Thickening of Al-induced Layer-exchanged Si$_{1-x}$Ge$_x$ Film for Improving Thermoelectric Output Power

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Abstract

Al-induced layer exchange enabled us to form thick Si$_{1-x}$Ge$_x$ (x: 0–1) layers up to 1000 nm. For Si and Ge, the grain size decreased with increasing thickness, while it was not remarkable for Si$_{0.4}$Ge$_{0.6}$. The SiGe provided high power factor even in thick films, reaching 850 µW mK^{-2}. Further, we demonstrated sequential layer exchange and achieved 2000-nm-thick SiGe, which exhibited the output power density of 37 nW cm^{-2} at room temperature.

1. Introduction

The SiGe alloy is an old, reliable, and tested thermoelectric material. If a SiGe layer can be formed onto plastic, it will be possible to create flexible thermoelectric devices with high performance. Recently, we developed the Al-induced layer exchange (ALILE) of SiGe and synthesized SiGe layers on glass substrates at ≤ 400 °C in the whole composition range, and investigated its thermoelectric properties [1,2]. However, as thermoelectric generators (TEGs) for sensing applications, higher output power is required. The output power of the thermoelectric conversion element is proportional to the volume. Therefore, the most reliable approach to high output is thickening film. In this study, we clarify the upper limit of ALILE-SiGe thickness and the thickness dependence of thermoelectric properties of ALILE-SiGe for the first time. Further, we demonstrated sequential LE, resulting in the highest output power density.

2. Experiment procedures

We prepared Al and amorphous (a-) Si$_{1-x}$Ge$_x$ (x: 0, 0.6, and 1) layers (t: 50, 300, 500, and 1000 nm each) on a SiO$_2$ glass substrate at room temperature (RT) by using radiofrequency (RF) magnetron sputtering (base pressure 3.0×10^{-4} Pa) with an Ar plasma. The RF power was set to 50 W. The samples were then annealed in an N$_2$ ambient for 30 h at 450 °C (Si), 400 °C (SiGe), and 350 °C (Ge). The Al layer was then etched away with an HF solution (HF 1.5%). Following the same procedure, the Si$_{0.4}$Ge$_{0.6}$ layer with t = 1000 nm was formed on a Si$_{0.4}$Ge$_{0.6}$ layer with t = 1000 nm.

3. Results and Discussion

The Raman spectra in Fig. 1(a) show the peaks corresponding to Si–Si, Si–Ge, and Ge–Ge vibration modes, which indicate that crystalline Si$_{1-x}$Ge$_x$ layers form on the substrates for all samples. Figure 1(b) shows that t of the resulting SiGe layer is approximately 1000 nm, as intended. Similar results were obtained for pure Si and Ge. Figure 1(c) shows that the 1000-nm-thick SiGe layer covers almost the entire surface of the substrate though it has some voids. We note that, when t = 2000 nm, the upper amorphous layer was crystallized before the SiGe layer reached the substrate, which inhibited the complete LE. Thus, in the Al-SiGe system under the current growth condition, the upper limit of t is approximately 1000 nm.
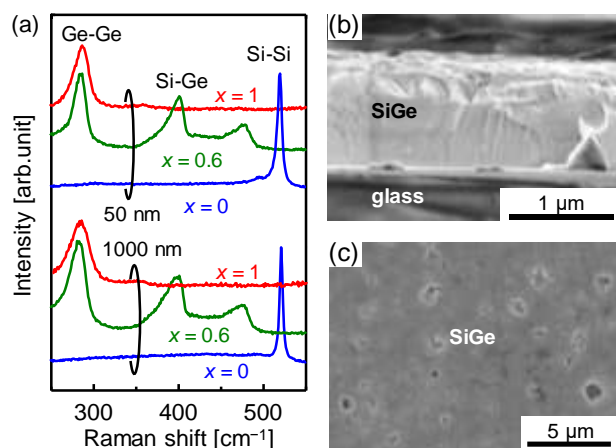
Figure 2 shows that the Si and Ge samples with t = 50 nm

Fig. 1 (a) Raman spectra of the samples after Al removal. (b) Cross-sectional and (c) surface SEM images of a Si$_{0.4}$Ge$_{0.6}$ layer with t = 1000 nm.
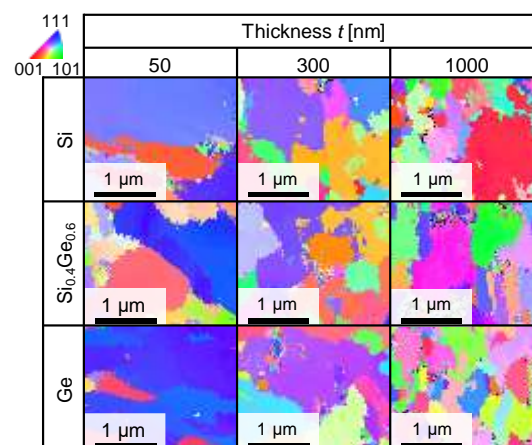

Fig. 2 EBSD images of the SiGe layers with t = 50, 300, 1000 nm

have grains of a several μm, which is an order of magnitude smaller than that of ALILE with a diffusion control layer. This is an advantage as TEGs because nanocrystalline grains scatter phonons and lower thermal conductivity. For Si and Ge, grain size decreases significantly with increasing t. This behavior is because the thicker the film is, the easier the crystal nucleus generate at the Al grain boundary and the higher the nucleation frequency is. The grains of SiGe is smaller than that of Si and Ge for $t = 50$ nm, similar to the case where the diffusion control layer is provided. Owing to this behavior, for SiGe, the decrease in grain size due to the increase in t is not remarkable.

