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Low-Temperature Sb-Induced Layer Exchange Crystallization for Slef-Limiting Formation of n-Type Ge/Insulator

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Abstract

Low-temperature (≤500°C) formation of n-type crystalline Ge on insulator is desired to merge optical devices onto large-scale integrated circuits. To achieve this, layer-exchange crystallization using a-Ge/Sb stacked structures is investigated. Annealing (450°C, 20 h) of a stacked structure with a-Ge/Sb film thicknesses of 100/100 nm results in layer exchange growth of Ge. However, thermal evaporation of Ge together with Sb has occurred. To solve this problem, a-Ge/Sb film thicknesses are modulated to 100/50 nm. This enables formation of n-type crystalline Ge without Ge evaporation at a low-temperature of 400°C.

1. Introduction

A technique for low temperature (≤500°C) formation of n-type crystalline Ge films on insulator should be developed to achieve the next-generation large-scale integrated circuits (LSI), where optical functions are merged. This is because n-type Ge shows high-efficiency optical functions owing to high electron population in the Γ band.

To obtain crystalline Ge films on insulator at low-temperatures, solid-phase crystallization (SPC) [1] and metal-induced layer-exchange crystallization (MIC) techniques, e.g., Al-induced crystallization (AIC) [2,3] and Au-induced crystallization (GIC) [4], have been developed. However, SPC of Ge results in formation of small grains (~200 nm). On the other hand, MIC enables formation of large grains (~2 μm). In addition, by combining inter-diffusion control between catalyst-metal/Ge, orientation-controlled very large grains (≥50 μm) are achieved. However, all of the films grown by previously-reported MIC show p-type conduction, due to residual Al atoms for AIC and vacancy-related defects for GIC.

In the present study, we investigate MIC using a group V element (Sb) as a catalyst. Formation of n-type Ge on insulator is realized through layer-exchange crystallization at a low temperature (400°C) by a-Ge/Sb thicknesses modulation.

2. Experiments and Results

The sample structure is illustrated in Fig 1. In the experiment, fused-quartz (amorphous SiO_2) chips were utilized as substrates. Stacked structures of a-Ge (thickness: 100 nm)/ Sb (thickness: 50, 100 nm) were formed on the substrates. The samples were annealed at 300°C−500°C in N_2 to induced crystallization. The grown layers were analyzed by Nomarski optical microscopy, Auger electron spectroscopy (AES), and micro-probe Raman spectroscopy.

The Raman spectra of samples (a-Ge/Sb thickness: 100/100 nm) before and after annealing at 300°C (100 h), 400°C (20 h), and 450°C (20 h) are shown in Fig. 2. Here, the measurements were performed from the back-side of the samples through transparent quartz substrates, as well as from the top-side of the samples. Before annealing, a peak due to Sb-Sb bonding in crystalline Sb is observed at ~150 cm^{-1} from the back-side. In Raman spectra observed from the back-side, with increasing annealing temperature, the intensities of the Sb-Sb peaks decrease, and a large peak due to Ge-Ge bonding in crystalline Ge appears at ~300 cm^{-1} after annealing at 450°C. On the other hand, in Raman spectra observed from the top-side, a large Sb-Sb peak together with a Ge-Ge peak is observed at 450°C, which suggests movement of Sb from the bottom layer to the top layer.

The concentration profiles in samples were analyzed by AES. The results of the samples (a-Ge/Sb thickness: 100/100 nm) before and after annealing at 400°C (20 h) and 450°C (20 h) are shown in Figs. 3(a)−3(c). Before annealing, a stacked structure of Ge/Sb is observed [Fig. 3(a)]. After annealing at 400°C, the Ge/Sb interface becomes broad [Fig. 3(b)]. After annealing at 450°C, Sb and Ge become dominant constituents in the top and bottom layers, respectively [Fig. 3(c)]. This indicates layer-exchange. The results of Raman and AES measurements evidence the layer-exchange growth by annealing at 450°C (20 h). However, as shown in Fig. 3(c), the total film thickness of the annealed sample (450°C, 20 h) is decreased to about one third of the initial thickness, which is due to thermal evaporation. Since evaporation is not observed in SPC of pure Ge at 450°C [5], the present result suggests that evaporation of Ge is induced by high-concentration Sb atoms.

In order to suppress the thermal evaporation, decrease in annealing temperature should be helpful. Thus, long time annealing (200 h) at a low temperature (400°C) was examined. The concentration profiles in a sample (a-Ge/Sb thickness: 100/100 nm) after annealing (400°C, 200 h) are shown in Fig. 4(a), which indicates that layer-exchange proceeds compared with the short time annealing result (20 h) [Fig. 3(b)]. However, thermal evaporation of Sb and Ge occurs for this sample. In addition, an unreacted Sb layer remains at the bottom due to the insufficient layer-exchange reaction.

To decrease the unreacted Sb layer, we examine thinning of the initial Sb layer. The concentration profiles in a sample (a-Ge/Sb thickness: 100/50 nm) after annealing (400°C, 200 h) are shown in Fig. 4(b). This indicates that the unreacted Sb layer at the bottom is significantly decreased by thinning of the initial Sb layer. In addition, interestingly, although thermal evaporation of Sb occurs, evaporation of Ge is significantly suppressed, which shows that this reaction is a self-limiting process depending on the Sb concentration. The thermo-electromotive-force measurements indicated n-type conduction of the grown layer. An EBSD image of the grown layer is also shown in Fig. 4(b). The grain sizes (1-2 μm) are almost the same as p-type Ge obtained by AIC and GIC without inter-diffusion control. These results cause an expectation that orientation-controlled very large n-type Ge grains will be obtained by combining inter-diffusion control.

