

High-purity β -SiC powder for the single-crystal growth of SiC

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High-purity β -SiC powder suitable for growing SiC single crystals was successfully synthesized from sol-gel precursors by carbothermal reduction. This was achieved through a two or three stage process that incorporated initial gasification, followed by gas phase reaction. To minimize the high loss that is typical of this process, and caused by the rate of evaporation in being faster than the gas phase reaction speed, the chemical structure of the precursor and heat treatment process were optimized. This found that a combination of tetraethyl orthosilicate and trimethyl phenylsilicate precursors, and a two-stage heat treatment, increases the production yield from 49.0% up to 84.4%. Furthermore, the purity of the β -SiC was also increased to 99.7%, with a metallic impurity content of just 130 ppm.

Key words: β -SiC powder, Crystal growth, High purity, Carbothermal.

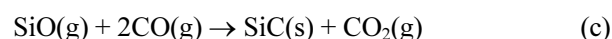
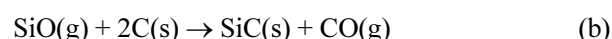
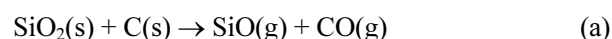
Introduction

The excellent physical, mechanical and electronic properties of silicon carbide (SiC) make it a promising material for use in next-generation electronic devices [1-4]. Indeed, single-crystal wafers of this material are already used in optical, high-frequency, heat-resistant vehicle and power devices, but are also becoming the focus of attention for expanding the current limits of silicon semiconductors [5-9]. Whatever the end use, however, creating large high-quality single crystals of SiC is essential to achieving the full potential of SiC-based devices.

At present, single crystals of SiC are normally produced through the sublimation of an alpha phase SiC (α -SiC) powder above 2200 °C. This alpha-phase powder is typically obtained through the Acheson process, which involves a lengthy carbothermic reaction between SiO₂ and carbon powders at around 2200-2400 °C. However, high-quality single crystals of SiC have been recently achieved using a beta phase SiC (β -SiC) powder [10-12]. This not only requires a significantly lower temperature for synthesis of 1700-1900 °C, but also allows for longer crystals to be grown at a higher speed. These β -SiC powders can be produced through a variety of different methods, which include: chemical vapor deposition (CVD) using organometallic silane precursors, direct carbonization from Si metal, pyrolysis of silane compounds, and the carbothermal reduction of silicon dioxide (SiO₂) with

carbon [13-16].

Of the various methods that have been developed for the growth of single crystals by sublimation and deposition, otherwise known as physical vapor transport (PVT) [17-20], carbothermal reduction is widely regarded as the most suitable for producing high-purity β -SiC. This involves the reduction of silica with carbon by the following reactions [21]:



More specifically, two separate reaction steps are involved: an initiation reaction (a), which can start from 1400 °C [22] and generates SiO and CO gases explosively; followed by SiC formation (b and c), which is either a gas-solid or gas-gas phase reaction. This process can therefore lead to a significant loss of silicon and carbon [23-30] at high temperatures, as the SiO and CO gases can escape the system faster than the rate of SiC deposition. Typically, β -SiC is produced between 1500 and 2000 °C, though a temperature of at least 1800 °C is needed to ensure high-purity and highly crystalline products.

In order to improve the yield of a carbothermal reaction, it needs to be stabilized by slowing the initiation reaction. To this end, this study explores the use of a silicon precursor prepared by a sol-gel method from tetraethyl orthosilicate (TEOS), along with a carbon source derived from the phenyl group of either trimethyl phenylsilicate (PTMS) or phenolic resin. The effect of these alternative precursors on the yield and

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quality of the resulting product is herein discussed, along with the use of a two-stage heating process.

