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Low temperature (250 °C) crystallization of amorphous Ge thin film on insulator through Ag-induced layer exchange

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Abstract

Polycrystalline Ge thin films are fabricated on glass substrates at 250 °C by using Ag as a catalytic metal for metal induced layer exchange crystallization.

1. Introduction

Ge-on-insulators are essential for high-speed thin-film transistors and high-efficiency solar cells. For these applications, methods to fabricate Ge thin films on insulators have been widely studied. Metal-induced layer exchange, using Al or Au as a catalyst, is one of the promising methods to form highly (111)-oriented and large-grained Ge thin films on insulators at low temperatures [1-3]. However, there are some problems: Al atoms remain in the resulting Ge films, reaching its solubility limit (~10^{20} cm^{-3}); Au is unusable for large-area devices because it is expensive.

We therefore focus on Ag as an alternative catalytic metal, which is not as expensive as Au and has a very low solubility in Ge (~10^{5} cm^{-3} at 250 °C) [4]. In this study, we investigate the Ag-induced layer exchange for fabricating a high-quality Ge thin film on an insulating substrate.

2. Experimental Procedures

Ag films were first prepared onto alkaline free glass substrates. Subsequently, an interlayer (Al_2O_3, SiO_2, TiO_2, SiN, and GeO_2) was prepared for inducing layer exchange. After that, amorphous Ge (a-Ge) films were deposited. The layer thicknesses of Ag and a-Ge were 50 nm each, and that of the interlayers was 2 nm. Al_2O_3, TiO_2, and GeO_2 interlayers were formed by depositions of Al, Ti, and Ge, followed by air exposure for 1 day. All depositions were carried out at room temperature using a radio-frequency magnetron sputtering method. Finally, the samples were annealed at 300 °C or 250 °C in a N_2 ambient to induce layer exchange (Fig. 1). These samples were evaluated using Nomarski optical microscopy, Raman spectroscopy, and energy dispersive X-ray (EDX) analysis. After Ag and oxide layers on the Ge layer were etched away using an acidic solution (H_3PO_4:HNO_3:CH_3COOH:H_2O=16:1:1:2), the samples were evaluated using scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD).

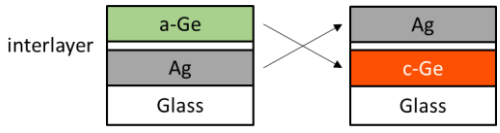

Fig. 1. Schematic of the Ag-induced layer exchange crystallization of amorphous Ge.

3. Results and Discussion

We explored interlayer materials for Ag-induced layer exchange. At first, we tried Al_2O_3, which is used for conventional layer exchange [1-3,5]. As shown in Fig. 2(a)-(c), although we see dendrite-like structures suggesting the process of layer exchange, the dendrite growth has stopped. Raman measurements revealed that the dendrite-like structures are crystalline Ge, while the top Ge layer is also crystallized, as representatively shown in Fig. 2(d). These results suggest that the Ag atoms diffused to the top a-Ge layer and crystallized the a-Ge, which stopped layer exchange. Therefore, it is important to choose an interlayer material which blocks Ag while allowing Ge passage.

We next attempted to use SiO_2, TiO_2, SiN, or GeO_2 as an interlayer material. As shown in Fig. 3(a) and 3(b), when the interlayer is SiO_2 or TiO_2, the lateral growth of crystalline

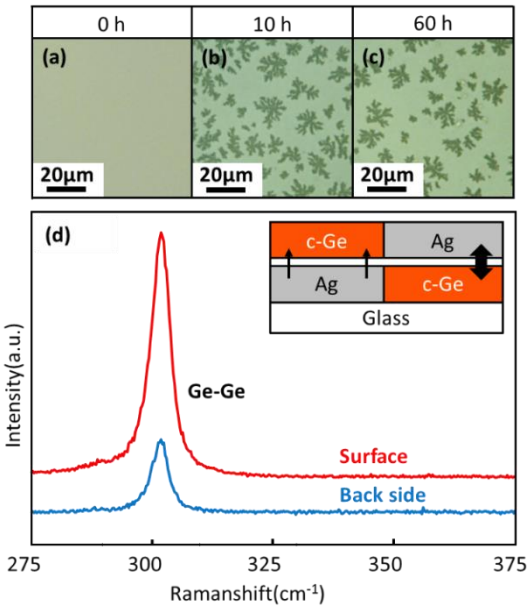

Fig. 2. Characterization of the sample with an Al_2O_3 interlayer annealed at 300 °C. (a)-(c) Nomarski optical micrographs obtained from the back side of the samples. (d) Raman spectra obtained from the surface and back sides of the sample annealed for 60 h. The expected sample structure is schematically shown.

