Thermoelectric Properties of p- and n-Type Si–Ge Dense Bodies Formed by Pulse-Current Sintering of Their Gas-Atomized and Pulverized Powders

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ガスアトマイズ粉及びその粉碎粉の放電焼結により得られた p 型, n 型 Si–Ge 緻密体の熱電特性

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Both p- and n-type $\text{Si}_{0.8}\text{Ge}_{0.2}$ powders were prepared by gas atomization of a mixture of Si and Ge with the addition of B or P. A part of the gas-atomized powders was further pulverized by ball-milling for 10 h in Ar. Then, dense bodies were formed from both the as-atomized and pulverized powders by pulse-current sintering. The thermoelectric properties such as the thermal conductivity, electric resistivity and Seebeck coefficient of the dense bodies were determined from room temperature to 1073 K, followed by the evaluation of the figure of merit (ZT). The thermal conductivities of p- and n-type fine-grained Si–Ge from pulverized powders were 8 and 10% lower on average in the temperature range of 300–1073 K, respectively, than those of the as-atomized powders. However, this phenomenon was accompanied with an increase in electric resistivity due to the reduced grain size and increased oxygen content, resulting in the decrease in ZT by 13 and 8% for p- and n-type Si–Ge, respectively. The ZT of n-type Si–Ge exceeded that of p-type because of the high Seebeck coefficient of n-type samples. Finally, the largest ZT value of 0.66 was obtained for the Si–Ge dense body from n-type gas-atomized powder. It was found that the application of the gas-atomized powder for fabricating Si–Ge sintered body has the advantage of the reduction in oxygen content and resistivity compared to the case of the pulverized powders. [Received August 5, 2003; Accepted September 30, 2003]

Key-words: Silicon–germanium, Ball-milling, Gas atomization, Pulse-current sintering, Thermoelectric property, Oxygen content

1. Introduction

Silicon–germanium (Si–Ge) alloy has been known to be a high-temperature thermoelectric element material, which can perform thermal-electrical energy conversion using the temperature difference between both ends of the element.^{1),2)} This alloy has been successfully applied to the power source for artificial satellites^{3)–5)} and is further expected to be applied for terrestrial use such as in environment-friendly power generation systems utilizing waste heat from energy-related facilities. Most of the experimental works on this alloy have been conducted on hot-pressed samples of Si–Ge powders obtained by pulverizing the corresponding ingots,⁶⁾ and $\text{Si}_{0.8}\text{Ge}_{0.2}$ has been determined to be the optimum composition with regard to thermoelectric properties.⁷⁾ Fleurial et al.⁸⁾ and Scoville and coworkers^{9),10)} attempted to improve the thermoelectric properties of GaP-doped n-type Si–Ge by controlling carrier concentration and mobility. Scoville et al.¹⁰⁾ and Beaty and coworkers^{11),12)} enhanced those of p-type Si–Ge by reducing thermal conductivity through the addition of BN powder.

An atomizing technique has been reported to be suitable for the preparation of homogeneous Si–Ge powders.¹³⁾ A pulse-current sintering (PCS) technique can yield a dense body of metal or ceramics in a very short period compared with other hot pressing techniques.¹⁴⁾ In the fabrication of Si–Ge dense bodies by the combination of two techniques, we found that ball-milling enhanced the sinterability of gas-atomized Si–Ge powders owing to the reduction of

grain size and the introduction of surface strain energy.¹⁵⁾ In this study, the Seebeck coefficient, electric resistivity and thermal conductivity of Si–Ge dense bodies that were prepared by PCS of the corresponding gas-atomized powders were determined to clarify the effect of the sample preparation methods, particularly paying attention to the grain size reduction by ball-milling.

2. Experimental

2.1 Sample preparation

Both p- and n-type Si–Ge powders were prepared by a gas atomizing method, as described in a previous paper.¹⁵⁾ The chemical compositions of as-prepared powders were Si 79.7 mol%, Ge 20.1 mol% and B 0.20 mol% for p-type, and Si 79.8 mol%, Ge 20.0 mol% and P 0.20 mol% for n-type. The mixing ratio of Si and Ge was determined to be 80 : 20 in mol% according to the report of Vining.⁷⁾ A part of the gas-atomized powders was further pulverized by ball-milling at 400 rpm for 10 h in argon. The densification of as-prepared or further pulverized powders was carried out using a PCS apparatus (Sumitomo Coal Mining Co., SPS-1030). A powder sample of 3 g was placed in a cylindrical carbon vessel with an inner diameter of 20 mm and then uniaxially compressed with a carbon punch at 49 MPa. Sintering was carried out to fabricate a compact for a soaking time of 180 s in vacuo, providing the pulse current through the punch. The sintering temperatures of as-atomized and pulverized powders were 1523 and 1433 K,

