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Crystallization of amorphous germanium in an Al/*a*-Ge bilayer film deposited on a SiO₂ substrate

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The crystallization of amorphous Ge(*a*-Ge) in an Al (134 nm) and *a*-Ge (108 nm) thin-film bilayer deposited on a SiO₂ substrate has been examined by a cross section transmission electron microscope technique. When crystallization of *a*-Ge begins at 125 °C, amorphous AlGe (*a*-AlGe) alloy is formed in the Ge layer. Then, the *a*-AlGe alloy layer also appeared at the surface of the bilayer. After complete crystallization, those amorphous layers disappeared and the bilayer film has been converted to a polycrystalline film. We discussed the crystallization of *a*-Ge and proposed the mechanism of the diffusion of Ge atoms from the inner *a*-Ge layer through the outer Al layer to the topmost surface that involves the formation of the metastable *a*-AlGe alloy in the Ge layer, followed by the crystallization of this alloy by the pseudo-eutectic reaction, leading to the decomposition into an equilibrium Al and Ge crystal mixture and *a*-Ge. Then, Ge atoms is released to the Al layer for the compensation of the Al diffusion down into the Ge layer and again forms the *a*-AlGe alloy in the Al layer. The *a*-AlGe alloy in the Al layer is also crystallized by the pseudo-eutectic reaction. Consequently, decomposed *a*-Ge is ejected from the inside to the surface of the bilayer, resulting in the surface Ge segregation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1359149]

I. INTRODUCTION

Amorphous semiconductors such as amorphous Ge (*a*-Ge) or amorphous Si (*a*-Si) are widely used for electronic applications and must have thermal stability to be reliably used. In metal-amorphous semiconductor bilayer or multilayer systems, the metals can dramatically reduce the temperature at which the amorphous semiconductor crystallizes. This phenomenon, which is usually called metal-contact induced crystallization or metal-mediated crystallization (MMC) is a subject of considerable interest both from a fundamental physics and technological viewpoint. Oki *et al.* first found the lower crystallization temperature to be related to the eutectic temperatures of the metal/*a*-Ge bilayer films.¹ For example, *a*-Ge in an Al/*a*-Ge bilayer film crystallize at 130–210 °C which is 60%–70% of the lowest eutectic temperature at 420 °C (in degrees Kelvin)^{1,2} though its crystallization temperature is normally reported to be 480 °C–530 °C.^{3,4} Hultman *et al.* studied the reaction between Au and *a*-Si in the Au/*a*-Si bilayer film and found that the formation of crystalline Si depends on the diffusion of the Au into *a*-Si and the formation of metastable Au–Si compounds, which act as transport phases for both Si and Au.⁵ In a recent study of the crystallization of *a*-Ge in the Al/*a*-Ge thin-film couples deposited onto a SiO₂ substrate, we have found that Al induces crystallization of Ge at

100 °C–125 °C and Ge atoms come out from the inner *a*-Ge layer and spread over the free surface of the outer Al layer, followed by the formation of crystalline Ge aggregates exhibiting complex substructures.⁶ Although the crystallization of *a*-Ge and the surface Ge segregation have been identified, the details of the structural change in the bilayer film during crystallization have not fully been understood.

The purpose of the study presented here is to examine the mechanism of the surface Ge segregation accompanied with crystallization of *a*-Ge in the Al/*a*-Ge bilayer film deposited on a SiO₂ substrate. A cross section transmission electron microscope (TEM) technique is employed to clarify an atomic process in the bilayer film.

II. EXPERIMENTAL

The Al/*a*-Ge bilayer film was prepared at room temperature by a vacuum evaporation technique under a pressure lower than 10^{−4} Pa. An *a*-Ge film was deposited on the degreased SiO₂ substrate, then, an Al layer was formed on the *a*-Ge film successively. The thickness of Al and *a*-Ge films, determined from a cross section TEM micrograph was about 134 and 108 nm, respectively. The thin film couples deposited onto the SiO₂ substrate was annealed at 125 °C in a vacuum of about 10^{−5} Pa.

