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Low-Temperature Bi-Induced Layer Exchange Crystallization for Formation of n-Type Ge on Insulator

Xiangsheng Gong, Sen Liu, Hongmiao Gao, and Taizoh Sadoh
Department of Electronics, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan
Phone: +81-92-802-3737 , E-mail : sadoh@ed.kyushu-u.ac.jp

Abstract

Low-temperature (≤500ºC) formation of n-type crystalline Ge (free electron concentration: >1×10^{19} cm^{-3}) on insulator is desired to merge optical devices onto large-scale integrated circuits. To achieve this, layer-exchange crystallization using a-Ge/Bi stacked structures is investigated. Annealing (≥270ºC, 20 h) of a-Ge/Bi stacked structures triggers layer exchange growth of Ge. The electrical properties of grown films significantly depend on the annealing temperature. By selecting an annealing temperature of 300°C, n-type Ge (free electron concentration: ~7×10^{19} cm^{-3}) is realized.

1. Introduction

A low temperature (≤500°C) growth technique of n-type Ge (free electron concentration: >1×10^{19} cm^{-3}) on insulator is necessary to realize the next-generation large-scale integrated circuits (LSIs), where optical functions are merged. This is because n-type Ge (free electron concentration: >1×10^{19} cm^{-3}) shows high-efficiency optical functions owing to high electron population in the Γ band [1].

To achieve crystalline Ge films on insulator at low-temperatures, various techniques, e.g., solid-phase crystallization (SPC) and metal-induced layer-exchange crystallization (MIC), have been developed [2]. Among these techniques, MIC enables formation of orientation-controlled large grains (≥50 μm), by combining with a nucleation control technique [2]. However, most of the films grown by MIC techniques show p-type conduction, due to residual metals and vacancy-related defects in grown layers. We previously reported MIC using a group V element (Sb) and obtained n-type Ge [3]. However, the free electron concentration was low (~2×10^{17} cm^{-3}).

In the present study, we investigate MIC using another group V element (Bi) as a catalyst. Formation of n-type Ge with a high free electron (~7×10^{19} cm^{-3}) is realized by selecting the annealing temperature (~300°C).

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)/Bi (thickness: 100 nm) were formed on the substrates. The samples were annealed at 250°C−350°C for 20 h in N_2 to induced crystallization. The grown layers were analyzed by micro-probe Raman spectroscopy, Auger electron spectroscopy (AES), and Hall effects measurements.

The Raman spectra of samples before and after annealing at 250°C−300°C 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, no Raman peak is detected. After annealing at 250°C, a small peak due to Ge-Ge bonding in crystalline Ge appears at ~300 cm^{-1} from the back-side, which suggests initiation of layer-exchange growth. For annealing temperatures above 270°C, the Raman peaks due to Ge-Ge bonding observed from the back-side become very large. On the other hand, the Raman peaks are also observed from the top-side after annealing at temperatures above ~270°C.

To reveal the phenomena, composition profiles for samples before and after annealing were analyzed using AES. The results are summarized in Fig. 3, where the x-axes are sputtering time. Before annealing, a stacked structure of Ge and Bi is formed, as shown in Fig. 3(a). Fig. 3(a) indicates that the region of Ge is wider than that of Bi. This is attributed to that the sputtering rate of Bi is significantly larger compared with Ge. The composition profiles after annealing at 250ºC are almost the same as those before annealing. On the other hand, after annealing at 270ºC, the Bi concentration is increased to ~30% in the surface region (etching time < 100 s), while the Ge concentration is increased to ~100% near the bottom interface (etching time: ~200 s). After annealing at 300ºC, the concentration of Ge in the bottom region (etching time: 100−200 s) is increased to above ~80%. These results indicate that the layer-exchange reaction is triggered by annealing at temperatures above 270°C. However, a large amount of Ge atoms (~70%) remain in the surface region. These results agree with the Raman spectra obtained from the top-side after annealing at temperatures above 270°C, where peaks due to Ge-Ge bonding are observed. We speculate that Bi atoms, which moved to the surface regions, are partially evaporated during the annealing, and thus, the surface region becomes Ge-rich.

The electrical properties of the grown layers are investigated by Hall effect measurements. The results are summarized as a function of the annealing temperature in Fig. 4(a). The conductive types of the grown layers depend on the annealing temperature. For annealing temperatures between 250−270°C, the grown layers show p-type, where the carrier concentrations are almost

constant (~2×10^{19} cm^{-3}), and the mobility decreases from ~140 to ~30 cm^2/Vs with increasing annealing temperature. At an annealing temperature of ~300°C, the grown layers show n-type with the carrier concentration of ~7×10^{19} cm^{-3} and the mobility of ~5 cm^2/Vs. For annealing temperatures of ~350°C, the grown layers again show p-type, which is probably due to phase separation of Ge and Bi by eutectic reaction.

