)$ as T approaches T_c is relatively abrupt in comparison with the experimental data. This is expected for a unique activation energy model. If we introduce a spectrum of activation energies and take into account the effect of Ge concentration gradient due to a recoil-implantation profile, a smearing out of the $\Phi_c(T)$ around T_c is expected.

It is interesting to note that the value of T_c we obtained is near the temperature at which Al vacancies become mobile upon annealing of an Al specimen irradiated at low temperature, e.g., 90 K , with 2 MeV electrons; the activation energy was measured to be 0.62 eV (Lwin, Doyoma and Koehler 1968). The mobility of the recoil-implanted Ge atoms in the Al matrix, therefore, must be correlated with the mobility of Al vacancies; i.e., Ge atoms migrate by a vacancy mechanism. Ge atoms are practically immobile in the low temperature range $0 - 160 \text{ K}$, as Al vacancies are immobile (Schilling, Berger, Isebeck and Wenzl 1970, Balluffi 1978). During an irradiation, this leads to a simple accumulation of Ge atoms at a

given depth of the Al layer with a rate independent of temperature. Consequently, c_{Ge} steadily increases and reaches $c_{Ge/Al}^{crit}$. Therefore, Φ_C remains constant in the low temperature regime. As T approaches T_C , Ge atoms become mobile as a result of the mobility of Al vacancies. This leads to a decrease in the accumulation rate of Ge atoms and, therefore, an increase in Φ_C . For $T \geq T_C$ the mobility of Ge atoms becomes sufficiently large to prevent c_{Ge} from reaching $c_{Ge/Al}^{crit}$ and, therefore, no amorphization occurs.

→ The monovacancy mechanism for the migration of Ge atoms is also implied by the fact that the activation energy of Ge atoms E_{Ge}^m (0.64 eV) is nearly equal to the migration energy of Al vacancies E_{1v}^m (0.65 eV). We recall that an electron irradiation of a specimen, e.g., Al, creates equal number of SIA's and vacancies. If SIA's and vacancies annihilate by direct recombination, it may be found that the self-diffusion coefficient of the atoms by the vacancy mechanism is $D = D' + D_{th}$, where D' is a measurement of the enhancement of self-diffusion due to irradiation and D_{th} is the thermal self-diffusion coefficient (Dienes and Damask 1958). D' and D_{th} depend exponentially on $1/T$ with the characteristic activation energies $E' = E_{1v}^m - \frac{1}{2} E_i^m \approx E_{1v}^m$ and $E_{th} = E_{1v}^m + E_{1v}^f$, respectively, where E_i^m is the self-interstitial migration energy, which is generally small compared with E_{1v}^m , and E_{1v}^f is the vacancy formation energy. Relevant diffusion data for Al and Al(Ge) systems at thermal equilibrium are listed in Table 1. We have $E' \approx E_{1v}^m = 0.65$ eV (Levy, Lanore and Hillairet 1973) and $E_{th} = 1.26$ eV (Peterson and Rothman 1970); E_{th} is about twice E' . In view of the exponential dependence of D' and D_{th} on $1/T$, D_{th} is negligible at low temperatures, e.g., $T < 200$ K, in comparison with D' , leading to $D \approx D'$. Therefore, during an irradiation at low temperatures, the atoms diffuse with an apparent activation energy equal to E_{1v}^m . In regard to the migration of Ge atoms in an Al matrix, since the binding energy between Ge atoms and Al vacancies is very small (Anthony 1970, Balluffi 1973), the effective vacancy jump frequency is not affected by the presence of Ge atoms. Consequently, the activation energy for the

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diffusion of Ge atoms via a vacancy mechanism is nearly identical to the activation energy for self-diffusion of Al atoms. For a system under irradiation, we therefore find $E_{Ge}^m \approx E' \approx E_{Al}^m = 0.65$ eV, as obtained previously; this is similar to a system at thermal equilibrium, i.e., $E_{th}^{Ge} = E_{th} = 1.26$ eV, where E_{th}^{Ge} is thermal activation energy for Ge atom diffusion in Al (Table 1).

Actually, the migration of Ge atoms may not only involve monovacancies, but also other point defects, such as divacancies and trivacancies with activation energies different from E_{Al}^m . Consequently, we should deal with a spectrum of activation energies, in particular for $T \approx T_c$. This would lead to a smearing out of the abrupt change in Φ_c at $T \approx T_c$, as we discussed earlier.

4. Conclusion

In situ HVEM studies have been performed on Ge/Al and Si/Al bilayer specimens, as well as on Al - 2.3 at.% Ge two phase alloy specimens. During an irradiation at 10 K, a c-to-a transition occurs in a Ge/Al bilayer specimen *only* when the Ge layer faces the incident beam, while the interfacial region of a Si/Al bilayer specimen can be rendered amorphous regardless of the direction of the incident beam with respect to the specimen. For the case of Al - 2.3 at.% Ge alloy specimens, amorphization of Ge precipitates in the Al matrix is also observed during an irradiation at 10 or 50 K. We obtained the critical fluence for amorphization to occur, $\Phi_c = 2.5 \times 10^{23} \text{ cm}^{-2}$ for the Ge-Al system (25 dpa and 15 dpa in Al); and $\Phi_c = 3 \times 10^{23} \text{ cm}^{-2}$ for the Si-Al system (19 dpa in Si and 18 dpa in Al). These results is explained based on an electron irradiation-induced recoil implantation mechanism.