JEOL JEM-200CX microscope was used for TEM observation at room temperature. TEM samples of as-deposited and annealed films were glued using Gatan G-1 bond at 80 °C, then ion milled the samples at 4 kV × 0.5 mA using a

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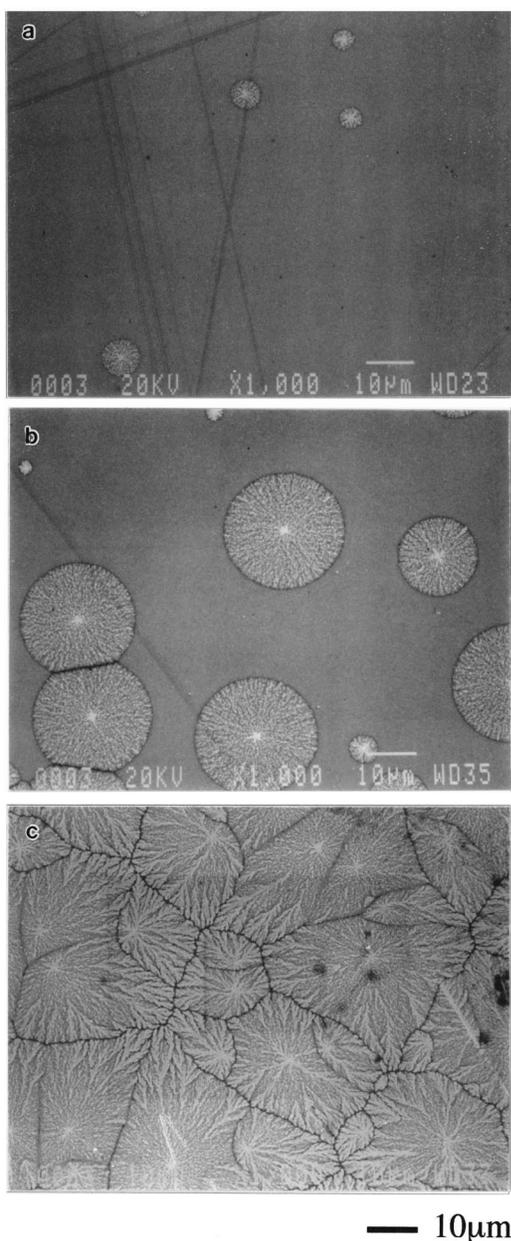


FIG. 1. SEM images of Ge aggregates on the free surface of the Al layer in the Al/*a*-Ge bilayer film deposited on the SiO₂ substrate : annealed at 125 °C for (a) 5, (b) 10, and (c) 50 h.

liquid nitrogen stage to avoid any reaction during sample preparation. A cross section TEM sample at the area, where the Ge aggregate has been formed, was prepared by using a focused ion beam technique. We used a Fei model-FIB200 with a Ga ion beam at 30 kV. In some specimens, we examined local concentrations by using energy dispersive x-ray spectroscopy (EDS) in JEOL JEM-3010 microscope which equipped with a 3 nm electron probe. The pattern evolution of the polycrystalline Ge aggregates on the free surface was observed by scanning electron microscope (SEM).

III. RESULTS

Figure 1 shows SEM images of the bilayer film annealed at 125 °C. After annealing 5 h, polycrystalline Ge aggregates

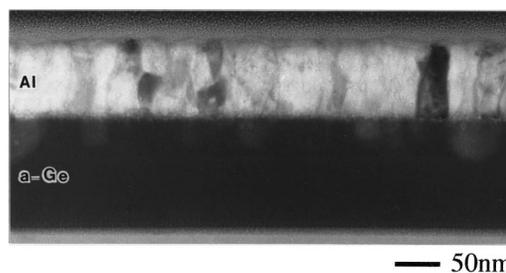


FIG. 2. Cross section TEM micrograph of the as-deposited Al(134 nm)/*a*-Ge(108 nm) bilayer film.

appear on the surface [Fig. 1(a)]. Then, those patterns grow radially [Fig. 1(b)] and cover the whole surface by annealing 50 h, as shown in Fig. 1(c).⁶ Previous Auger electron spectroscopy measurements have indicated that each pattern consisted of the light and dark grains which are crystalline Ge and Al phases respectively.^{6,7}

Figure 2 is a cross section bright field (BF) TEM micrograph of the as-deposited Al/*a*-Ge bilayer film. The *a*-Ge layer appear uniformly gray in the BF image because of its homogeneous and weakly scattering.⁸ In the BF image it is also revealed that the Al layer consists of columnar crystal grains.