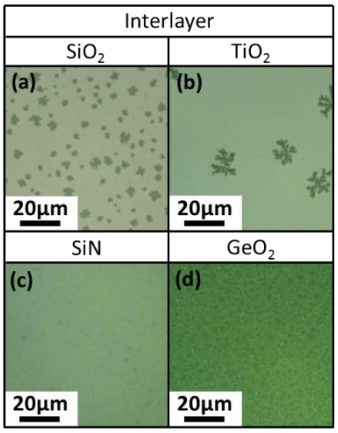

Fig. 3. Nomarski optical micrographs obtained from the back side of the samples with a SiO_2, TiO_2, SiN, or GeO_2 interlayer, annealed at 300 °C for 10 h.

Ge stopped, resulting in the insufficient coverage of Ge on the substrate as is the case in the Al_2O_3 interlayer. As shown in Fig. 3(c), when the interlayer is SiN, Ge crystallization, i.e., Ge diffusion to Ag, is not observed. As shown in Fig. 3(d), when the interlayer is GeO_2, Ge and Ag are mixed without layer exchange. From these results, we conclude that it is difficult to selectively suppress Ag diffusion to Ge only by changing the interlayer material.

Since diffusion coefficients strongly depend on temperature, we lowered the annealing temperature from 300 °C to 250 °C to suppress the Ag diffusion. The results are shown in Fig. 4. As shown in Fig. 4(a), 4(c), and 4(d), when the interlayer is Al_2O_3, TiO_2, or SiN, the growth morphology is the same as that obtained by the 300 °C annealing. On the other hand, a complete layer exchange is confirmed as shown in Fig. 4(b) and 4(e) for samples with a SiO_2 or GeO_2 interlayer. This means that Ag-induced layer exchange of a-Ge is possible by modulating both the interlayer material and annealing temperature.

After the top Ag layers of the layer-exchanged samples were removed, the crystal quality of Ge layers were evaluated. As shown in Fig. 5(a) and 5(b), Ge thin films uniformly cover glass substrates. As the result of EDX measurement, Ag concentration in the Ge was lower than the detection limit (1%). Fig. 5(c) shows Ge-Ge peaks at 300 cm^{-1} for each sample. Their full widths at half maximum (FWHMs) are relatively small [1-3], indicating the good crystallinity of Ge formed through Ag-induced layer exchange. Fig. 5(d) and 5(e) show that the grain size of both Ge layers is approximately a few μm. Although the grain size is smaller than that of conventional Ge layers obtained by Al- or Au-induced crystallization, the hole concentrations were as low as the order of 10^{17} cm^{-3}.

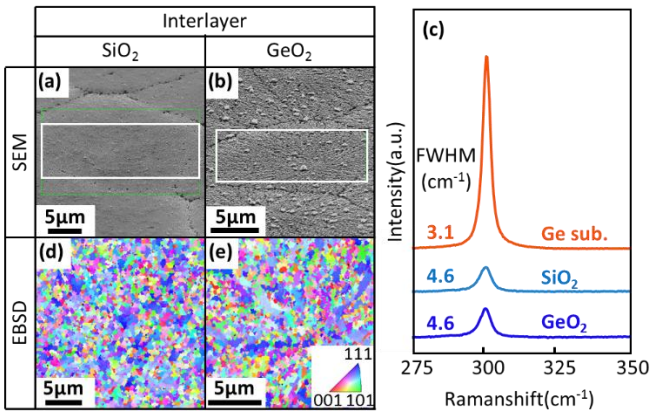

Fig. 5. Characterization of the layer-exchanged samples after removing the top Ag layers. (a),(b) SEM images of the Ge layers where the samples are tilted by 70°. (c) Raman spectra. A spectrum obtained from a bulk Ge substrate is shown for comparison. (d),(e) EBSD images in the normal direction where coloration indicates crystal orientation according to the legend.

4. Conclusion

We focused on Ag as a catalytic metal on metal induced layer exchange crystallization of a-Ge. We investigated the effects of interlayer materials and annealing temperature on the layer exchange. By combining appropriate interlayers (GeO_2 or SiO_2) and annealing temperature (250 °C), we succeeded in making uniform Ge thin films on grass substrates through layer exchange crystallization. The detailed crystal quality and the electrical properties are discussed in the presentation.

References

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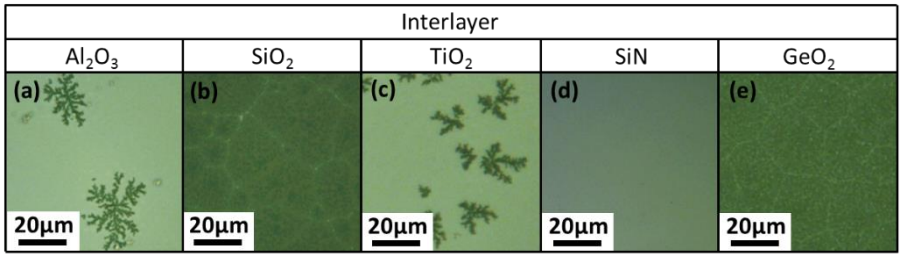

Fig. 4. Nomarski optical micrographs obtained from the back side of the samples with an Al_2O_3, SiO_2, TiO_2, SiN, or GeO_2 interlayer, annealed at 250 °C for 100 h.