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Thin-Film Thermoelectric Generators with $Si_{1-x}Ge_x$ Formed by Layer Exchange

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Abstract

We have studied the fabrication of thermoelectric SiGe thin films using a layer exchange technique with various metal catalysts. Here, we achieve both p- and n-type SiGe at 500 °C using Ag-induced layer exchange. The thermoelectric power factor reaches 1000 μW m^{-1} K^{-2} for n-type, which is the record high value for SiGe formed below 1000 °C. Further, for the first time ever, we demonstrate the thermoelectric generator operation using the low-temperature polycrystalline SiGe layers.

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 generators (TEGs) with high performance. Metal-induced layer-exchange (LE) has attracted interest as a method for lowering the growth temperature of amorphous (a-) Si and Ge thin films on insulators. [1,2] We achieved p-type SiGe with high power factors *PF* (400 μW m^{-1} K^{-2}) at RT in low temperature process (< 500 °C) using metal-induced LE with Zn [3] and Al. [4] Further, we achieved n-type SiGe at 350 °C using Zn: As-induced LE. [5] However, *PF* remained at a very low value (<30 μW m^{-1} K^{-2}). In this study, we review thermoelectric SiGe formed by Metal-induced LE, and report Ag-induced LE allowed for fabricating both p- and n-type SiGe on glass at 500 °C and demonstrate the TEG operation. The resulting n-type SiGe exhibits the highest recorded *PF* (1000 μW m^{-1} K^{-2}) as SiGe formed at low temperature (< 1000 °C).

2. Experiment procedures

We prepared metal layers (Al, Al:B (1% B-doped Al), Ag, Ag:B (10%), Ag:As (10%), Zn, Zn:As (10%)) and an amorphous $Si_{1-x}Ge_x$ (x: 0, 0.15, 0.3, 0.6, 0.8, and 1) layers (50-nm-thick each) on a SiO_2 glass substrate by RT using radio frequency (RF) magnetron sputtering (base pressure: 3.0×10^{-4} Pa) with an Ar plasma. The RF power was set to be 30W for Ag, Ag:B, and Ag:As, and 50 W for Al, Al:B, Zn, Zn:As, and a- $Si_{1-x}Ge_x$. The samples were then annealed at T_g of 80–550 °C for 1-100h in an N_2 ambient chamber until exchange of the layer was complete (Fig.1). The Al, Ag, and Zn layers of the sample after layer exchange were etched away with HF solution (HF: 1.5%), an acidic solution (H_3PO_4: HNO_3: CH_3COOH: H_2O = 16: 1: 1: 2), and an HCl solution (HCl: 36%), respectively.

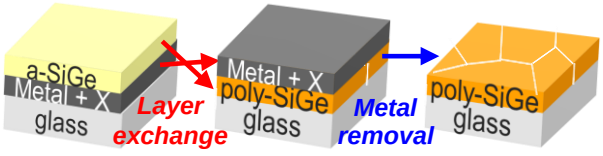

Fig. 1. Schematic of the sample preparation.

3. Results and Discussion

Although the process temperature range of layer exchange varies depending on the metal catalysts and *x*, we succeeded in crystallizing below the heat-resistant temperature of polyimide (500 °C) under all conditions. In particular, Ge crystallization was observed at extremely low temperatures

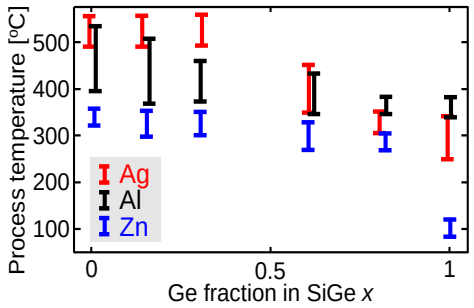

Fig. 2. Process temperature of LE for each metal catalyst.

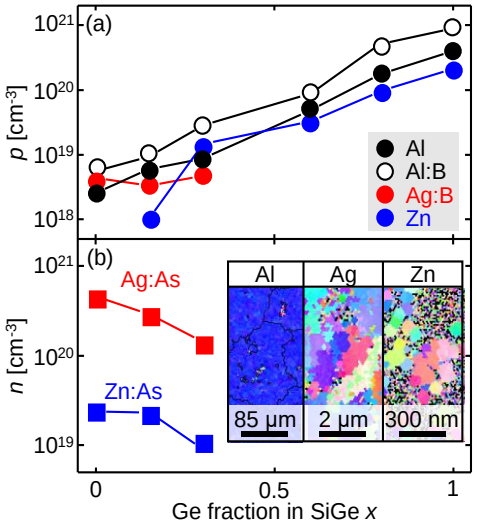

Fig. 3. (a) *p* and (b) *n* of the samples as a function of *x*. EBSD images of the Si samples are also shown in (b).

(80 °C) in Zn-induced LE (Fig. 2). The hole concentration p increased with increasing x due to the solid solubility limit of the p-type metal dopant [Fig. 3(a)]. It was also found that the addition of B in Al increases p. On the other hand, the electron concentration n varied with the metal catalyst and increased with the decrease in x, reflecting the solid solubility limit of As in SiGe [Fig. 3(b)]. In Ag:As-induced LE, a high n of more than 10^{20} cm^{-3} was obtained. The grain size of the $Si_{1-x}Ge_x$ layers was Al > Ag > Zn, and a significant difference was confirmed by the metal catalysts. The thermal conductivity reflects the grain size, and a low value (2.9 W/mK for Ge) was obtained especially in the Zn-induced LE due to the small grain size (< 300 nm).