After annealing at 125 °C for 2 h, although any surface Ge aggregate has not been observed, small grains (dark contrast in BF image) appear at the Al/*a*-Ge interface and the crystallization proceeds to the substrate, as shown in Fig. 3(a). The diffraction pattern taken from the whole bilayer film shows a Ge {111} diffraction ring, indicating that *a*-Ge is crystallized, as shown in Fig. 3(c). The high-resolution picture [Fig. 3(b)] shows the details of the bilayer more clearly. As shown here, the Al columnar structure is slightly ambiguous and from the EDS analysis Al and Ge layer have a significant amount of Ge and Al, respectively (arrows **a–h**). In Fig. 3(b), it can also be noted that the Al atoms diffuse into the uniformly gray amorphous region, as indicated by arrow **h**.

Figure 4(a) is the cross section BF image of the bilayer film where the small Ge aggregate is formed on the topmost surface by annealing at 125 °C for 5 h. As the picture shows, considerable mixing that involves crystallization of *a*-Ge layer and destruction of the Al columnar structure has occurred. The selected area diffraction (SAD) pattern taken in this mixed region shows diffraction rings of the Al {111} and Ge {111}, indicating that the bilayer film is mixture of Al and Ge crystal grains, as shown in Fig. 4(b). Also, as can be seen from Fig. 4(a), uniformly gray amorphous layers are observed both in the Ge layer and at the topmost surface (arrows). Figure 4(c) is the EDS line scan profile across the thickness of the bilayer film. The EDS analysis qualitatively shows that both amorphous layers are rich in Ge.

Further annealing at 125 °C for 50 h, the surface of the bilayer is completely covered with the Ge aggregates, as shown in Fig. 1(c). The cross section BF image shows that the bilayer film has transformed into a polycrystalline structure, as shown in Fig. 5. The amorphous layer at the topmost

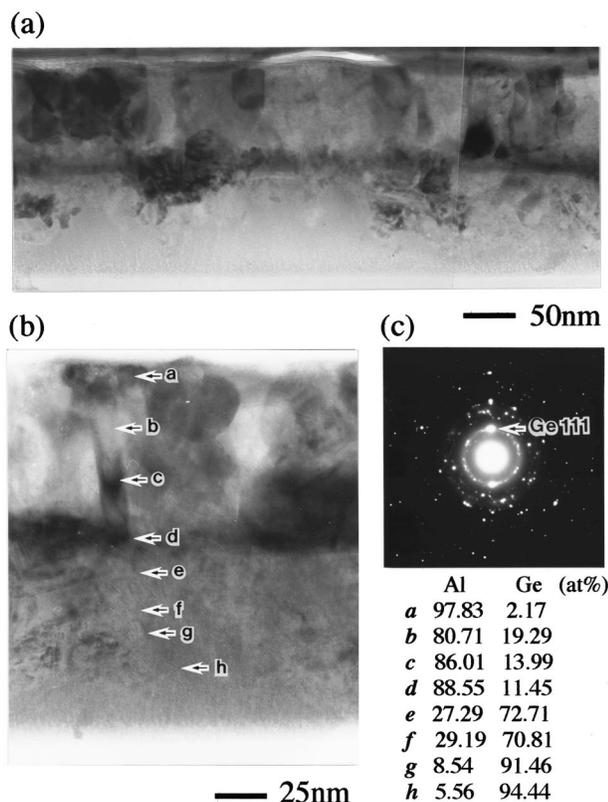


FIG. 3. Cross section images of the Al/Ge bilayer, annealed at 125 °C for 2 h, (a) BF, (b) high-resolution images, and (c) the diffraction pattern. The EDS analysis shows Al and Ge layer have a high concentration of Ge and Al, respectively (arrows a–h).

surface has disappeared, while the amorphous layer close to the SiO₂ substrate is still visible (arrow).

