Effect of interlayer on silver-induced layer exchange crystallization of amorphous germanium thin film on insulator

Ryota Yoshimine, Kaoru Toko*, and Takashi Suemasu

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

*E-mail: toko@bk.tsukuba.ac.jp

Metal-induced layer exchange (MILE) is an advanced crystallization technique for fabricating high-quality semiconductor thin films on insulating substrates at low temperatures. Here, we focused on Ag as a catalytic metal for crystallizing amorphous germanium thin films on glass through MILE. The layer exchange between Ag and a-Ge was not simple because Ag diffused into a-Ge so fast that it crystallized the top a-Ge layer before the completion of layer exchange. To suppress Ag diffusion into a-Ge, we explored the kind of interlayer material between them as well as the growth temperature. Preparing SiO_2 and GeO_2 interlayers allowed for a complete layer exchange, resulting in the formation of polycrystalline Ge thin films on glass at temperatures as low as 250 °C. These findings are essential for further understanding and controlling the layer exchange phenomenon.

1. Introduction

Polycrystalline germanium (poly-Ge) thin films on insulators have attracted the attention of many researchers to realize next-generation electronic devices, such as system-in-displays, three-dimensional integrated circuits, and multijunction thin-film solar cells.[1-4] Researchers have developed the following growth techniques for poly-Ge thin films on insulators: magnetron sputtering,[4] chemical vapor deposition,[5] laser annealing,[6,7] and solid-phase crystallization (SPC).[8,9] Those poly-Ge thin films, however, consist of small grains (< 1 μm) and their carrier mobilities are limited to 140 cm^2 V^{-1} s^{-1}.[4,8,9] In addition, because vacancies in Ge act as acceptors, the poly-Ge thin films are highly p-doped ($> 5 \times 10^{17}$ cm^{-3}).[8,9] The high carrier concentration makes it difficult to control the conduction type.

Metal-induced layer exchange (MILE) has been widely investigated to form large-grained Si,[10-15] SiGe,[16-18] and Ge [19-30] thin films on insulators. In MILE, Al [19-24] and Au [25-27] have been used as catalytic metals for crystallizing amorphous Ge (a-Ge). The MILE with these catalysts has allowed for the formation of large-grained (> 100 μm), (111)-oriented Ge thin films.[20,26] In addition, these catalysts have significantly lowered the growth temperature of a-Ge, leading to the formation of poly-Ge on plastic substrates.[22,25,26] The use of poly-Ge as a seed layer has enabled us to directly synthesize vertically aligned Ge nanowires on glass [28] and plastic substrates.[29] However, in an Al-Ge system, the resulting Ge layer shows a high hole concentration of $p = 2 \times 10^{20}$ cm^{-3} owing to the residual Al atoms in Ge activated as acceptors.[25] Although poly-Ge is useful for a p-type layer in solar cells,[12] it cannot be used as an active layer for transistors. On the other hand, in a Au-Ge system, the resulting Ge layer shows relatively good electrical properties ($p = 2 \times 10^{17}$ cm^{-3} and hole mobility: 160 cm^2 V^{-1} s^{-1}).[25] This has allowed for the formation of a thin-film transistor by an all-low-temperature process.[30] However, Au has difficulty in being used for large-area devices because it is expensive and unstable.

We have focused on Ag as a catalytic metal for the MILE growth of a-Ge on insulators. In a Ag-Si system, MILE has been demonstrated.[31] Since the solubility of Ag in Ge is low (~10^5 cm^{-3} at 250 °C),[32] the amount of residual Ag in Ge should be small. Moreover, the phase diagram of the Ag-Ge system suggests that the layer exchange occurs at low temperatures because Ge is soluble in Ag at temperatures lower than those in the case of Al and Au. In fact, catalytic Ag has formed crystalline Ge below 400 °C.[33,34] Here, we investigate the effect of an interlayer, a diffusion barrier layer between Ag and Ge, to achieve the layer exchange crystallization of a-Ge on an insulating substrate.

