Electrical and thermal properties of off-stoichiometric SiC prepared by spark plasma sintering

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1. Introduction

Silicon carbide (SiC) is a promising high-power semiconductor material because it has a wide band gap and high electron-mobility [1–3]. The electrical properties of highly pure SiC, mainly single crystalline SiC, prepared by chemical vapor deposition and sublimation, has been intensively investigated [4–6]. SiC can be also used as an electrical heating element because of its high electrical conductivity, good oxidation resistance, and high thermal shock resistance [7,8]. SiC heating elements are fabricated from relatively impure SiC powder containing various impurities such as Al, Fe, and O. Moreover, commercial SiC powder, commonly fabricated by the Acheson method using SiO2 and C, does not have a stoichiometric composition; the powder contains excess C or Si. The electrical properties of SiC are strongly dependent on the impurities; however, the properties of impure SiC, in particular, off-stoichiometric SiC, have scarcely been investigated. The thermal conductivity of a SiC heating element should also be controlled, because the thermal shock of a SiC heater and thermal conduction from a SiC heater to an electrode and/or insulation element are important for the design of a SiC heater. To develop a high-performance SiC heater, it is essential to understand the effects of excess C and Si in SiC on the electrical and thermal conductivity of SiC.

In this study, C- and Si-added SiC bodies were prepared by spark plasma sintering (SPS) by using a relatively impure commercial SiC powder, and the effects of C and Si addition on the electrical and thermal properties of the SiC body were investigated.

2. Experimental procedures

Commercial SiC powder (α-type, 6H, OY-15, Yakushima Denko Co., Ltd, Tokyo, Japan) with an average particle size of 1.2 µm was used as the source material. The reagent grade C (graphite; average particle size of 20 µm, Kojundo Chemical Laboratory Co., Ltd, Saitama, Japan) and Si powders (average particle size of <1 µm, Kojundo Chemical Laboratory Co., Ltd, Saitama, Japan) were used as additives. Table 1 shows the chemical analysis of the SiC source powder obtained from the supplier. The C and Si contents in the off-stoichiometric SiC were 1, 3, and 5 mol%. The C- and Si-added SiC are hereafter named C-SiC and Si-SiC, respectively. The C-SiC and Si-SiC powders were mixed by ball milling in a small amount of ethanol for 5 h. After drying, the powders were poured in a graphite die (inner diameter of 10 mm) and sintered in a vacuum using SPS equipment (SPS-210LX, Fuji Electronic Industrial, Kawasaki, Japan) at 2373 K for 5 min. The heating rate was 100 K min⁻¹ at a pressure of 50 MPa. The density of the SiC bodies was measured by the Archimedes method. The relative density was calculated using the theoretical density of SiC (3.21 Mg m⁻³).

REFERENCES

[1] J. Wu et al., J. Solid State Chem. 161 (2001) 355.
[2] A. Hara et al., J. Am. Ceram. Soc. 85 (2002) 298.
[3] Y. Taki et al., J. Eur. Ceram. Soc. 34 (2014) 1150.
[4] J. Wu et al., J. Solid State Chem. 151 (1999) 250.
[5] Y. Taki et al., J. Eur. Ceram. Soc. 34 (2014) 1150.
The crystal phases and lattice parameters were examined by X-ray diffraction (XRD; CuKα, Ultima IV, Rigaku Corp., Tokyo, Japan) using high-purity silicon powder as an internal standard. The microstructures were observed using a scanning electron microscope (SEM; S-3400N, Hitachi High-Technologies Corp., Tokyo, Japan) and a transmission electron microscope (TEM; EM-002B, Topcon, Tokyo, Japan). The electrical conductivity (\(\sigma\)) was measured with a dc four-probe method in vacuum at 298–1123 K. The Seebeck coefficient (\(S\)) was measured in a He atmosphere at 298–973 K by changing the temperature gradient (ZEM-3, ULVAC-RIKO, Kanagawa, Japan). The thermal conductivity (\(\kappa\)) was measured with a laser flash method (TC-7000, ULVAC-RIKO, Kanagawa, Japan) in a vacuum at 298–973 K.

3. Results and discussion

The XRD patterns of the SiC source powder and the sintered SiC bodies are shown in Figure 1. The SiC source powder and the SiC bodies were identified as 6H-SiC (ICSD #01-072-0018). The added C and Si were identified by XRD prior to the sintering. The peak of Si in the mixed powder increased corresponding to the added Si content. A small peak of C (graphite) was also observed in the mixed powder. After sintering, no peaks of C or Si were found in the C-SiC and Si-SiC bodies. The added C and Si could be dissolved in a solid solution in the SiC bodies.

