

Thermoelectric p-type Ge Film Formed by Zn-induced Layer Exchange at 80 °C

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Abstract

Zn-induced layer exchange allowed us to fabricate nanocrystalline Ge on insulators at 80 °C. The Ge layer had a high hole concentration p ($> 10^{20} \text{ cm}^{-3}$) and therefore exhibited a high electrical conductivity σ ($> 200 \text{ S/cm}$). These properties enabled the power factor P to reach 240 and 160 $\mu\text{W/mK}^2$ for Ge on glass and even flexible plastic substrates, respectively. Grain boundary phonon scattering reduced the thermal conductivity to 3 W/mK.

1. Introduction

The SiGe alloy is the oldest, reliable and proven thermoelectric material. If a SiGe layer can be formed on plastic, it will be possible to create flexible thermoelectric devices with high performance. Metal-induced layer exchange (MILE) has attracted interest as a method for lowering the growth temperature T_g of amorphous (a-) Si and Ge thin films on insulators.^[1] We developed the SiGe layer on a heat-resistant plastic (polyimide) and demonstrated high thermoelectric performance by the Al-induced layer exchange (ALILE).^[2] However, because the synthesis temperature was above 300 °C, the types of flexible substrates are strictly limited to engineering plastics. In this study, we report the Zn-induced layer exchange (ZILE) of Ge allowed for nanocrystalline Ge on a plastic substrate at 80 °C, which exhibited high thermoelectric performance.

2. Experiment procedures

We prepared Zn and a-Ge layers (50-nm-thick each) on a SiO₂ glass substrate by RT using radio frequency (RF) magnetron sputtering (base pressure: $3.0 \times 10^{-4} \text{ Pa}$) with an Ar plasma. The RF power was set to be 50 W. Between the two deposition cycles, the Zn film was exposed to air (air-exposure-time (t_{air}): 0–1 h) to form a native Zn-oxide layer, which acted as a diffusion-limiting layer. The samples were then annealed at T_g of 80–200 °C in an N₂ ambient chamber until exchange of the layer was complete. The Zn and oxide layers were then etched away with an HCl solution (HCl: 36%) for 20 s. Following the same procedure, a Ge layer was fabricated at 80 °C on a flexible polyimide substrate (125- μm thick, Du Pont-Toray Co., Ltd.) pre-covered with a sputtered SiO₂ layer (100-nm thick).

3. Results and Discussion

The areas of dark contrast in Figs. 1(a)–1(c) show Ge and bright contrast indicates Zn. These images indicate that the Ge atoms diffuse to the back surface and then cover the entire

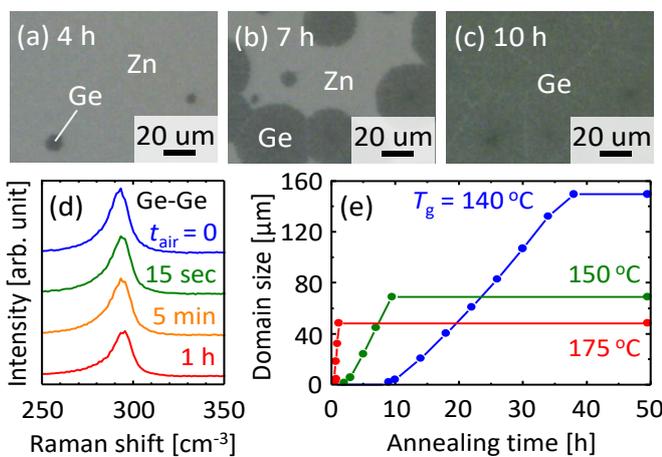


Fig. 1 (a-c) Optical microscope images of the ZILE growth of a-Ge. (d) Raman spectra of the samples ($T_g = 150 \text{ }^\circ\text{C}$) before Zn removal. (e) Annealing-time dependence of the domain size of crystalline Ge derived from the images for $t_{\text{air}} = 5 \text{ min}$.

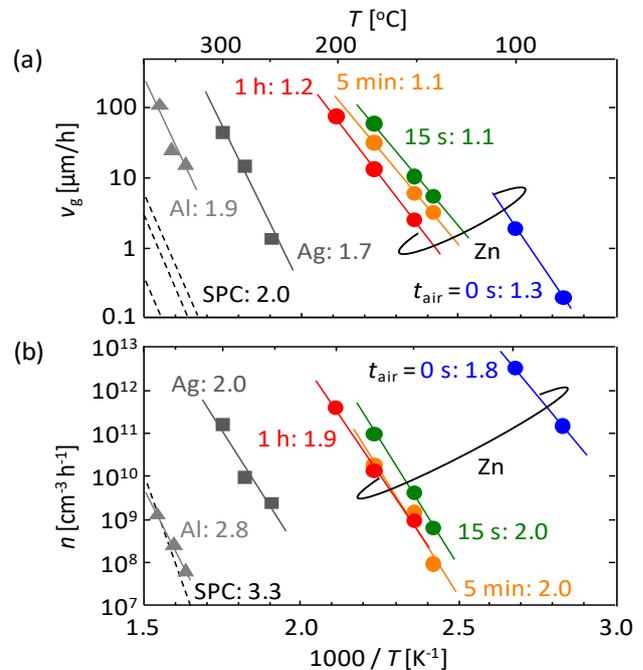


Fig. 2 Growth properties of the ZILE of Ge. Arrhenius plots of the (a) v_g and (b) n determined by the *in-situ* observations. Values indicate the activation energies of (a) E_v [eV] and (b) E_n [eV] obtained from the Arrhenius equation and the slopes of the lines.

surface of the substrate during annealing. Raman peaks near 300 cm^{-1} corresponding to crystalline Ge [Fig. 1(d)] are found for all samples, indicating that poly-Ge layers are formed on glass by ZILE. Fig 1(e) shows the domain size increase with increasing annealing time, which saturate as the layer exchange completed. In addition, n was determined by counting the number of Ge domains per unit area and dividing the number by the thickness of the Ge layer. Both v_g and n for ZILE are far greater than those of SPC and even larger than those of MILE based on Al and Ag catalysts (Fig. 2). We used the Arrhenius equation and the results from Fig. 2, to determine the activation energies of the lateral growth E_v and nucleation E_n . The E_v and E_n of the ZILE samples are much lower than those of the other samples. These results suggest that the diffusion of Ge into Zn is strongly suppressed by the native Zn-oxide interlayer. These properties contributed to the layer exchange at $80\text{ }^\circ\text{C}$ in ZILE-Ge, which is the lowest temperature reported for the layer exchange phenomenon.