2. Experimental methods

Ag films were first prepared on alkaline free glass substrates. Subsequently, an interlayer (Al_2O_3, SiO_2, TiO_2, SiN, or GeO_2) was prepared as a diffusion control layer.[20,25] After that, amorphous Ge (a-Ge) films were prepared. The thickness of each Ag or Ge layer was 50 nm and that of each interlayer was 2 nm. The Al_2O_3, TiO_2, and GeO_2 interlayers were formed by preparing Al, Ti, and Ge followed by air exposure for 1 d, respectively. All depositions were carried out at room temperature by radio-frequency (RF) magnetron sputtering (base pressure: 3.0×10^{-4} Pa) using Ar plasma (flow rate: 10 sccm, pressure: 0.25 Pa). The RF power was set to 30 W for Ag, 100 W for SiO_2, and 50 W for other materials. The deposition rates were 32 nm/min for Ge, 35 nm/min for Ag, 12.5 nm/min for Al, 8.7 nm/min for SiO_2, 5 nm/min for Ti, and 6.7 nm/min for SiN. In the sputtering system, the error of the deposition thickness is within 10 %. Finally, the samples were annealed at 300 or 250 °C in N_2 ambient to induce layer exchange (Fig. 1). The resulting samples were evaluated by Nomarski optical microscopy and Raman spectroscopy (spot size: 1 μm, wavelength: 532 nm, detection depth: approximately 10 nm in crystalline Ge). After layer exchange, Ag and interlayers on poly-Ge were etched away using an acidic solution (H_3PO_4: HNO_3: CH_3COOH: H_2O = 16: 1: 1: 2) and a HF solution (HF: 1.5%) for 1 min each. The resulting Ge layers were evaluated by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and electron backscatter diffraction (EBSD).

3. Results and discussion

An interlayer between metal and amorphous semiconductor layers is essential for inducing layer exchange and fabricating a high-quality crystalline semiconductor layer on insulators. First, we employ Al_2O_3 as an interlayer because it is used in the conventional layer exchange including Al-Si,[11] Al-Ge,[20] and Au-Ge.[25]

Figures 2(a)-2(c) show the Nomarski optical micrographs showing the back surface in the samples, observed through transparent substrates. Figure 2(a) shows the bottom Ag layer before annealing. Figure 2(b) shows that dendrite structures appear after 10 h annealing, which is a representative image of the process of layer exchange.[20] However, as shown in Fig. 2(c), those dendrite structures do not grow after annealing for longer than 10 h. The 10-h-annealed sample was evaluated by Raman spectroscopy. The representative results are shown in Fig. 2(d). The dendrite structures, observed from the back surface of the sample, had a peak at around 300 cm^{-1}, corresponding to the vibration mode of Ge-Ge bonds.[26] This result proves that the dendrite structures are crystalline Ge. On the other hand, Ge-Ge peaks were also observed on the front surface of the sample. This result indicates that the top a-Ge layer crystallized during annealing without layer exchange. From these results, the sample structure is illustrated in Fig. 2(d). Since the crystallization temperature of a-Ge is generally above 400 °C,[8,9] this case, the crystallization of the top a-Ge layer at 300 °C, is likely due to the catalytic effect of Ag atoms.[33,34] Therefore, Ag diffusion into the top a-Ge layer is a possible reason why the dendrite growth, i.e., layer exchange, stopped.

This behavior is explained from the perspective of the diffusion coefficient. The diffusion coefficient is defined as

$$D = D_0 \exp\left(-\frac{E}{RT}\right),$$

where D is the diffusion coefficient (m^2 s^{-1}), D_0 is the diffusion constant (m^2 s^{-1}), E is the activation energy of diffusion (kJ mol^{-1}), R is the gas constant (kJ mol^{-1} K^{-1}), and T is the absolute temperature (K). Here, D_0 and E vary between materials where the atoms diffuse. Therefore, D is determined by the material used and the growth temperature. In conventional layer exchange systems (Al-Ge and Au-Ge), the D of metal atoms in Ge (D_{metal}) is smaller than that of Ge atoms in metals (D_{Ge}).[32,35,36] The Ag-Ge system has an opposite property: D_{metal} is larger than D_{Ge}.[32,36] These findings suggest that layer exchange occurs in the system where $D_{\mathrm{metal}} < D_{\mathrm{Ge}}$. We note that D is determined in crystalline Ge or metals. In MILE, metals diffuse into a-Ge and Ge into the grain boundaries of metals.[13] There is an assumption that the magnitude relation of D remains unchanged against the crystal state. According to the discussion, if an interlayer material blocks Ag but allows Ge to pass, the layer exchange between Ag and Ge layers is likely to occur despite $D_{\mathrm{metal}} > D_{\mathrm{Ge}}$. We therefore explored the interlayer material between Ag and Ge layers for completing layer exchange.

We employed SiO_2, TiO_2, SiN, or GeO_2 as an interlayer material. As shown in Figs. 3(a) and 3(b), when the interlayer was SiO_2 or TiO_2, dendrite growth stopped. This results in the insufficient coverage of Ge on the substrate as is the case of the Al_2O_3 interlayer. As shown in Fig. 3(c), when the interlayer was SiN, the sample remained unchanged after annealing. This result suggests that the 2-nm-thick SiN layer suppressed the diffusion of both Ge and Ag atoms. Figure 3(d) shows that, when the interlayer was GeO_2, Ge and Ag were mixed without layer exchange. The mixed structure was determined by the naked eye and Nomarski optical microscopy: both sides of the sample showed the same color and morphology. This result is the same as that observed in the sample without an interlayer. Thus, Ag and Ge atoms rapidly passed through the 2-nm-thick GeO_2 layer. We varied the thickness of the interlayer from 1 to 5 nm; however, the layer exchange was not achieved. From these results, we conclude that it is difficult to selectively suppress Ag diffusion into Ge only by changing the interlayer material.