Figure 3(a) shows that the hole concentration p increases with increasing x, while it does not depend on t. This behavior is due to the ALILE feature that p is determined by the solubility limit of Al in $Si_{1-x}Ge_x$. For Si and Ge, the electrical conductivity σ decreases with increasing t (Fig. 3(b)). Considering that grain size decreases significantly with increasing t (Fig. 2), this behavior likely reflects a lower carrier mobility because of the smaller grain size. For $Si_{0.4}Ge_{0.6}$, σ is almost constant for t, likely because the grain size is almost constant for t (Fig. 2). Figure 3(c) shows that the Seebeck coefficient S decreases with increasing x, which is consistent with the basic physical properties of $Si_{1-x}Ge_x$ and the behavior of p (Fig. 3(a)). Figure 3(d) shows that the power factor PF has a t dependence reflecting σ. The highest PF larger than 850 μW $m^{-1} K^{-2}$ was obtained for SiGe with $t = 500$ nm. The PF is the record high value among p-type SiGe obtained at low temperature (< 500 °C).

Figure 4(a) shows that a 2000-nm-thick SiGe layer forms on a glass substrate after Al removal by the sequential LE. Thus, we have demonstrated that the sequential LE of SiGe is possible, meaning in principle that, there is no limit to thickening. Figure 4(b) shows that the PF increases with increasing the measurement temperature, which is similar to the general thermoelectric properties of SiGe [3]. The PF value for $t = 2000$ nm exhibits relatively high value (500 μW $m^{-1} K^{-2}$) at room temperature. Figure 4(c) shows that for each t, the open-circuit voltage is almost consistent with the value calculated from S. The short-circuit current increases with increasing t.
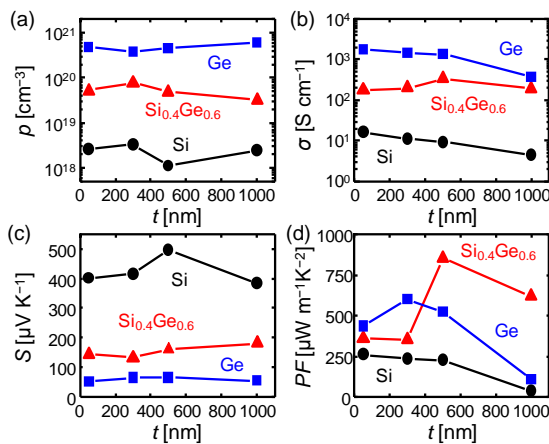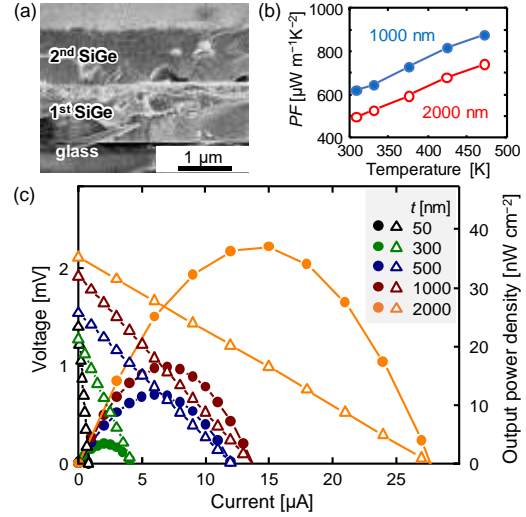

Fig. 4 (a) Cross-sectional SEM image of the resulting sample of sequential LE after Al removal. (b) PF of the SiGe samples for $t = 1000$ and 2000 nm with respect to the measurement temperature. (c) Voltage-current (open triangles) and output power density (solid circles) at RT for the SiGe samples with $t = 50$, 300, 500, 1000, and 2000 nm obtained under a constant temperature difference of 10 K.

The maximum output power density increases with increasing t and reaches 37 nW cm^{-2} for $t = 2000$ nm. This is a high value for environmentally friendly inorganic thin films synthesized below the heat resistant temperature of plastic substrates (400 °C). This result means that a several-cm device can output μW power, which is potentially useful for future wearable sensors.

4. Conclusion

The upper limit of ALILE-SiGe thickness is approximately 1000 nm. We demonstrated that a 2000-nm-thick SiGe layer forms by the sequential LE and it has excellent characteristics as a thermoelectric film while maintaining low process temperatures (≤ 400 °C), meaning in principle that, there is no limit to thickening. ALILE-SiGe provides high PF even in thick films, reflecting the t dependence of σ and S. The maximum power density improves with increasing t, reaching 37 nW cm^{-2}. These achievements will accelerate the realization of thin film TEGs.

References

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Fig. 3 Electrical and thermoelectric properties of ALILE-SiGe (a) p, (b) σ, (c) S, and (d) PF at RT as a function of t.