Figs. 3(a)–(d) indicate that the actual grain size of the Ge layer is much smaller than the Ge domain size determined by optical microscopy (Fig. 1). All samples showed p-type conduction where p was of the order of 10^{20} cm^{-3} , as shown in Fig. 3(e). Considering that Zn is not a p-type dopant for Ge and a smaller grain size provides higher p (Fig. 3), we attribute the high p to defect-induced acceptors in Ge. The value of σ increases with p [Fig. 3(e)]. The value of S ranged from 60 to $100\text{ }\mu\text{V/K}$ [Fig. 3(f)], which is reasonable for p-type Ge with p of the order of 10^{20} cm^{-3} . The power factor P exhibits a maximum value ($240\text{ }\mu\text{W/mK}^2$) for $t_{\text{air}} = 0\text{ s}$ and $T_g = 80\text{ }^\circ\text{C}$ reflecting the high σ value [Fig. 3(g)]. This sample also exhibited a cross-plane κ of 2.95 W/mK . This κ value is much lower than that of bulk-Ge, likely because of the nanocrystal structure, which induces GB phonon scattering. The dimensionless figure of merit at RT was determined to be 0.024, which is the highest level among the thermoelectric films syn-

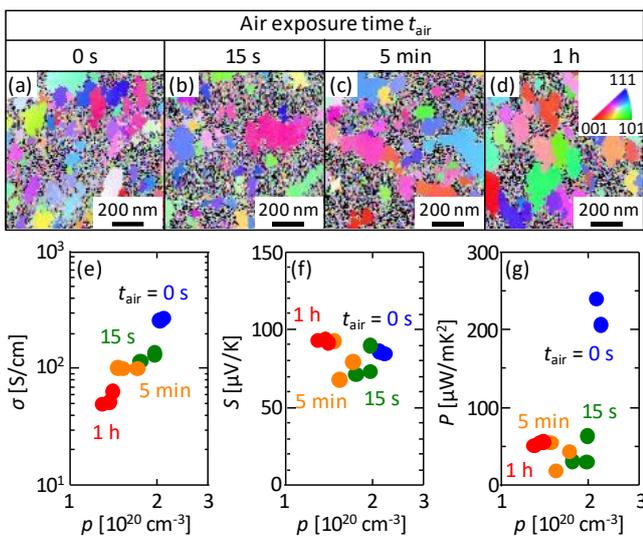


Fig. 3 (a–d) EBSD images of the Ge layers for $t_{\text{air}} = 0\text{ s}$ ($T_g = 80\text{ }^\circ\text{C}$) and $t_{\text{air}} = 15\text{ s}$, 5 min , and 1 h ($T_g = 150\text{ }^\circ\text{C}$), (e) σ , (f) S , and (g) P at RT as a function of p .

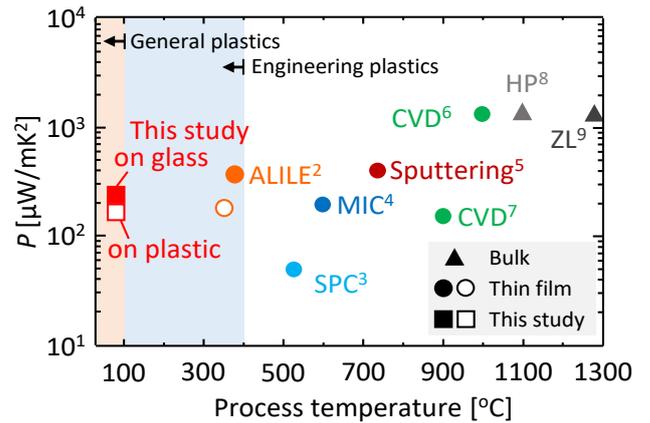


Fig. 4 Power factor of SiGe as a function of process temperature.

thesized below $100\text{ }^\circ\text{C}$. Fig. 4 shows that SiGe generally requires high process temperature to obtain high power factor. The current ZILE technique uses defect-induced acceptors in nanocrystalline Ge to form highly p-doped Ge, resulting in a P of $240\text{ }\mu\text{W/mK}^2$ at a processing temperature of $80\text{ }^\circ\text{C}$, which is compatible with many kinds of plastics. The P value is highest in thermoelectric films synthesized over such a low temperature range. Furthermore, κ in ZILE-Ge is comparable to that of the poly-SiGe layers owing to the nanocrystal structuring.

3. Conclusion

The ZILE growth of a-Ge has the following two features: (i) ultralow temperature growth ($< 100\text{ }^\circ\text{C}$) owing to the strong catalytic effects of Zn; (ii) nanocrystalline Ge formation allowing for high p ($> 10^{20}\text{ cm}^{-3}$) and low κ ($< 3\text{ W/mK}$). With these features, ZILE-Ge simultaneously achieved both high thermoelectric performance and a low thermal budget at the highest level. These achievements will accelerate the realization of thin film thermoelectric elements.

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