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## Thermoelectric Properties of Single-Crystalline SiC and Dense Sintered SiC for Self-Cooling Devices

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We investigated the thermoelectric properties of 4H-SiC substrates and dense sintered SiC, which are expected to be candidate materials for use in self-cooling devices because of their high Seebeck coefficient, low electrical resistivity, and high thermal conductivity. The carrier concentration of 4H-SiC samples doped with nitrogen is in the range of  $10^{16}$  to  $10^{19}$  cm<sup>-3</sup>. The sintered SiC samples of the  $\alpha$ -type and  $\beta$ -type contain less than 1000 ppm of cation impurities and have a relative density higher than 98% with respect to single-crystalline SiC. 4H-SiC with a carrier concentration of  $10^{19}$  cm<sup>-3</sup> has the highest power factor of  $2.7 \times 10^{-3}$  W·K<sup>-2</sup>·m<sup>-1</sup> and a high thermal conductivity of 260 W·K<sup>-1</sup>·m<sup>-1</sup> at room temperature. One-dimensional calculations for heat distribution indicate that a Si chip in a self-cooling device, which consists of 4H-SiC with a carrier concentration of  $10^{19}$  cm<sup>-3</sup>, could be refrigerated more strongly than one on a copper plate under specific operating conditions.

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### 1. Introduction

In our modern world, the use of silicon semiconductor devices is widespread. Recently, the amount of heat generated in highly integrated Si devices such as central processing units (CPUs) and power devices that include metal oxide semiconductor field-effect transistors (MOSFETs) and insulated gate bipolar transistors (IGBTs) has been markedly increasing. On the other hand, electrical equipment incorporating Si devices has been reducing in size, and heat dissipation modules in the equipment are becoming smaller in volume. The temperature increases in Si devices affect the performance of these devices and the equipment. Improvement of cooling techniques is a key issue.

Peltier modules, which contain thermoelectric materials, are used to cool electrical devices. The figure of merit  $Z$ , which represents the performance of a thermoelectric material, is defined by the equation  $Z = \alpha^2 / \rho\kappa$ , where  $\alpha$ ,  $\rho$ , and  $\kappa$  are the Seebeck coefficient, the electrical resistivity, and the thermal conductivity, respectively. The Peltier modules use the Peltier effect to cool devices. To increase the cooling efficiency, it is required that thermoelectric materials in the Peltier module have a high Seebeck coefficient, a low electrical resistivity, and a low thermal conductivity.

Silicon carbide, SiC, is a next-generation material to be used in semiconductor power devices. SiC has been expected to be a potential thermoelectric material for use at high temperatures because of its high mechanical strength, high melting point, nontoxicity, and high Seebeck coefficient. However, its high thermal conductivity leads to a low figure of merit  $Z$ . To decrease the thermal conductivity of SiC, researchers have developed porous SiC by controlling the porosity using various types of sintering methods and additives.<sup>1-9)</sup>

Yamaguchi *et al.* have proposed a new scheme for cooling electronic devices and have called these devices “self-cooling devices”.<sup>10-12)</sup> The cooling process uses both

the Peltier effect and thermal conduction. The device current drives the Peltier effect. In the proposed scheme, it is required that thermoelectric materials have a high Seebeck coefficient, a low electrical resistivity, and a high thermal conductivity. The requirement of high thermal conductivity is different from that for typical thermoelectric materials. Single-crystalline SiC and dense sintered SiC are expected to be good candidate materials for use in self-cooling devices because of their high Seebeck coefficient and high thermal conductivity.<sup>12)</sup>

The aims of this study are to investigate the thermoelectric properties of n-type single-crystalline 4H-SiC and n-type dense sintered SiC with a low cation impurity concentration in the temperature range of 300 to 400 K and to discuss briefly the potential of SiC as a material for use in self-cooling devices.

### 2. Experimental Methods

The samples were three substrates of single-crystalline 4H-SiC with (0001) orientation (hereafter labeled as SC) and six sintered SiC samples (ST). Table I shows the specifications of the samples.