Figure 2 shows the lattice parameters of the source powder, pristine SiC, C-SiC, and Si-SiC. The lattice parameters of the SiC source powder (\(a = 0.3090\) nm and \(c = 1.5121\) nm) were greater than those of the standard values (\(a = 0.3081\) nm and \(c = 1.5117\) nm), which might be owing to the incorporation of impurities during the powder manufacturing process. The lattice parameters of the pristine SiC bodies (\(a = 0.3090\) nm and \(c = 1.5120\) nm) were close to those of the source powder, whereas the lattice parameters of C-SiC and Si-SiC slightly increased. If C or Si atoms dissolved in SiC, considering the tetrahedral covalent radius of C (\(r_{\text{cov(C)}} = 0.077\) nm) and Si (\(r_{\text{cov(Si)}} = 0.107\) nm) [9], then the lattice parameters of

| Chemical analysis of SiC source powder. | mol% |
|----------------------------------------|------|
| SiC                                    | 97.80|
| Free carbon                            | 1.59 |
| SiO₂                                   | 0.56 |
| AI                                     | 0.03 |
| Fe                                     | 0.02 |

Figure 1. XRD patterns of (a) SiC source powder, and SiC bodies: (b) pristine SiC, (c) 5 mol % C-added SiC and (d) 5 mol % Si-added SiC.

Figure 2. Effect of the added amount of C or Si on the lattice parameters: (a) \(a\)-axis and (b) \(c\)-axis.
C-SiC would be smaller and those of Si-SiC would be greater than those of pristine SiC. Gadzira et al. [10] reported that the solid solution of C atoms in β-SiC (3C) powder prepared by self-propagation high-temperature synthesis caused a decrease in the a-axis value, whereas that of C dissolved in the SiC body increased to the standard value after heating at a high sintering pressure and temperature. The C dissolved in SiC was disintegrated and precipitated at the grain boundary. Bernie et al. [11] prepared Si- and C-dissolved and saturated SiC powders by heat treatment at 2673 K. The SiC (3C) powder with excess Si was still 3C after the heat treatment, whereas the SiC (3C) powder with excess C changed to 6H-SiC. The lattice parameters of both SiC bodies were somewhat higher than the standard values. Although the reasons for the increase in the lattice parameters of C-SiC and Si-SiC in this study are still unclear, these changes were similar to those reported by Bernie et al. [11]. Because C and Si are the major components of SiC, a small amount of C and Si dissolved in SiC could not be precisely identified. The present results suggest that C and Si may interstitially dissolve in SiC because the lattice parameters of C-SiC and Si-SiC were both somewhat greater than those of pristine SiC.

Figure 3 shows the effects of the added amount of C or Si on the relative density of the SiC body. The C-SiC exhibited an increase in relative density from 80.2 to 84.8% with the increasing amount of C addition, whereas the Si-SiC showed the maximum of 89.5% at 1 mol% Si then a slight decrease to 85.4% with the addition of more Si content. C and B additives have been commonly employed as sintering additives for pressureless sintering of SiC to achieve fully dense bodies [12–14]. The addition of C has been used to enhance the sinterability by reducing the SiO2 phase on the SiC powder surface by forming CO and CO2 gases. The addition of too much C would result in the segregation of graphite at the grain boundary, impeding the densification [15]. The appropriate amount of C addition was reported to be in the range of 1.7–12.2 mol% [14–17]. It was reported that the density of Si-added SiC tended to decrease with increasing Si content, in particular, at a high Si content [18]. The density of C-SiC and Si-SiC in the present study was almost the same as the commercial SiC sintering element [7]; they are appropriate to further study the electrical and thermal conductivities for the application to the heater.

Figure 4 shows the SEM images of pristine SiC, C-SiC, and Si-SiC. No precipitates of C and Si were observed at the grain boundary and triple points. The added C and Si might be dissolved in a solid solution in the SiC body. Stobierski [15] studied the effect of carbon additive amount on the sintering of SiC and reported that the unreacted C (graphite) precipitated at the grain boundary was found in SiC bodies with the excess of C content of 12 and 23 mol%. In the present study, it was not confirmed whether the 5 mol% of C additive was all dissolved, but a partial amount of the C could be dissolved in the SiC body.