respectively. The low sintering temperature of the pulverized powders was due to the mechanochemically increased surface energy by ball-milling. The carbon vessel was enclosed inside a carbon thermal insulator to realize temperature uniformity of the charged powder. The sintering temperature was measured with a Pt-(Pt-13%Rh) thermocouple inserted into the vessel wall adjacent to the sample. Sintered bodies from p-type and n-type as-prepared powders were labeled A_p and A_n , respectively, and those from pulverized powders, P_p and P_n , respectively.

2.2 Characterization

A rectangular sample of 3 mm × 3 mm × 15 mm size was cut from a sintered body of 20 mm diameter and 4 mm thickness, and fixed between high- and low-temperature parts in a sample holder of a thermoelectric measurement apparatus (ULVAC-RIKO, ZEM-1), where it was brought into contact with a pair of probes for the measurement of both voltage and temperature, which were 10 mm apart. Seebeck coefficient and electric resistivity were simultaneously measured from room temperature to 1073 K in He with the temperature differences of 20, 30 and 40 K between the two probes.

Thermal diffusivity α (cm²·s⁻¹) and specific heat C_p (Jg⁻¹·K⁻¹) were measured in vacuo from room temperature to 1073 K with a laser flash thermal constant analyzer (ULVAC-RIKO, TC-7000) using a disk sample of 10 mm diameter and 2 mm thickness which was cut from the above sintered body. One side of the sample was heated with a ruby laser flash, and the temperature of the back surface was measured with a thermocouple or infrared detector. Specific heat was calibrated with a sapphire sample. The oxygen content of both the powder and sintered body was determined by measuring the amount of carbon dioxide generated from the melted sample in a carbon crucible using an oxygen/nitrogen analyzer (Horiba, EMGA-620W).

3. Results and discussion

3.1 Thermoelectric properties

A_p and A_n had the density of 99.6%, and P_p and P_n had that of 100%; the former included large grains more than 20 μ m in size, and the latter consisted of small grains less than 5 μ m in size.¹⁵⁾ The XRD patterns of these sintered bodies all indicated a well-crystallized Si-Ge single phase (Fig. 1).

Thermal conductivity is obtained by multiplying thermal diffusivity, specific heat and density. The temperature dependences of thermal conductivity, electric resistivity and Seebeck coefficient of p-type sintered bodies (A_p and P_p) are shown in Fig. 2. It is well known that the thermal conductivity of a thermoelectric material decreases with decreasing grain size.^{16),17)} In this study, the thermal conductivity of P_p having a smaller grain size was small in the temperature range of 300–1073 K compared with that of A_p , and those of P_p and A_p became almost constant above 880 K, as shown in Fig. 2(a). Thermal conductivity (κ) is, in general, expressed by the sum of lattice thermal conductivity (κ_{ph}) and electronic thermal conductivity (κ_{el}) as³⁾

$$\kappa = \kappa_{ph} + \kappa_{el} \quad (1)$$

Thus, the slight decrease in κ up to 873 K is due to the decrease in κ_{ph} with increasing temperature as κ_{el} is almost invariable, and the constant value over this temperature is due to the balance of the decrease in κ_{ph} and the increase in κ_{el} , because the latter increases with carrier concentration as the temperature rises.¹⁷⁾ Furthermore, κ_{ph} becomes smaller by the phonon scattering at the grain boundary of polycrystalline materials. It has been demonstrated that κ_{ph} of Si-Ge sintered bodies decreased with the reduction of the grain size.^{18),19)} The lower thermal conductivity of P_p than that of A_p seems to be attributed to the decrease in κ_{ph} with

Fig. 1. Typical XRD pattern of Si_{0.2}Ge_{0.8} dense body formed by pulse-current sintering. Sample: the dense body from gas-atomized p-type powder (A_p).

Fig. 2. Thermoelectric parameters of Si-Ge sintered bodies from as-prepared and pulverized p-type powders (A_p and P_p).

increasing phonon scattering of the fine-grained structure.