The free electron concentration obtained at 300°C in the present study is compared with thermal equilibrium solid-solubility of Bi in Ge in Fig. 4(b), where the broken line shows extrapolation of reported values of Bi solubility [4]. It is found that the free electron concentration obtained in the present study is significantly higher compared with the solubility of Bi at 300°C. Further study is needed to reveal the origin of the high free electron concentration (~7×10^{19} cm^{-3}).

3. Conclusion

Low-temperature Bi-induced crystallization of Ge on insulator has been developed. Layer exchange reaction is initiated by annealing above ~270°C. The electrical properties of the grown layers significantly depend on the annealing temperature. As a result, n-type Ge (free electron concentration: ~7×10^{19} cm^{-3}) is obtained at ~300°C. This technique will be useful for realization of advanced LSI combined with optical functions.

References

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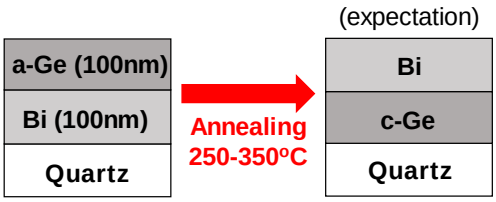


Fig.1. Schematic sample structure.

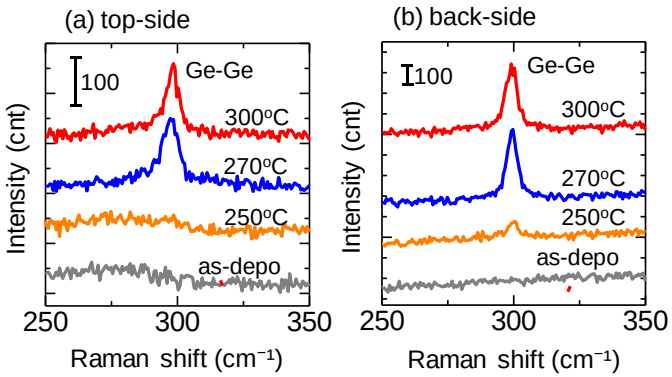


Fig.2. Raman spectra obtained from top-side (a) and back-side (b) of samples before and after annealing.

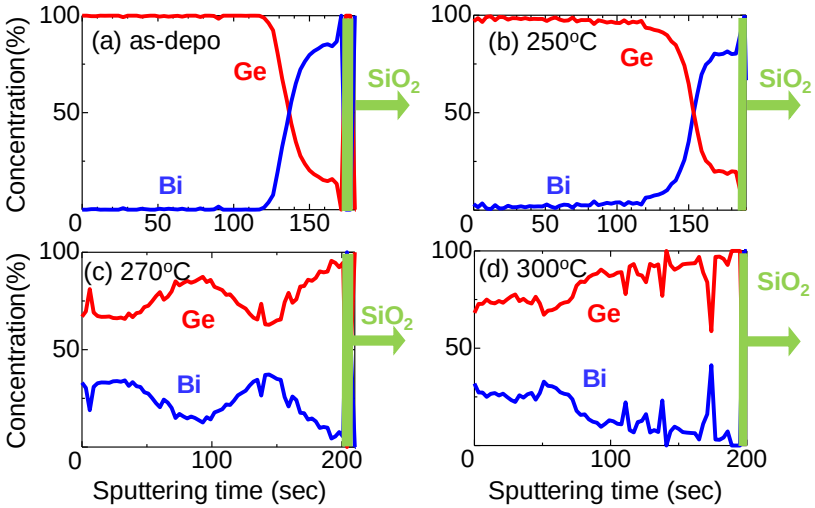
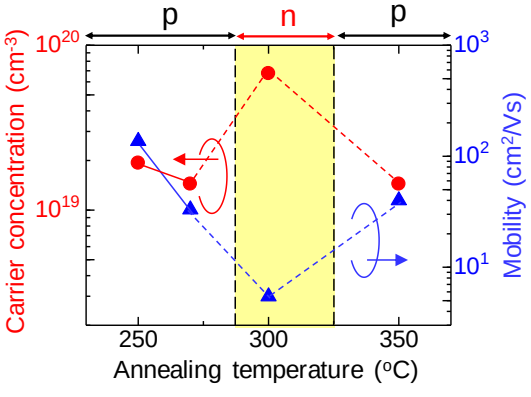


Fig.3. In-depth profiles of Ge and Bi concentrations in samples before and after annealing.



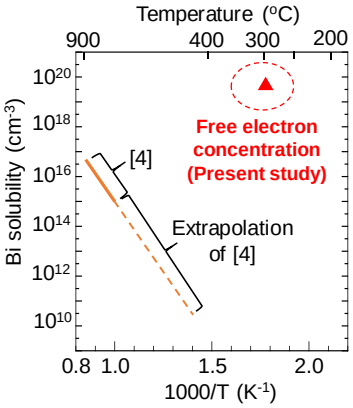


Fig.4. (a) Annealing temperature dependence of carrier concentration and mobility in grown films and (b) comparison between free electron concentration and thermal equilibrium solid-solubility of Bi in Ge.