The SC samples were prepared at the National Institute of Advanced Industrial Science and Technology (AIST). Substrates with rectangular shapes were cut out from single-crystalline ingots grown at AIST. The surfaces, Si and C planes of the substrates, were polished using diamond slurry and had a mirror-like gloss. Four nickel electrodes were fabricated on both surfaces as follows: 1) nickel films with a thickness of 200 Å were evaporated on the substrates and 2) the substrates were annealed at 1300 K in a vacuum for 1 min to form ohmic contact between the substrates and the nickel electrodes. Two electrodes for current supply were arranged on the ends of the surfaces. The other electrodes for voltage measurement had a size of  $1 \times 0.5$  mm<sup>2</sup> and were arranged on the surfaces with a distance larger than 5 mm between them.

The ST samples were commercial products fabricated by sintering fine-particle powders pressed without additives in

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**Table I.** Specification of sample structure, purity, density, and carrier concentration.

Sample	Structure	Purity (%)	Density <sup>a)</sup> (%)	$n_c$ <sup>b)</sup> (cm <sup>-3</sup> )	Thickness (mm)
ST $\alpha$ 1	$\alpha$	99.99	99.2	—	1.0
ST $\alpha$ 2	$\alpha$	99.9	99.5	$1 \times 10^{18}$	1.0
ST $\beta$ 1	$\beta$	99.9	98.8	—	1.0
ST $\beta$ 2	$\beta$	99.9	99.2	—	1.0
ST $\beta$ 3	$\beta$	99.9	99.2	$2 \times 10^{20}$	1.0
ST $\beta$ 4	$\beta$	99.999	98.8	—	1.0
SC16	4H	—	—	$\sim 10^{16}$	1.1
SC18	4H	—	—	$\sim 10^{18}$	2.4
SC19	4H	—	—	$\sim 10^{19}$	0.4

a) Relative density with respect to single-crystalline SiC.

b) Carrier concentration.

argon atmosphere. They contained cation impurities (less than 1000 ppm) and had a relative density higher than 98%, with respect to single-crystalline SiC. It was not necessary to form an electrode on the surface of the samples because ohmic contact could be easily maintained.

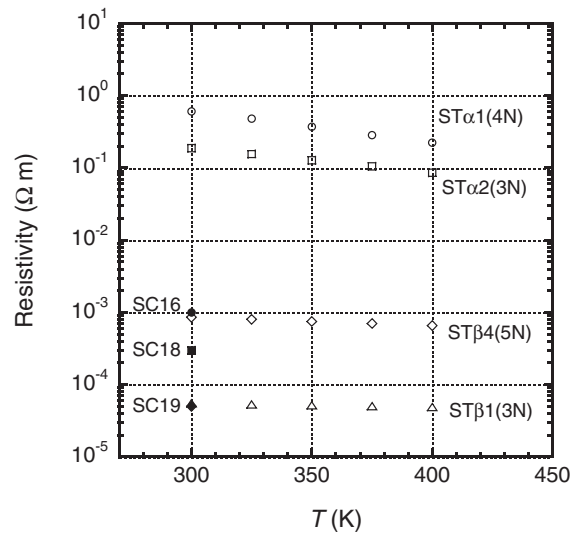
The measurement procedure has been described in our previous paper.<sup>12)</sup> The electrical resistivity, the Seebeck coefficient, and the thermal conductivity of the samples were measured from 300 to 400 K in a vacuum (perpendicular to the *c*-axis of SC samples). The electrical resistivity of the ST samples was measured by the DC four-contact method and that of the SC samples was measured by the van der Pauw method. The Seebeck coefficient was estimated from the temperature difference and thermoelectromotive force. The difference in temperature between the two ends of the sample was controlled to be within the range of 0 to 3 K using small heaters. The thermal conductivity was measured by the steady-state method. All the measurements were carried out in a steady state. The temperature-measurement errors of this equipment have been estimated to be below  $\pm 1$  K. The Seebeck coefficient of a calcium cobalt oxide, Ca<sub>3</sub>Co<sub>4</sub>O<sub>9-x</sub>, sample obtained using the equipment was 6% higher than that of the same sample obtained using TOYO ResiTest8300.