The Seebeck coefficient $|S|$ of Ag-LE SiGe samples increases with an increasing measurement temperature for all samples [Fig. 4(a)]. This is a typical trend of degenerated semiconductor exhibiting metallic behavior, which is attributed to the high p and n. Fig. 4(b) shows that the PF at RT reaches approximately 230 μW m^{-1} K^{-2} for p-type Si and 1000 μW m^{-1} K^{-2} for n-type $Si_{0.85}Ge_{0.15}$. The PF of the n-type SiGe layer is the highest value for SiGe thin films synthesized at <1000 °C.

Fig. 5(a) shows the measurement setup of the output power of the in-plane π-type TEG fabricated using the p- and n-type $Si_{0.85}Ge_{0.15}$. The open-circuit voltage of 5.0 mV and the short-circuit current of 0.50 μA were obtained at ΔT = 10 K [Fig. 5(b)]. These values were almost consistent with the estimated values (open-circuit voltage: 4.7 mV, short-circuit current: 0.56 μA) from $|S|$ and σ. The maximum output power reaches 1.4 nW at ΔT = 15 K. Considering that the output power is proportional to the volume, thickening the film is the next issue for improving the power.

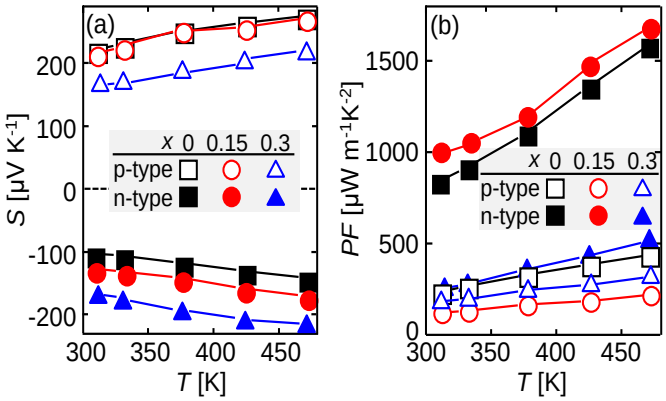

Fig. 4 Thermoelectric properties of $Si_{1-x}Ge_x$ (x=0, 0.15, and 0.3) formed by Ag-LE as a function of measurement temperature T.

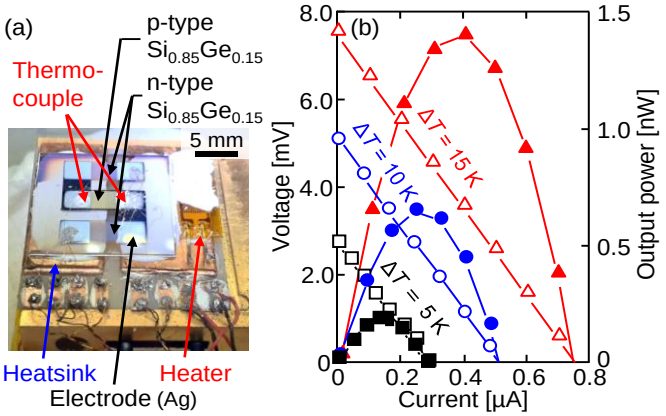

Fig. 5 Thermoelectric measurement of the TEG of the p- and n-type $Si_{0.85}Ge_{0.15}$ (50 nm thick each) formed by Ag-induced LE. (a) Photograph of the TEG ready for the measurement, and (b) Thermoelectric current–voltage and the power-voltage curves of the TEG.

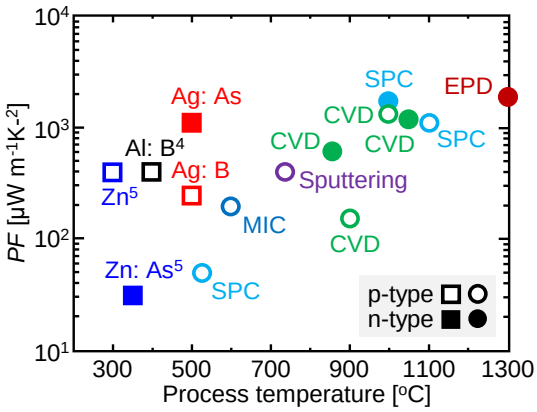

Fig. 6 PF of SiGe thin films as a function of process temperature.

As shown in Fig. 6, SiGe generally requires high processing temperatures to obtain high values of PF. For p-type SiGe, the Al:B- and Zn-induced LE enabled us to achieve both, a high PF (400 μW m^{-1} K^{-2}) and a low processing temperature (≤ 500 °C). Further, the Ag:As-induced LE using provides n-type SiGe with a high PF (1000 μW m^{-1} K^{-2}) even in 500 °C process. Combining with p-type SiGe formed by Al:B- or Zn-induced LE will fabricate the excellent TEGs at low processing temperature.

4. Conclusion

We clarified the crystallinity and thermoelectric properties depending on the metal catalysts in SiGe thin film formed by metal-induced LE. In particular, Ag-induced LE allowed us to fabricate both p- and n-type SiGe on glass at 500 °C. The n-type SiGe exhibited the highest recorded PF (1000 μW m^{-1} K^{-2}) as SiGe formed at low temperature (< 1000 °C). The TEG formed using the SiGe layers output 1.4 nW with ΔT = 15 K at RT even for thin films (50 nm thick). These achievements will accelerate the realization of thin-film TEGs for future micro-energy harvesting.

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