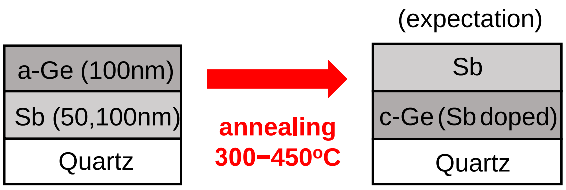

Fig.1. Schematic sample structure.

3. Conclusion

The film-thickness-modulated Sb-induced layer exchange crystallization of Ge on insulator has been developed. Self-limiting formation of n-type Ge without Ge evaporation is achieved at a low temperature (400°C) by modulation of a-Ge/Sb thicknesses to 100/50 nm. This technique will facilitate realization of advanced LSI combined with optical functions.

References

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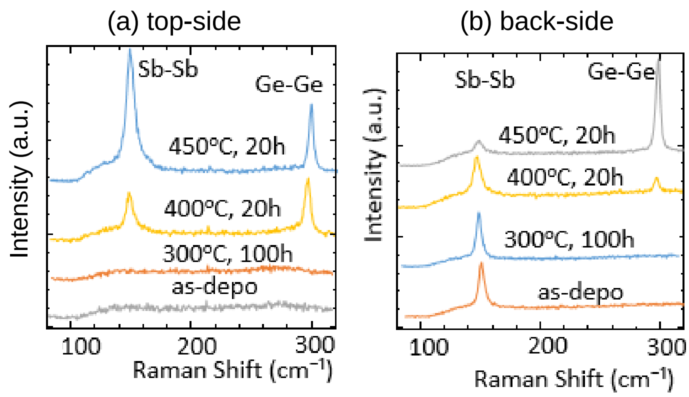


Fig.2. Raman spectra obtained from top-side (a) and back-side (b) of samples before and after annealing. Initial a-Ge/Sb film thicknesses are 100/100 nm.

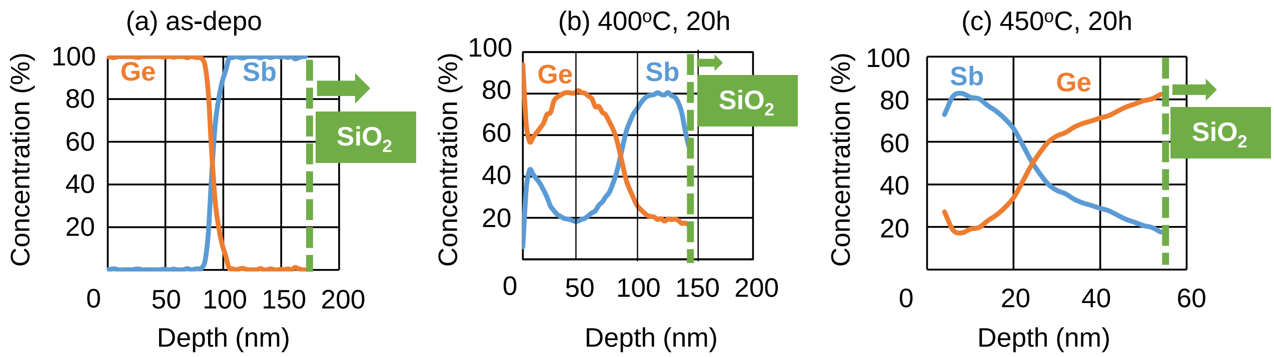
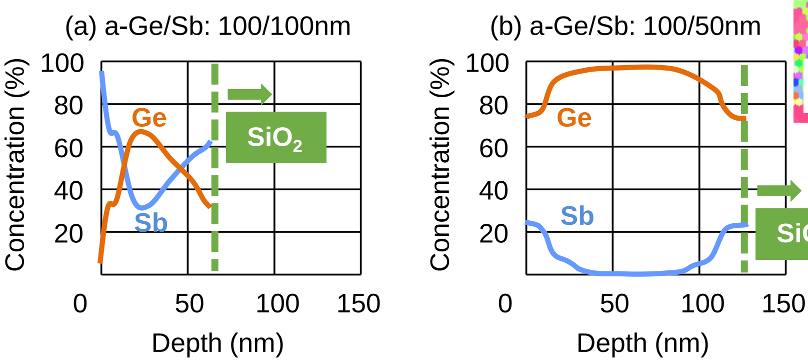


Fig.3. In-depth profiles of Ge and Sb concentrations in samples before and after annealing. Initial a-Ge/Sb film thicknesses are 100/100 nm.



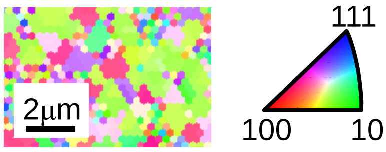


Fig.4. In-depth profiles of Ge and Sb concentrations in samples before and after annealing (400°C, 200 h). Initial a-Ge/Sb film thicknesses are 100/100 (a) and 100/50 nm (b). An EBSD image of a sample (100/50 nm) is also shown in (b)