### 3. Results and Discussion

#### 3.1 Thermoelectric property

Figure 1 shows the temperature dependence of the electrical resistivity of the ST and SC samples. ST $\beta$ 4 (5N) has a resistivity that decreases with increasing temperature. The electrical resistivity of  $\beta$ -ST samples with 3N purity, ST $\beta$ 1 (3N), ST $\beta$ 2 (3N), and ST $\beta$ 3 (3N), is lower than that of ST $\beta$ 4 (5N) and negligibly changes with temperature. It is considered that the carrier concentration of ST $\beta$ 4 (5N) is lower than those of the other  $\beta$ -ST samples with 3N, which is about  $10^{20}$  cm<sup>-3</sup>, compared with the temperature and carrier concentration dependence of the electrical resistivity for heavily N-doped polycrystalline SiC samples.<sup>13)</sup> The  $\alpha$ -ST samples have a resistivity above  $10^{-1}$   $\Omega$ ·m, which is 100 times higher than that of the  $\beta$ -ST samples. It can be seen that the electrical resistivity of the  $\beta$ - and  $\alpha$ -ST samples decreases with increasing impurity concentration. SC19 has the lowest electrical resistivity of  $5 \times 10^{-5}$   $\Omega$ ·m among the SC samples.

Table II shows the Seebeck coefficient of  $\beta$ -SiC with n-type conduction at room temperature.<sup>13-16)</sup> In all the



**Fig. 1.** Temperature dependence of electrical resistivity for ST and SC samples.

**Table II.** Comparison of the Seebeck coefficients on  $\beta$ -SiC with literature data at room temperature.

Author	Sample	$n_c$ <sup>a)</sup> (cm <sup>-3</sup> )	$\alpha$ ( $\mu$ V·K <sup>-1</sup> )	Ref.
This work	$\beta$ 1(3N) <sup>b)</sup>	$\sim 10^{20}$	-111	
	$\beta$ 4(5N)		-158	
Maeda <i>et al.</i>	N <sub>2</sub> : 4(+5) <sup>c)</sup>		-60	14
	N <sub>2</sub> : 0		-100	
Ageel <i>et al.</i>	194C <sup>d)</sup>		-10	15
	164A		-28	
Golikova <i>et al.</i>	1 <sup>e)</sup>	$8 \times 10^{20}$	-70	13
	3	$2.2 \times 10^{20}$	-120	
Pohl	— <sup>f)</sup>		-106	16

a) Carrier concentration.

b) Sintered bulk from fine SiC particles.

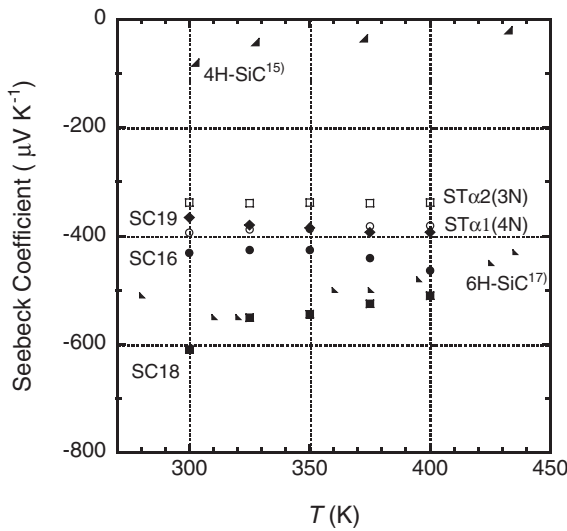
c) Sintered bulk fabricated from rice hulls.

d) Films deposited on quartz.