The Seebeck coefficients of A_p and P_p monotonically increased with temperature, as shown in Fig. 2(b). No significant difference between A_p and P_p was observed, indicating the independence from the grain size. Slack and Hussain theoretically suggested that Seebeck coefficient is affected by grain size only when the grain size is less than 0.01 μ m of the electron mean-free path.²⁰⁾ Figure 2(c) shows that the resistivities of A_p and P_p increased linearly with temperature. The resistivity of P_p was higher than that of A_p in the entire temperature range considered, probably due to the difference in grain size. Electrical conductivity σ is expressed as

$$\sigma = 1/\rho = ne\mu \quad (2)$$

where n , e and μ denote the concentration, charge and mobility of charge carriers, respectively. The carrier concentration of P_p appeared to be the same as that of A_p ,

Fig. 3. Thermoelectric parameters of Si-Ge sintered bodies from as-prepared and pulverized n-type powders (A_n and P_n).

judging from the result that these samples had the same Seebeck coefficient (Fig. 2(b)). Therefore, the higher resistivity of P_p than that of A_p may be attributed to the decrease in the mobility of the charge carriers caused by the fine-grained structure. The thermoelectric parameters of n-type Si-Ge sintered bodies are also shown in Fig. 3. There was no significant difference in the temperature dependences of these parameters between those of p- and n-type samples, except for the slightly increased thermal conductivities of A_n and P_n at a temperature higher than 873 K, as shown in Fig. 3(a). As in the case of p-type, P_n have a lower thermal conductivity and higher resistivity than A_n probably due to the fine-grained structure. However, the Seebeck coefficient of P_n was slightly lower than that of A_n (Fig. 3(b)), and the difference in resistivity between P_n and A_n was smaller than that of p-type (Fig. 3(c)). As carrier concentration increases, electrical conductivity increases proportionally while Seebeck coefficient decreases logarithmically.³⁾ Thus, the slight enhancement of the carrier concentration of P_n possibly occurred through ball-milling, followed by the slight decrease in the resistivity and the Seebeck coefficient of the sample.

The thermal conductivities of P_p and P_n were 8 and 10% lower on average in the temperature range of 300–1073 K than those of A_p and A_n , respectively, as shown in Figs. 2(a) and 3(a). The specific heat of P_p was found to be slightly higher than that of A_p , although it is known to be insensitive to the microstructure of the material (Table 1).²¹⁾ The thermal diffusivity of P_p was lower than that of A_p . The n-type Si-Ge also had the same tendency of specific heat and thermal diffusivity as the p-type. These results indicated that the decreases in the thermal conductivities of P_p and P_n by ball-milling were attributed to the decrease in their thermal diffusivities.

3.2 Figure of merit

The conversion efficiency from heat to electrical energy in

Table 1. Specific Heat, Thermal Diffusivity and Thermal Conductivity (at 873 K)

		p-type		n-type	
		A_p	P_p	A_n	P_n
Specific Heat	C_p / Jg ⁻¹ K ⁻¹	0.74	0.78	0.72	0.74
Thermal Diffusivity	α / cm ² s ⁻¹	0.022	0.019	0.022	0.019
Thermal Conductivity	κ / m ⁻¹ K ⁻¹	4.8	4.4	4.5	4.2

Fig. 4. Figure of merit ZT of Si-Ge sintered bodies from as-prepared and their pulverized powders.

a thermoelectric generator depends on the thermoelectric figure of merit which is determined by³⁾

$$ZT = S^2 T / \rho \kappa \quad (3)$$

where ZT is dimensionless figure of merit, S Seebeck coefficient ($V \cdot K^{-1}$), ρ resistivity ($\Omega \cdot m$) and κ thermal conductivity ($Wm^{-1} \cdot K^{-1}$). Figure 4 shows that the ZT of n-type Si-Ge exceeded that of p-type, which was based on the difference in Seebeck coefficient, as shown in Figs. 2(b) and 3(b). The ZT of A_p and P_p increased monotonically from 300 to 1073 K, but the value of P_p was lower than that of A_p in this temperature range. Those of A_n and P_n increased monotonically from 300 to 873 K and the slopes of the lines of these samples slightly decreased above 873 K due to the slight increase in thermal conductivities (Fig. 3(a)). The lowering of the ZT of P_n compared to that of A_n was also observed from 300 to 873 K.