Figure 6 shows the temperature dependence of the electrical conductivity (σ) of pristine SiC, C-SiC, and Si-SiC. The pristine SiC showed extrinsic (impurity) conduction below approximately 800 K, and the activation energy of σ was 0.1 eV. With increasing temperature to the range of 800–1150 K, the activation energy increased to 0.7 eV, which was less than the half of the band gap of 6H-SiC (3.02 eV) [1] and lower than the Fermi energy level. The electrical conductivity of C-SiC increased with increasing content of C additive. The activation energy of C-SiC decreased with increasing C content and was almost zero below 800 K. The temperature-independent behavior of σ is beneficial for the application of SiC in a heater. The σ values of Si-SiC were lower than those of C-SiC. The σ of Si-SiC containing 1–3 mol% Si additive was lower than that of pristine SiC. The σ of Si-SiC containing 5 mol% Si additive was greater than that of pristine SiC. The activation energy of σ for Si-SiC was almost the same as that of pristine SiC. Wei et al. [19] reported that a high Si content in SiC increased the carrier concentration and improved σ of foam-shaped SiC ceramics. Okamoto et al. [18] reported that a small amount of Si additive (1.4 mol

![Figure 3](image-url) Figure 3. Effect of the added amount of C or Si on the relative density.
\% Si) did not increase \( \sigma \), whereas a Si additive content of more than 1.4 mol\% increased \( \sigma \) by two to three orders of magnitude. In the present study, at least 5 mol\% of Si additive content was required to enhance the electrical conductivity. The temperature dependence of \( \sigma \) of Si-SiC was similar to that of pristine SiC.

Figure 7 shows Seebeck coefficient for pristine SiC, C-SiC, and Si-SiC. The pristine SiC had \( n \)-type conductivity with a Seebeck coefficient of approximately...
−70 to −200 µV K−1. The commercial SiC source powder is synthesized by the Acheson method, in which N impurities from air are dissolved in the SiC source powder, causing n-type conduction [20,21]. The Seebeck coefficient of C-SiC with 3 and 5 mol% C additive changed from n- to p-type at approximately 660 and 820 K, respectively. The present results imply that the addition of C to SiC could cause p-type conduction. A small amount of additive C content (1 mol%) could not compensate for the n-type impurity (N donor), whereas more than 3 mol% C additive was enough to compensate for the n-type (N donor) impurity. This also implies that a certain amount of C can dissolve in a solid solution in SiC. The Seebeck coefficient of Si-SiC was negative, which corresponded to n-type conduction. The Si content did not have much influence on the Seebeck coefficient of SiC, as reported by Wei et al. [19]. The maximum absolute Seebeck coefficient for Si-SiC with 3 mol% Si was approximately 300 µV K−1 at 800 K.

The excess C and Si might form a solid solution in SiC lattice as the evidence of lattice parameter change and no precipitate phase was observed from TEM. The C-SiC showed the considerable change of Seebeck coefficient from n-type to p-type with the increasing amount of C implying the change of carrier concentration in SiC. The σ values of C-SiC increased by two orders of magnitude and exhibited low activation energy indicated that the excessive C forms a shallow impurity level in SiC. On the other hand, Si-SiC showed a small difference of Seebeck coefficient and electrical conductivity with varying Si amount. The Si solid solution would form a deeper impurity level in SiC compared to that of C.

Figure 6. Temperature dependence of the electrical conductivity of (a) C-added SiC and (b) Si-added SiC.

Figure 7. Temperature dependence of the Seebeck coefficient of (a) C-added SiC and (b) Si-added SiC.
Figure 8 shows the temperature dependence of the thermal conductivity for pristine SiC, C-SiC, and Si-SiC. The temperature dependence of the SiC bodies decreased with increasing temperature. This suggested that phonons, and not free electrons, were responsible for the thermal conduction in SiC bodies. According to the Wiedemann–Franz law, the thermal conductivity by free-electron was less than 1/1000 than that of phonon (lattice vibration) in the present study. The thermal conductivities of C-SiC and Si-SiC improved compared to that of pristine SiC. Si-SiC had a slightly higher thermal conductivity than that of C-SiC. At room temperature, the thermal conductivity of the SiC bodies was approximately 180–250 W m⁻¹ K⁻¹, whereas at 973 K, the thermal conductivity was 50–70 W m⁻¹ K⁻¹. The difference in the thermal conductivity between pristine SiC, C-SiC, and Si-SiC could be caused by the density; the higher the density the greater the thermal conductivity, as shown in Figure 3.

