High Temperature Transport Property of B- and P-Doped GeSi Single Crystals Prepared by a Czochralski Method

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B-doped (p-type) and P-doped (n-type) $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals were prepared by a Czochralski (CZ) method. The anisotropy of Seebeck coefficient (α), electrical conductivity (σ) and thermal conductivity (κ) among the [001], [110] and [111] directions was determined and the values were compared with those of polycrystalline materials. The Seebeck coefficient of B-doped specimen in the [111] direction (α_{111}) was the same as that in the [110] direction (α_{110}), and was greater than that in the [001] direction (α_{001}) measured at all temperature. The α_{111} , α_{110} and α_{100} of the P-doped specimens were in agreement above 600 K, but anisotropy of α values was observed below 500 K, ($|\alpha_{001}| > |\alpha_{111}| > |\alpha_{110}|$). No anisotropy of σ and κ was observed in both B- and P-doped specimens. The thermal conductivity of B- and P-doped single crystal specimens were much greater than that of polycrystalline materials.

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1. Introduction

GeSi alloy is a well-known thermoelectric material in the temperature range between 900 and 1200 K.^{1,2)} Many studies have been conducted to lower thermal conductivity and to improve the thermoelectric performance.³⁻⁵⁾ Theoretical calculation suggested that the thermoelectric figure-of-merit values should be improved by the scattering of phonon at grain boundaries.^{6,7)} Previous research showed that fine grained hot pressed GeSi has low conductivity and high figure-of-merit values.⁸⁻¹⁰⁾

Thermoelectric properties of GeSi have been mainly investigated by using arc melted, hot pressed and sintered materials. The thermoelectric properties of GeSi with high Si contents by a Czochralski method (CZ method) has been also reported.⁵⁾ However, it is difficult to make large homogeneous GeSi single crystals because of the significant miscibility gap in the Ge-Si system.¹¹⁻¹³⁾ Therefore, the detailed anisotropy of GeSi alloy has not been well understood. In this paper, homogeneous large GeSi single crystals were prepared by a CZ method. The anisotropy among [100], [110] and [111] directions of thermoelectric properties (Seebeck coefficient, the electrical conductivity, the thermal conductivity) was studied.

2. Experimental

The single crystals of B-doped and P-doped GeSi were prepared by a Czochralski method. Because the composition and the amount of dopant were gradually changed during the growth of single crystal, the composition and the carrier concentration of the obtained specimen were determined by an EPMA analysis and a Hall coefficient measurement, respectively. To obtain the relatively homogeneous specimens, large single crystals (60 mm in diameter) were prepared and was cut into thin sheets (2 mm in thickness). The sheet at a composition of $\text{Ge}_{0.07}\text{Si}_{0.93}$ was used. The single crystal sheet was cut to three sizes ($2 \times 3 \times 12 \text{ mm}^3$, $\phi 10 \times 1.2 \text{ mm}^3$ and $5 \times 5 \times 0.5 \text{ mm}^3$), for measurements of Seebeck coef-

ficient and electrical conductivity, thermal conductivity, and Hall coefficient, respectively.

The electrical conductivity (σ) was measured by a d.c. four-probe method in Ar gas at 300 to 1000 K. The Hall coefficient measurement was carried out by a Van der Paw method in vacuum at room temperature. The Seebeck coefficient (α) was determined from the slope of the linear relationship between thermoelectric power and temperature difference. The thermoelectric power was measured using R-type thermocouples in Ar gas at 300 to 1010 K. Thermal conductivity (κ) was measured by a laser flush method (TC-7000, Shinku Riko) in vacuum at 290 to 1060 K.

The figure-of-merit (Z) was calculated from eq. (1).

$$Z = \alpha^2 \sigma / \kappa. \quad (1)$$

3. Results and Discussions

Figure 1 shows the electrical conductivities as functions of reciprocal temperature for B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals. The electrical conductivities decreased with increasing temperature, indicating a degenerated semiconductivity. No anisotropy of electrical conductivity was observed in both B- and P-doped specimens. B-doped specimens showed a higher conductivity than P-doped specimens, which is attributed to the difference of carrier concentration as shown in Fig. 2.