The differences in ZT between Si-Ge dense bodies sintered with as-prepared and pulverized powders were 13% in p-type and 8% in n-type, respectively, in the temperature range of 300–1073 K. A_p and A_n displayed better thermoelectric abilities than P_p and P_n since the effect of the decrease in resistivity exceeded that of the increase in thermal conductivity, according to Eq. (3). Vining et al. also reported that the thermal conductivity of the Si-Ge sintered body from powders with various grain sizes ranging from 1 to 100 μm decreased with decreasing grain size; however, the figure of merit did not significantly increase due to a compensating reduction in electrical conductivity.²²⁾ In this study, the thermoelectric properties were not improved by the reduction in the grain size of the Si-Ge sintered body by ball-milling.

The oxygen contents of sintered bodies with their starting powders are shown in Fig. 5. The oxygen contents of P_p , P_n , and their powders were found to be approximately 20 times

Fig. 5. Oxygen content of Si-Ge powders and their sintered bodies.

Fig. 6. Figure of merit ZT of (a) p-type and (b) n-type $\text{Si}_{0.8}\text{Ge}_{0.2}$ sintered bodies.

more than those of A_p , A_n , and their powders. The metal oxide, that is SiO_2 and GeO_2 , probably formed on the grain surface in air after ball-milling, and then the resistivity of P_p and P_n may have been enhanced by this metal oxide layer which existed at the grain boundary, as suggested by Slack and Hussain.²⁰⁾ It was also observed that the oxygen contents of all the sintered bodies were slightly lower than those of the corresponding starting powders, which was probably attributed to the reducing atmosphere of the PCS process due to the use of a carbon vessel in vacuo.

The ZT of A_p was higher than that of Noguchi's sample²³⁾ from 300 to 1073 K, however, slightly lower than that of Vining's sample²²⁾ above 700 K (Fig. 6(a)). The ZT of A_n was almost the same as that of Noguchi's sample but lower than that of Vining's sample above 500 K (Fig. 6(b)). The thermal conductivity, Seebeck coefficient and resistivity of

Table 2. Seebeck Coefficient, Resistivity, Thermal Conductivity of p- and n-Type $\text{Si}_{0.8}\text{Ge}_{0.2}$ (at 873 K)

	Dopant /mol%	Powder	Sintering	κ /Wm ⁻¹ K ⁻¹	S / μ VK ⁻¹	ρ / $\mu\Omega$ m	
A_p	p-type	0.20B	Atomized	PCS	4.8	251	24.7
Noguchi ²¹⁾		0.20B	Pulverized	PCS	4.9	241	27.1
Vining et al. ²⁰⁾		0.23B	Pulverized	Hot Pressing	3.6	236	25.7
A_n	n-type	0.20P	Atomized	PCS	4.5	-325	33.2
Noguchi ²¹⁾		0.30P	Pulverized	PCS	4.7	-292	25.9
Vininga et al. ²⁰⁾		0.59P	Pulverized	Hot Pressing	3.6	-267	23.0

p- and n-type $\text{Si}_{0.8}\text{Ge}_{0.2}$ sintered bodies at 873 K are summarized in Table 2. The Seebeck coefficient of n-type samples seems to strongly depend on dopant concentration, while resistivity seems to be affected by both dopant concentration and the microstructure. The resistivity of A_p was the lowest probably due to the large grain size and low oxygen content. Thus, the larger ZT of A_p than that of Noguchi's sample was attributed to the low resistivity of this sample, as shown in Fig. 6(a), which may be caused by the powder preparation method. The difference in thermal conductivity between this study and that of Noguchi was obscure, while the thermal conductivity of Vining's samples was significantly lower than those of the other two samples. Thus, the ZT values of both Vining's p- and n-type samples were relatively high.

4. Conclusions

The thermoelectric properties of p- and n-type $\text{Si}_{0.8}\text{Ge}_{0.2}$ dense bodies formed by pulse-current sintering of their gas-atomized and pulverized powders by ball-milling were investigated in the temperature range from room temperature to 1073 K. The pulse-current sintering of the gas-atomized and pulverized powders possibly yielded the shaped bodies with a density of more than 99% at 1523 and 1433 K, respectively, in a short time of 3 min. The results obtained in this study were all attributed to the thermoelectric properties such as the thermal conductivity, electric resistivity and Seebeck coefficient of the dense bodies. It has been proved that the figure of merit of sample A_n was the highest among the four kinds of dense bodies tested and that further pulverization of the gas-atomized powders by ball-milling was ineffective.

Acknowledgment The authors wish to express their appreciation to Mr. Takayoshi Shimizu and Dr. Koichi Morii of Daido Steel Company for their assistance in the preparation of gas-atomized powders.

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