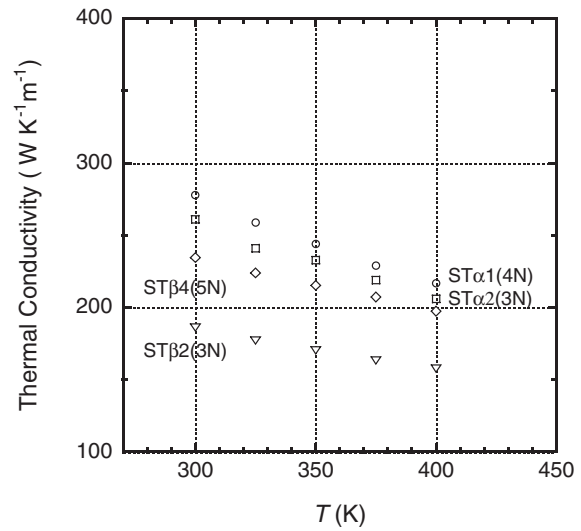
e) Decomposing methyl trichlorosilane vapor.

f) Monocrystal.

samples, the Seebeck coefficients negligibly or slightly increase with increasing temperature. Figure 2 shows the temperature dependence of the Seebeck coefficient for single-crystalline samples with a hexagonal structure and  $\alpha$ -ST samples. The absolute values of  $\alpha$ -ST, SC18, 4H-SiC,<sup>15)</sup> and 6H-SiC<sup>17)</sup> decrease with increasing temperature. In contrast, the temperature dependences of SC16 and SC19 are opposite. In Ioffe's theory,<sup>18)</sup> the Seebeck coefficient decreases with increasing carrier concentration. The phenomenon that both carrier concentration and the absolute value of the Seebeck coefficient for a semiconductor sample increase with temperature cannot be explained by means of a simple semiconductor theory taking into account only the electron diffusion generating the thermoelectromotive force under the temperature gradient. It is considered that this temperature dependence of the Seebeck coefficient is due to the phonon-drag effect, where the carrier electrons are predominantly dragged by the phonons scattered by the boundaries such as grain surfaces, stacking fault planes, and dislocations.<sup>2,3,9)</sup>



**Fig. 2.** Temperature dependence of Seebeck coefficient for  $\alpha$ -ST and single-crystalline SiC. Solid symbols represent single-crystalline samples.



**Fig. 3.** Temperature dependence of thermal conductivity for ST samples.

**Table III.** Thermal conductivity of single-crystalline SiC with a hexagonal structure.

Author	Sample	Polytype	$n_c^a$ ( $\text{cm}^{-3}$ )	$\kappa$ ( $\text{W}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ )	$-s$ ( $T > 300\text{K}$ )	Ref.
This work	SC16	4H	$\sim 10^{16}$	320	-1.05	
	SC18	4H	$\sim 10^{18}$	360	-1.02	
	SC19	4H	$\sim 10^{19}$	260	-0.81	
Jenny <i>et al.</i>		4H	High purity	490	-1.68	20
		4H	$8 \times 10^{18}$	420	-1.45	
Morelli <i>et al.</i>	1	6H	$3.5 \times 10^{16}$	430		21
	2	6H	$2.9 \times 10^{18}$	300		
Burgemeister <i>et al.</i>	1	6H	$8 \times 10^{15}$	387	-1.49	22
	3	6H	$1 \times 10^{19}$	295	-1.02	
Slack	R66	6H	$1 \times 10^{17}$	490	-1.2 <sup>b)</sup>	23

a) Carrier concentration.

b) Calculated from extrapolated data.

The electrical resistivity and the Seebeck coefficient depend on sintering conditions such as the nitrogen pressure in an atmosphere,<sup>2,14</sup> the temperature, and time.<sup>9</sup> The sintering conditions for the  $\beta$ -ST samples were the same. The electrical resistivity and the Seebeck coefficient of the  $\beta$ -ST samples with 3N purity are lower than those of ST $\beta$ 4 (5N). This indicates that the ST samples with higher metal impurities such as Al and Fe acting on an acceptor have a higher carrier concentration. However, the Seebeck coefficient measurement shows that the  $\beta$ -ST samples show n-type conduction and an electron is a major carrier. Moreover, it has been reported that  $\alpha$ -SiC samples sintered in Ar showed p-type conduction possibly due to a dominant effect of the acceptor impurities such as Al and Fe contained in the starting powder.<sup>2,9</sup> In contrast, the  $\alpha$ -ST samples sintered in Ar show n-type conduction. It is considered that metal impurities in the ST samples increase nitrogen incorporation into the ST samples and/or enhance nitrogen ionizing as a donor.