Figure 2 shows the carrier concentrations as functions of reciprocal temperature for B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals. The carrier concentrations of B- and P-doped specimens were independent of temperature under 800 K (extrinsic region), and increased with increasing temperature above 800 K (intrinsic region).

Figure 3 summarizes the relationship between mobility and concentration of carrier for specimens of zone leveled polycrystals⁵⁾ and arc melted polycrystals.¹⁴⁾ There is a general trend that mobility decreases with increasing concentration of carrier. The decrease for P-doped specimens is larger than that for B-doped specimens. The carrier mobility of P-doped

Fig. 1 Electrical conductivities of B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals.

Fig. 2 Concentration of carriers in B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals.

specimen in the present work was much greater than other specimens prepared by arc melting and by zone leveling. This trend is well coincident with the difference in grain size of specimens. The carrier mobility of B-doped specimen in the present work was almost the same as the reported values of polycrystal specimens prepared by arc melting. The influence of grain size was small in B-doped specimens as discussed below.

The relation between the mobility of carrier (μ) and the effective mass of carrier (m^*) is represented as eq. (2).

$$\mu = q\tau/m^* \quad (2)$$

Here q is electric charge of carrier and τ is relaxation time. The carrier mobility increases with the decreasing effective mass. The effective mass of electron is usually smaller than

Fig. 3 Mobility of carrier in GeSi alloys as functions of carrier concentration at 300 K. (arc: arc melting, zone: zone leveling) (poly: polycrystal, single: single crystal).

that of hole.¹⁵⁾ This is in good agreement with the result that the carrier mobility of electron is higher than that of hole in Fig. 3. Equation (2) also represents that the influence of relaxation time on the mobility is smaller for larger effective mass. Supposing that the change in the relaxation time by the scattering at grain boundary is the same for B- and P-doped GeSi, the change in the mobility for P-doped GeSi is larger than that for B-doped GeSi. This is one of the reasons why the influence of grain size was small in B-doped specimens in Fig. 3.

Figure 4 shows the temperature dependence of the Seebeck coefficients (α) for B- and P-doped specimens. The Seebeck coefficients of B-doped specimens showed positive values with a weak dependence on temperature. The weak temperature dependence behavior was different from the previous report for B-doped GeSi which showed a maximum at 1000 to 1200 K.^{10,16)} The α values of B-doped specimens in the [110] and [111] directions (α_{110} and α_{111}) were almost same and greater than those in the direction of [111] (α_{111}).

The absolute values of ($|\alpha|$) for P-doped specimens showed a maximum and minimum at about 800 and 500 K, respectively. The temperature where the Seebeck coefficient showed maximum corresponded to the boundary between intrinsic region and extrinsic region in Fig. 2. The previous reports on P-doped GeSi showed an increase in $|\alpha|$ with increasing temperature and a maximum at higher temperatures.^{10,17)} Nevertheless, the minimum point at lower temperature was not reported. The similar behavior was observed for p-type and n-type Si under room temperature,¹⁸⁾ which was explained by phonon drag effect.¹⁹⁾ However the present report was carried out above room temperature and the phonon drag effect was reported under room temperature where the mean free path of phonon was long. Accordingly, the present behavior may have no relation with phonon drag effect. The α values of P-doped specimens in the [001], [110] and [111] directions were almost the same as those above 600 K. Below 500 K, the

anisotropy of α was observed, where $|\alpha_{001}| > |\alpha_{111}| > |\alpha_{110}|$. The reason of anisotropy of α values remains unclear now.