As we mentioned above, the diffusion coefficient D also depends on the growth temperature T. In addition, its dependence is related to the activation energy E, which depends on the kind of material. To suppress Ag diffusion into Ge, we therefore lowered the growth temperature from 300 to 250 °C for samples with different interlayers. The results are shown in Fig. 4. As shown in Figs. 4(a), 4(c), and 4(d), when the interlayer was Al_2O_3, TiO_2, or SiN, growth morphologies were almost the same as those obtained at 300 °C. On the other hand, when the interlayer was SiO_2 or GeO_2, dendrite growth was completed and covered the entire substrate as shown in Figs. 4(b) and 4(e). These results suggest that the layer exchange was completed because the SiO_2 and GeO_2 interlayers well suppressed Ag diffusion into Ge at 250 °C. Thus, the Ag-induced layer exchange growth of a-Ge was achieved by modulating both the interlayer material and the growth temperature.

After removing the top-Ag layers in the layer-exchanged samples, the crystal quality of the resulting Ge layers was evaluated. As shown in Fig. 5(a), the Ge layers have Ge-Ge peaks whose positions were the same as that of the bulk-Ge substrate. This result suggests that the Ge layers had no stress. The full widths at half maximum (FWHMs) of the Ge layers were relatively small (4.6 cm^{-1}),8,21,26) indicating good crystallinity. Figures 5(b) and 5(c) show that the Ge layers cover the glass substrates. The cracks in the Ge layers correspond to the collisions of the grown dendrites, which became obvious during Ag etching. The sample prepared with a GeO_2 interlayer has small Ge islands on the surface [Fig. 5(b)], which usually appear in layer-exchanged Si [10] and Ge.[23] In contrast, the sample with a SiO_2 interlayer has a smooth surface without Ge islands [Fig. 5(a)]. For the latter sample, Ge islands are considered to be removed together with Ag by wet etching likely because of the poor interface adherence between the Ge islands and the SiO_2 interlayer.[5] As a result of the EDX measurement, the Ag concentration in the Ge layers was lower than the detection limit (1%), attributed to the low solubility of Ag in Ge.[32] Figures 5(d) and 5(e) show that the grain size of the Ge layers in both samples is approximately a few μm. This grain size is two orders larger than that of conventional SPC-Ge;[8,9] however, it is smaller than that of the Ge layers obtained by Al- and Au-induced layer exchange.[20,25] Further optimization of growth conditions is necessary to improve the crystal quality of the Ge layer obtained by Ag-induced layer exchange.

4. Conclusions

We focused on Ag as a catalytic metal for the MILE growth of a-Ge. We found that the layer exchange between Ag and Ge was not simple because Ag diffused into Ge so fast that it crystallized the top a-Ge layer before layer exchange. By selecting appropriate interlayers (SiO_2 and GeO_2) between the Ge and Ag layers and by lowering the growth temperature from 300 to 250 °C, we achieved a complete layer exchange growth of a-Ge on a glass substrate. These findings are essential for understanding the layer exchange mechanism and for fabricating high-quality semiconductor thin films on insulating substrates.

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Figure Captions

Fig. 1. (Color online) Schematic of the Ag-induced layer exchange crystallization of a-Ge on a glass substrate.

Fig. 2. (Color online) Characterization of the sample with an Al_2O_3 interlayer annealed at 300 °C. (a)-(c) Nomarski optical micrographs obtained from the back surface of the samples. (d) Raman spectra obtained from the front and back surfaces of the sample annealed for 10 h. The expected sample structure is schematically shown in (d).

Fig. 3. (Color online) Nomarski optical micrographs obtained from the back surface of the samples with a (a) SiO_2, (b) TiO_2, (c) SiN, or (d) GeO_2 interlayer, annealed at 300 °C for 10 h.

Fig. 4. (Color online) Nomarski optical micrographs obtained from the back surface of the samples with a (a) Al_2O_3, (b) SiO_2, (c) TiO_2, (d) SiN, or (e) GeO_2 interlayer, annealed at 250 °C for 100 h.

Fig. 5. (Color online) Characterization of the layer-exchanged samples after removing Ag and interlayers. (a) Raman spectra obtained from the front surface of the samples. A spectrum obtained from a bulk Ge substrate is shown for comparison. The FWHMs of the Ge-Ge peaks are shown for each spectra. (b, c) SEM images of the Ge layers where the samples are tilted by 70°. (d, e) EBSD images of the Ge layers in the normal direction, corresponding to the regions framed by white squares. The coloration indicates the crystal orientation according to the legend inserted in (e).