Figure 3 shows the temperature dependence of the thermal conductivity of the ST samples. The thermal conductivity decreases with increasing impurity concentration, which is due to electron carriers and cation impurities acting

as scattering centers of phonons.<sup>19</sup> Table III shows the thermal conductivity of single-crystalline SiC with a hexagonal structure at room temperature. The term  $-s$  represents the slope in a  $\log T$ - $\log \kappa$  plot, that is,  $\kappa \propto T^{-s}$ . The thermal conductivity basically decreases and the absolute value of  $-s$  decreases with increasing carrier concentration. The SC16 sample has a lower thermal conductivity than that of the SC18 sample possibly due to structural defects such as micropipes and dislocations.

The figure of merit  $Z$  is not a good indicator for self-cooling devices because self-cooling devices need high Seebeck coefficients, low electrical resistivity, and high thermal conductivity. Thus, we use the power factor,  $\text{PF} = \alpha^2/\rho$ , to discuss the performance of self-cooling devices. Figure 4 shows the temperature dependence of PF. The PF of the  $\beta$ -ST samples is about  $10^{-4} \text{ W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$ . The  $\alpha$ -ST samples have a high Seebeck coefficient but also a high resistivity of  $\sim 10^{-1} \Omega\cdot\text{m}$ . Therefore, the PF of  $\alpha$ -ST samples is below  $10^{-6} \text{ W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$ . SC18 and SC19 have PFs of  $1.2 \times 10^{-3}$  and  $2.7 \times 10^{-3} \text{ W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$  at 300 K, respectively.

Figure 5 shows the PF and thermal conductivity of SiC, bismuth-telluride alloy (BiTe), gallium-arsenic (GaAs), and

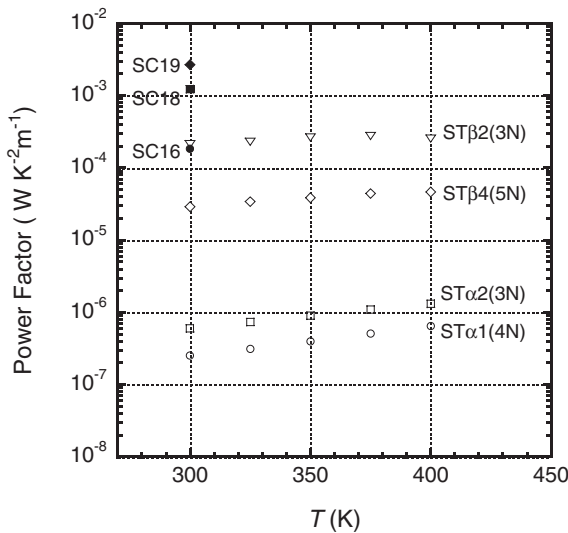


Fig. 4. Temperature dependence of power factor.

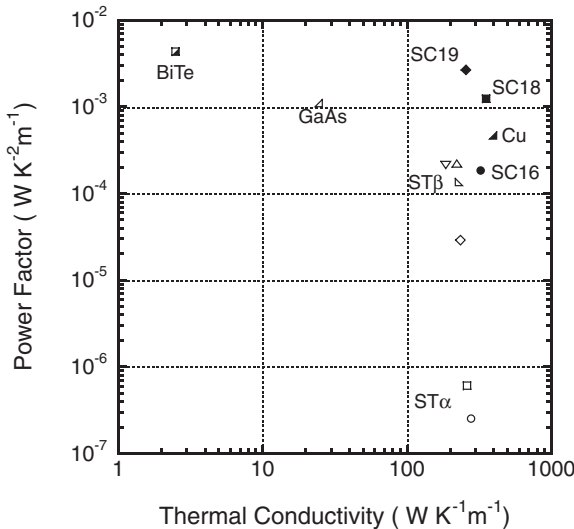


Fig. 5. Power factor vs thermal conductivity at room temperature.

copper at room temperature. Because BiTe has a low thermal conductivity it is not an ideal material for use in a self-cooling device, even though the PF of BiTe is high. SC19 has the highest PF among all the samples and a high thermal conductivity.