Figure 5 shows the α values of B- and P-doped specimens as functions of carrier concentration reported in literatures.^{5,14} The $|\alpha|$ values increase with decreasing carrier concentration as indicated in a conventional semiconductor theory.²⁰ The $|\alpha|$ values obtained in the present work fell into this relationship between $|\alpha|$ and carrier concentration.

Figure 6 shows the temperature dependence of thermal conductivity (κ) for B- and P-doped specimens. The κ values decreased with increasing temperature, independent of crystal directions. No difference was observed between B-doped and P-doped specimens. Figure 6 also contains the κ values of zone leveled polycrystal specimens ($\text{Ge}_{0.07}\text{Si}_{0.93}$, $\text{Ge}_{0.2}\text{Si}_{0.8}$, $\text{Ge}_{0.3}\text{Si}_{0.7}$)^{4,5} for comparison. The κ values for single crystals in the present study was much larger than those of reported values. This indicates that the grain boundary is the reason to

reduce the thermal conductivity for GeSi alloys. The effect of grain boundary on the κ values was also reported by Slack *et al.*¹⁶ They illustrated that the lattice thermal conductivity increased from 0.9 to $4.7 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing the grain size from 10^{-8} to 10^{-5} m . The contribution of carrier electron on the thermal conductivity should be negligible in the present study because the carrier concentration of the present specimens are significantly low (less than 10^{26} m^{-3}).

Figure 7 shows the temperature dependence of the dimension-less figure-of-merit (ZT) for B- and P-doped specimens. The ZT values for both B- and P-doped specimens showed a maximum at certain temperature (T_{max}). The T_{max} of the B-doped specimens were higher than those of P-doped specimens. It is predicted from the conventional semiconductor theory that the T_{max} increases with increasing carrier concentration, which is in agreement with the present study.^{16,17}

Fig. 4 Seebeck coefficients of B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals.

Fig. 6 Thermal conductivities of B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals.

Fig. 5 Seebeck coefficients of GeSi alloys as functions of carrier concentration at 300 K.

Fig. 7 Dimension-less figure-of-merits for B- and P-doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals.

Vining¹⁷⁾ calculated the optimum carrier concentration ($3 \times 10^{26} \text{ m}^{-3}$) to maximize the ZT values for GeSi alloys. At this carrier concentration, the electrical conductivity is 10^5 Sm^{-1} , Seebeck coefficient $200 \mu\text{VK}^{-1}$ and thermal conductivity $5 \text{ Wm}^{-1}\text{K}^{-1}$. In the present study, the carrier concentration was $2.3 \times 10^{25} \text{ m}^{-3}$ in B-doped specimens, and $4.3 \times 10^{24} \text{ m}^{-3}$ in P-doped specimens, respectively. Since the carrier concentrations were smaller than the optimum value, the Seebeck coefficients were larger (about $400 \mu\text{VK}^{-1}$), the electrical conductivities were smaller (about 10^4 Sm^{-1}), and the ZT 's were lower (about 0.09). The increase in the dopant density would be needed for the improvement of the dimension-less figure-of-merit values in the present specimens.

4. Conclusion

B- and P- doped $\text{Ge}_{0.07}\text{Si}_{0.93}$ single crystals were prepared by a Czochralski (CZ) method and the anisotropy of thermoelectric properties (α : Seebeck coefficient, σ : electrical conductivity and κ : thermal conductivity) among [001], [110] and [111] directions were evaluated.

(1) The anisotropy of α for B-doped specimens was observed independent of temperature, where $\alpha_{110} = \alpha_{111} > \alpha_{001}$. The anisotropy of α for P-doped specimens was observed at less than 500 K, where $|\alpha_{001}| > |\alpha_{111}| > |\alpha_{110}|$. No obvious anisotropy of σ nor κ was observed for both B- and P-doped specimens.

(2) The carrier mobility of P-doped specimens was greater than those of B-doped specimens and polycrystalline materials.

(3) The κ values for single crystals were much greater than those of polycrystalline materials.

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