IV. DISCUSSIONS

The atomic process in the Al/*a*-Ge bilayer film on the SiO₂ substrate taking place during low temperature annealing at 125 °C is now considered.

The interactions between films of Ag and *a*-Si,⁹ Ag and *a*-Ge⁸ have been extensively studied by Konno and Sinclair using *in situ* TEM. In their work, any amorphous alloy or metastable compound was not detected in these films. On the other hand, metastable phase formation has been reported during the crystallization of *a*-Si in contact with Au.^{5,10,11} The difference between the Au–Si and the Ag–Si systems is that the former possesses an unusually deep eutectic phase diagram, whereas the latter exhibits a shallow eutectic. A deep eutectic point indicates that the affinity between Au and Si atoms is stronger than that of Ag and Si, resulting in the formation of the metastable phase in the former, but not in the latter.¹²

The model in Fig. 6 gives a tentative description of the interaction between thin films of Al and *a*-Ge. Amorphous AlGe (*a*-AlGe) alloy phase have been found between the transformed polycrystalline region and the SiO₂ substrate, as shown in marked h of Fig. 3(b). This alloy phase is rich in Ge but the concentration of Al is higher than the equilibrium solid solubility at 125 °C (less than 1 at% Al). The Al–Ge

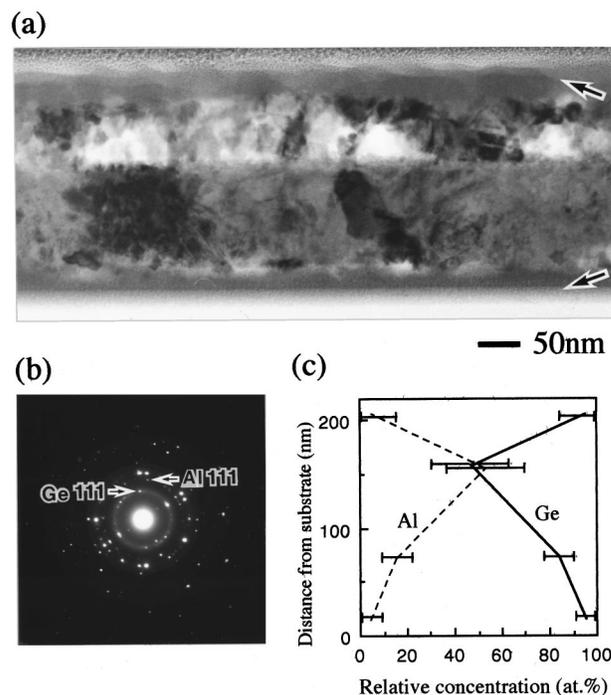


FIG. 4. (a) Cross section image of the film annealed at 125 °C for 5 h, where the small Ge aggregate is formed on the topmost surface as shown in Fig. 1(a). Uniformly gray layers are observed in the Ge layer and at the topmost surface (arrows). (b) The inset SAD pattern taken in this mixed region. (c) A representative EDS line scan profile across the thickness of the bilayer.

phase diagram which we show in Fig. 7, though approximate, contains all of the essential features required to interpret the present results. According to the phase diagram, the eutectic point of the Al–Ge system (420 °C) is much lower than that of the Ag–Ge system (651 °C). Therefore, *a*-AlGe would be formed in the *a*-Ge layer because of the strong affinity between Al and Ge atoms¹³ [Fig. 6(a)]. The concentration of Al in *a*-Ge would be extrapolated by the extension of the liquidus line below the eutectic temperature.¹² This extrapolation indicates that the solubility limit of Al in *a*-Ge at 125 °C would be given by composition x_1 .