### 3.2 Heat flow in self-cooling devices

Figure 6 shows heat flow directions in a plate when the temperature  $T_h$  at the top surface of the plate is higher than the temperature  $T_c$  at the bottom surface of the plate when Peltier heat is taken into account. In the case that a Si chip is an n-channel MOSFET with an electrical current flowing from the  $T_c$  side to the  $T_h$  side, an n-type conducting thermoelectric material is needed because Peltier heat flows in a direction opposite to the current in n-type materials. In the opposite current direction, a p-type conducting material is needed.

Heat flux  $Q$  at the top of the plate with a cross section of  $A \text{ mm}^2$  and a thickness of  $d \text{ mm}$  is approximately represented in eq. (1),

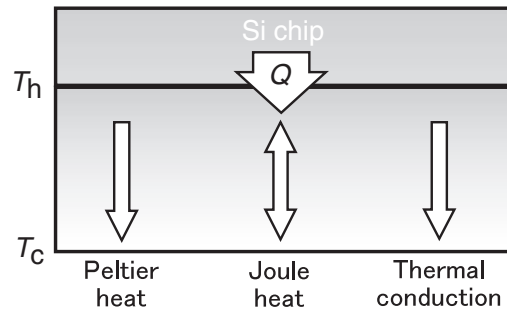


Fig. 6. Heat flow in a plate when electrical current flows.

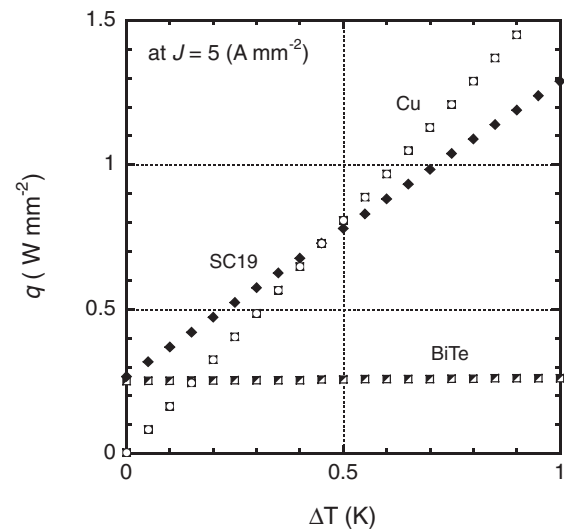


Fig. 7. Heat flux density in a plate as a function of temperature difference between top and bottom surfaces of the plate.

$$Q = \alpha T_h A J - \frac{1}{2} (A J)^2 \rho \frac{d}{A} + \kappa \frac{A}{d} \Delta T, \quad (1)$$

where  $J$  is the electrical current density and  $\Delta T$  is the temperature difference between  $T_h$  and  $T_c$ . Figure 7 shows the heat flux density  $q = Q/A$  for BiTe, SC19, and copper plates obtained by one-dimensional calculation. All the plates have a thickness of 0.25 mm. The vertical axis shows the heat flux from the silicone chip, and the horizontal axis is the temperature difference. If the temperature difference is small, the heat flux of SC19 is larger than that of copper. That is, the Si chip in a self-cooling device could be refrigerated more strongly than one on a copper plate under a specific operating condition.

### 4. Conclusions

The present study leads to the following conclusions:

- 1) Sintered  $\beta$ -SiC has a power factor of approximately  $10^{-4} \text{ W} \cdot \text{K}^{-2} \cdot \text{m}^{-1}$  and a thermal conductivity of  $190 \text{ W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$  at 300 K.
- 2) The highest power factor,  $2.7 \times 10^{-3} \text{ W} \cdot \text{K}^{-2} \cdot \text{m}^{-1}$ , is found for single-crystalline SiC with a carrier concentration of  $10^{19} \text{ cm}^{-3}$ , the thermal conductivity of which is  $260 \text{ W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$  at 300 K.

For single-crystalline SiC, the electrical resistivity, the thermal conductivity and the absolute value of the Seebeck

coefficient decrease with increasing carrier concentration from  $10^{18}$  to  $10^{19}$   $\text{cm}^{-3}$ . We should optimize the carrier concentration in SiC to develop the best materials for use in self-cooling devices.

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