The temperature dependence of Φ_c for a Ge/Al specimen with the Ge side facing the incident electron beam has been studied. It is found that Φ_c remains constant in the low temperature range from 10 - 160 K, then increases rapidly with increasing T in the range 160 - 190 K, and finally becomes immeasurably large at $T = T_c = 190$ K; T_c is the critical

temperature above which no amorphization can be observed. In terms of the mobility of the recoil-implanted Ge atoms in the Al matrix, our results are qualitatively accounted for by a rate-theory model. It is found that the migration of Ge atoms during an irradiation is via a vacancy mechanism with an effective activation energy $E_{Ge} = 0.64$ eV. The fact that E_{Ge} is nearly equal to the migration energy of Al monovacancies may be understood based on an irradiation-enhanced diffusion mechanism.

5. Acknowledgements

Dr. X. W. Lin received support from the Robert R. McCormick School of Engineering and Applied Science for this research. Additional support was received through the use of the central facilities of Northwestern University's National Science Foundation funded Materials Research Center. This research was made possible through the use of the High Voltage Electron Microscope Facility at Argonne National Laboratory. The aid of Messrs. E. Ryan and S. Ockers of this facility is gratefully acknowledged. Dr. P. R. Okamoto was supported by the U. S. Department of Energy, BES-MS, under contract number W-31-109-Eng-38. We wish to thank Dr. G. Martin for useful discussions which were made possible by a National Science Foundation US-France Cooperative Science grant (Dr. Christine Glenday, contract officer).

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Table Caption

Table 1: The parameters used for numerical calculations of the critical fluence (Φ_c) as a function of temperature (T), along with relevant point diffusion data for Al and Al(Ge) systems at thermal equilibrium.

Figure Captions

Figure 1: A TEM micrograph exhibiting Ge precipitates in an Al - 2.3 at.% Ge alloy specimen after a combined quenching and aging heat treatment. The inset is the corresponding SADP with a $[110]$ zone axis. The strong spots correspond to reflections from the Al matrix and the weak ones from Ge precipitates.

Figure 2: A schematic diagram illustrating the two configurations of Ge/Al or Si/Al specimens used in our 1 MeV electron beam irradiation experiments: (a) The Ge or Si layer is facing the incident beam. (b) The Al layer is facing the electron beam.

Figure 3: HVEM dark-field micrographs and their corresponding SADP's of an Al -2.3 at.% Ge specimen irradiated to a sequence of fluences at 50 K; the dark-field images were from a Ge (220) diffraction spot as shown in the SADP's: (a) before irradiation; (b), (c), and (d) irradiated to 5.9×10^{22} , 1.8×10^{23} , and 2.4×10^{23} cm⁻², respectively. Note that the intensity of the Ge (220) reflection decreases with increasing fluence, while the crystalline Ge precipitates gradually disappear from the irradiated zone.

Figure 4: HVEM micrographs of a Ge/Al bilayer specimen prior to irradiation: (a) Bright-field micrograph showing Al grains on the Ge layer. (b) The corresponding SADP. The indexed strong spots are from Ge single crystal reflections and the weak spots, forming concentric rings, are from the polycrystalline Al layer.

Figure 5: HVEM SADP's of a Ge/Al bilayer specimen after an irradiation to 5.3×10^{23} cm⁻² at 10 K. The strong indexed spots are Ge single crystal reflections, while the weak spots forming rings are from the polycrystalline Al layer. (a) The Ge layer faces the incident

beam (Fig. 2a). The presence of diffuse scattering rings indicates formation of an amorphous phase. (b) The Al layer faces the incident beam (Fig. 2b). No diffuse rings are present.

Figure 6: HVEM SADP's of a Si/Al bilayer specimen after an irradiation to $6.3 \times 10^{23} \text{ cm}^{-2}$ at 10 K. The strong indexed spots are Si single crystal reflections, while the weak spots forming rings are from the polycrystalline Al layer. (a) The Si layer faces the incident beam (Fig. 2a). (b) The Al layer faces the incident beam (Fig. 2b). The presence of diffuse scattering rings (a) and (b) is an indication of the formation of an amorphous phase.

Figure 7: The variation of the critical fluence for amorphization to occur (Φ_c) with temperature (T) of a Ge/Al bilayer specimen subjected 1 MeV electron irradiation at a constant flux (ϕ) of $3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$. The Ge layer of the bilayer specimen faced the incident beam. No amorphization can be observed above a critical temperature of $\approx 190 \text{ K}$. The calculated Φ_c as a function of T is denoted by the dashed curve.

Table 1

Parameters	Notation	Value	Reference
Electron irradiation fluence	ϕ	$3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$	[a]
Critical fluence at 10 K	Φ_c	$3 \times 10^{23} \text{ cm}^{-2}$	[a]
Ge atom attempt jump frequency in Al	ν_0	10^{13} s^{-1}	[a]
Activation energy for Ge atom migration in Al under irradiation	E_{Ge}	0.64 eV	[a]
Al vacancy formation energy	E_{1v}^f	0.69 eV	[b]
Al vacancy migration energy	E_{1v}^m	0.65 eV	[c]
Thermal self-diffusion activation energy in Al	E_{th}	1.26 eV	[d]
Thermal activation energy for Ge atom diffusion in Al	E_{th}^{Ge}	1.26 eV	[d]

[a] This study

[b] Tzanetakis, Hillairet and Revel 1976

[c] Levy, Lanore and Hillairet 1973

[d] Peterson and Rothman 1970

100 nm $\bar{B}[110]$

5000

5000

5000

Al-Ge alloy
X-ray diffraction

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