As shown in Figs. 3 and 4, the crystallization of the *a*-Ge occurs at the Al/*a*-Ge interface and proceeds toward the SiO₂ substrate. In the present experiment, the crystallization of *a*-Ge at temperature 125 °C, which is far below the crystallization temperature, is a consequence of MMC typi-

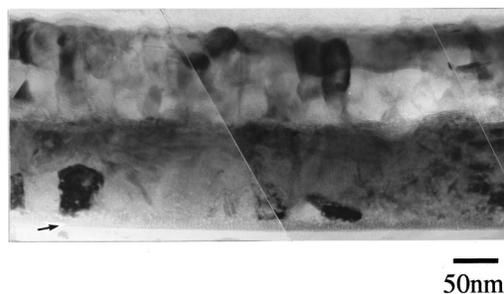


FIG. 5. Cross section TEM micrograph of the bilayer film annealed at 125 °C for 50 h. The amorphous layer close to the SiO₂ substrate is still visible (arrow).

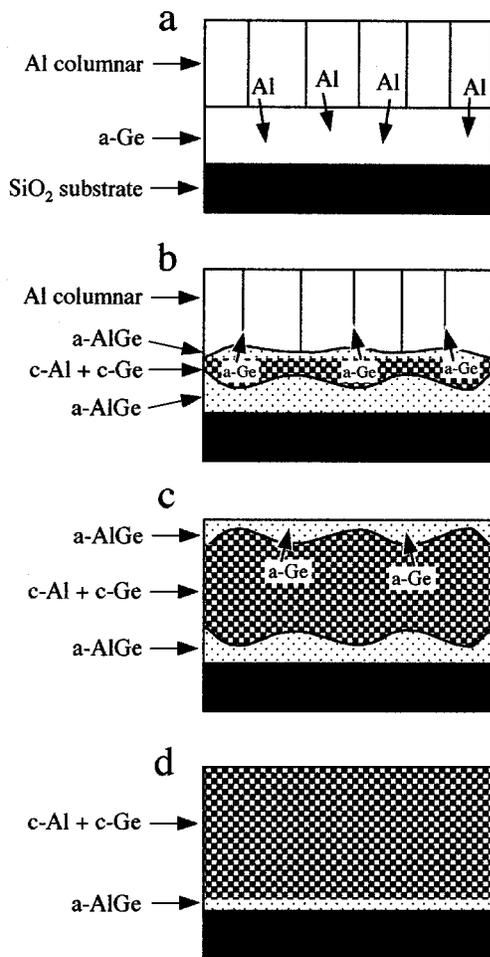


FIG. 6. Cross section diagrams giving a tentative description of the interaction between thin films of Al and *a*-Ge. (a) as deposition, (b) beginning of the reaction, (c) further annealing, and (d) the crystallization is complete.

cal in low temperature eutectic systems.^{14–16} It has been shown by Oki *et al.* that the crystallization temperature of MMC is strongly related to the eutectic temperature of the Ge-metal systems.¹ Therefore, the metastable *a*-AlGe alloy, which has been formed by Al diffusion into the *a*-Ge layer,

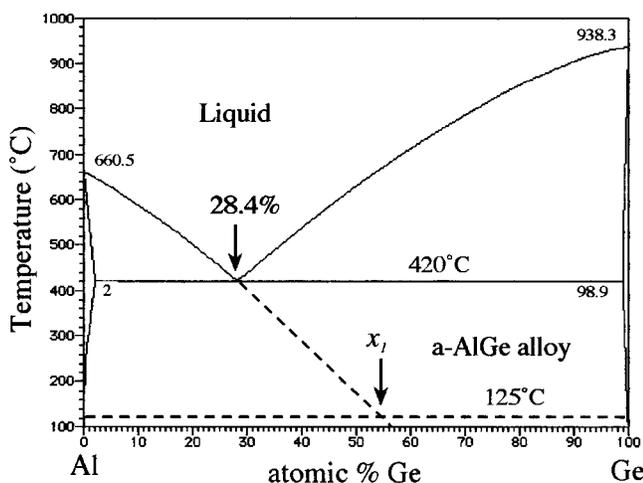
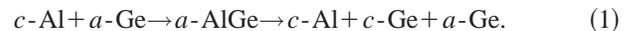