4. Conclusion

Off-stoichiometric SiC, C-added (C-SiC), and Si-added SiC (Si-SiC), were prepared by SPS at 2373 K. The C-SiC and Si-SiC bodies were 6H-SiC polytype. C and Si could be dissolved in a solid solution in SiC. The addition of a small amount of Si (1 mol%) significantly increased the densification of SiC. The addition of 3–5 mol% C improved the electrical conductivity ($\sigma$) of SiC and caused less temperature dependence, which is beneficial for application in heaters. C-SiC changed from $n$- to a $p$-type conduction with increasing C additive content, whereas Si-SiC had $n$-type conduction independent of the amount of Si content. The thermal conductivities of C-SiC and Si-SiC (180–250 W m⁻¹ K⁻¹) were greater than that of pristine SiC (100 W m⁻¹ K⁻¹) at room temperature. This could be caused by the difference in density.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Casady JB, Johnson RW. Status of silicon carbide (SiC) as a wide-bandgap semiconductor for high-temperature applications: A review. Solid-State Electron. 1996;39:1409–1422.
[2] Morkoç H, Strite S, Gao GB, et al. Large-band-gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies. J Appl Phys. 1994;76:1363–1398.
[3] Choyke WJ, Pensl G. Physical properties of SiC. MRS Bull. 1997;22:25–29.
[4] Hwang JD, Fang YK, Song YJ, et al. High mobility $\beta$-SiC epilayer prepared by low-pressure rapid thermal chemical vapor deposition on a (100) silicon substrate. Thin Solid Films. 1996;272:4–6.
[5] Neyret E, Di Cioccio L, Bluet JM, et al. Deposition, evaluation and control of 4H and 6H SiC epitaxial layers for device applications. Mater Sci Eng B. 2001;80:332–336.
[6] Foti G. Silicon carbide: from amorphous to crystalline material. Appl Surf Sci. 2003;184:20–26.
[7] Pelissier K, Chartier T, Laurent JM. Silicon carbide heating elements. Ceram Int. 1998;24:371–377.
[8] Sōmiya S, editor. Silicon carbide ceramics 1: fundamental and solid reaction. London: Elsevier Applied Science; 1991.

[9] Tajima Y, Kingery WD. Solid solubility of aluminum and boron in silicon carbide. J Am Ceram Soc. 1982;65:C-27–C-29.

[10] Gadzira M, Gnesin G, Mykhaylyk O, et al. Solid solution of carbon in β-SiC. Mater Lett. 1998;35:277–282.

[11] Birnie DP, Kingery WD. The limit of non-stoichiometry in silicon carbide. J Mater Sci. 1990;25:2827–2834.

[12] Hojo J, Miyachi K, Okabe Y, et al. Effect of chemical composition on the sinterability of ultrafine SiC Powders. J Am Ceram Soc. 1983;66:c114–c115.

[13] Rijswijk W, Shanefield DJ. Effects of carbon as a sintering aid in silicon cCarbide. J Am Ceram Soc. 1990;73:148–149.

[14] Clegg WJ. Role of carbon in the sintering of boron-doped silicon carbide. J Am Ceram Soc. 2000;83:1039–1043.

[15] Stobierski L, Gubernat A. Sintering of silicon carbide I. Effect Carbon Ceram Int. 2003;29:287–292.

[16] Ermer E, Wiesław P, Ludosław S. Influence of sintering activators on structure of silicon carbide. Solid State Ion. 2001;141–142:523–528.

[17] Prochazka S, Scanlan RM. Effect of boron and carbon on sintering of SiC. J Am Ceram Soc. 1975;58:72.

[18] Okamoto Y, Inai H, Morimoto J. Temperature dependence of the thermoelectric properties of Si doped SiC. J Jpn Soc Powder Powder Metall. 1998;45:905–908.

[19] Wei W, Cao X, Tian C, et al. The influence of Si distribution and content on the thermoelectric properties of SiC foam ceramics. Micropor Mesopor Mater. 2008;112:521–525.

[20] Takeda Y, Nakamura K, Maeda K, et al. Effects of elemental additives on electrical resistivity of silicon carbide ceramics. J Am Ceram Soc. 1987;70:C-266–C-267.

[21] Ogihara S, Maeda K, Takeda Y, et al. Effect of impurity and carrier concentrations on electrical resistivity and thermal conductivity of SiC ceramics containing BeO. J Am Ceram Soc. 1985;68:C-16–C-18.