FIG. 7. Schematic phase diagram of the Al-Ge system with the solubility limit of the metastable *a*-AlGe alloy.

is probably crystallized by the pseudo-eutectic reaction, resulting in an equilibrium mixture of Al and Ge micrograins. Further annealing at 125 °C causes growth of the crystallized region by Al diffusing into the Ge layer. Here, the concentration of Ge at the eutectic point, 28 at %, must be lower than x_1 , as just mentioned. This lower concentration suggests that *a*-AlGe alloy would be decomposed into an equilibrium Al and Ge crystal mixture (28 at % Ge) and *a*-Ge by the pseudo-eutectic reaction.¹⁶

From the aforementioned discussions, a model for the Al/*a*-Ge interaction can be put forward that describes MMC of *a*-Ge



where the *c*-Al and *c*-Ge is crystalline Al and Ge, respectively. Common for these steps is the weakening of the bonding of Ge atoms in contact with Al. As a result, a higher atomic mobility is obtained. The system lowers its energy by forming a metastable *a*-AlGe alloy and ultimately crystallization occurs.¹⁷

When the inner *a*-Ge layer is crystallized, the columnar structure of the outer Al layer has been completely lost and transformed into a polycrystalline structure, as shown in Fig. 4. It has been also revealed that Ge-rich amorphous layer appeared at the topmost surface. It is well known that the void structure in grain boundaries of the columnar structure is a short-cut diffusion path.¹⁶ Therefore, Ge atoms in the Ge layer are probably released to the grain boundaries of the Al columnar crystals in order to compensate the Al diffusion down into the Ge layer [Fig. 6(b)]. The released Ge again forms the *a*-AlGe alloy and nucleation occurs at the grain boundaries, leading to the destruction of the columnar structure. Then, *a*-Ge, which has been decomposed by the pseudo-eutectic reaction, is squeezed out from the inside of the Al layer, resulting in the surface segregation [Fig. 6(c)]. The surface amorphous layer reacts with the adjacent Al crystallites, finally, the bilayer film is completely transformed into a polycrystalline film [Fig. 6(d)]. The diffusion of released Ge through the Al-layer is proposed to be driven by the difference in free energy of *a*-Ge and *c*-Ge. The amorphous layer was slightly left close to the SiO₂ substrate, as shown in Fig. 5, probably due to relax the residual stress in the film deposited onto the substrate.¹⁸

VI. CONCLUSIONS

The crystallization of *a*-Ge in an Al(134 nm)/*a*-Ge(108 nm) bilayer film deposited onto a SiO₂ substrate has been examined by cross section TEM technique. We have found that Al induces crystallization of Ge in the bilayer film at 125 °C. When crystallization of *a*-Ge begins at the Al/*a*-Ge interface, *a*-AlGe alloy is formed in the Ge layer, the alloy layer also appeared at the topmost surface of the film. After complete crystallization, those amorphous layers disappeared except that close to the substrate, and the bilayer film has been converted to the polycrystalline film. We discussed the crystallization of *a*-Ge and proposed the mechanism of the diffusion of Ge atoms from the inner *a*-Ge layer to the topmost surface through the outer Al layer that

involves the formation of the α -AlGe alloy in the Ge layer, followed by the crystallization of the alloy by the pseudo-eutectic reaction, leading to the decomposition into an equilibrium Al and Ge crystal mixture and α -Ge. Then, Ge atoms is released to the Al layer for the compensation of the Al diffusion down into the Ge layer. The released Ge forms again the α -AlGe alloy and nucleation occurs at the grain boundaries, leading to the destruction of the columnar structure. Finally, α -Ge, which has been decomposed by the pseudo-eutectic reaction, is squeezed out from the inside of the Al layer, resulting in the surface segregation. These results indicate that formation of the metastable phase and the subsequent eutectic reaction is an important factor for stability of the metal-amorphous semiconductor bilayer or multilayer systems.

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