Experimental Procedure

Reagent-grade tetraethyl orthosilicate (TEOS, 98% $\text{Si}(\text{OC}_2\text{H}_5)_4$, Aldrich), trimethyl phenylsilicate (PTMS, 98% $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$, Aldrich), ammonia solution (25%, Daejung), and oxalic acid (99%, Aldrich) were used for the preparation of the sol-gel precursors by a previously described method [31]. For Precursor-1, a phenyl-containing silica sol was obtained from TEOS and PTMS under basic conditions (pH 11 achieved with ammonia solution); whereas Precursor-2 was prepared under acidic conditions (pH 1-2 achieved with oxalic acid) after mixing TEOS and phenolic resin.

Both precursors were calcined at 1000 °C, and then characterized by ^{29}Si solid NMR spectroscopy (Varian Unity INOVA600) at 600 MHz using a CP/MAS technique to obtain better signal-to-noise ratios. After analysis, the SiC precursors were placed into graphite crucibles and subjected to either direct heating up to 1800 °C at a rate of 20 °C/min, or a two-step heat-treatment method of heating first to 1550 °C, and then to 1800 °C.

X-ray powder diffraction (XRD) analysis was performed using a P/MAX 2200V/PC (Rigaku Corp.) with a Cu target ($K\alpha = 1.54 \text{ \AA}$) to identify the crystalline phase of the β -SiC powder. The shape and size of particles in each powder was then determined by scanning electron microscopy (SEM: JSM-6700F, JEOL). The purity of each powder was measured in accordance with Korean Industrial Standards (KS L 1612), and the amount of metallic impurities was determined using glow discharge mass spectrometry (GDMS).

Results and Discussion

The different carbon sources used to prepare the SiC precursors resulted in distinctly different chemical structures: Precursor-1 containing Si-C bonds due to the phenyl structure in PTMS that remained even after calcination at 1000 °C, whereas the phenolic resin used for Precursor-2 resulted in an absence of Si-C bonds. The chemical structures of these precursors have been previously confirmed by FT-IR and solid NMR spectroscopy [31], with their estimated structures and NMR spectra shown in Figure 1 and 2. Figure 1(a) shows the Si-C bonds in the Si-O network of Precursor-1, the presence of which is confirmed by the three significant split peaks at -36.9, -70.8, and -106.5 ppm in the ^{29}Si NMR spectrum (Figure 2(a)). The chemical shifts were attributed to SiC_2O_2 , SiCO_3 , and SiO_4 , respectively. In contrast, the absence of Si-C bonds in Precursor-2 (Figure 1(b)) is confirmed by the fact that only Si-O bonds appear in its NMR spectrum (Figure 2(b)).

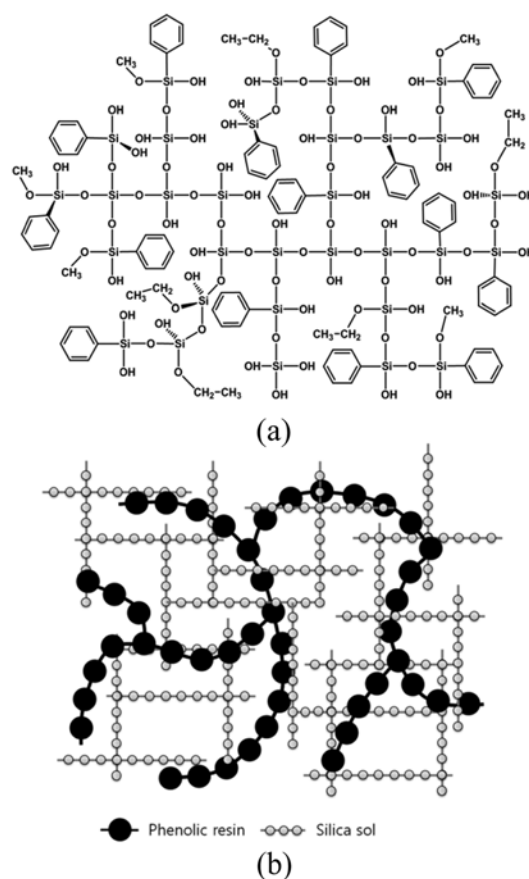


Fig. 1. Proposed structure of (a) precursor-1 and (b) precursor-2, as prepared by sol-gel method using different carbon sources.

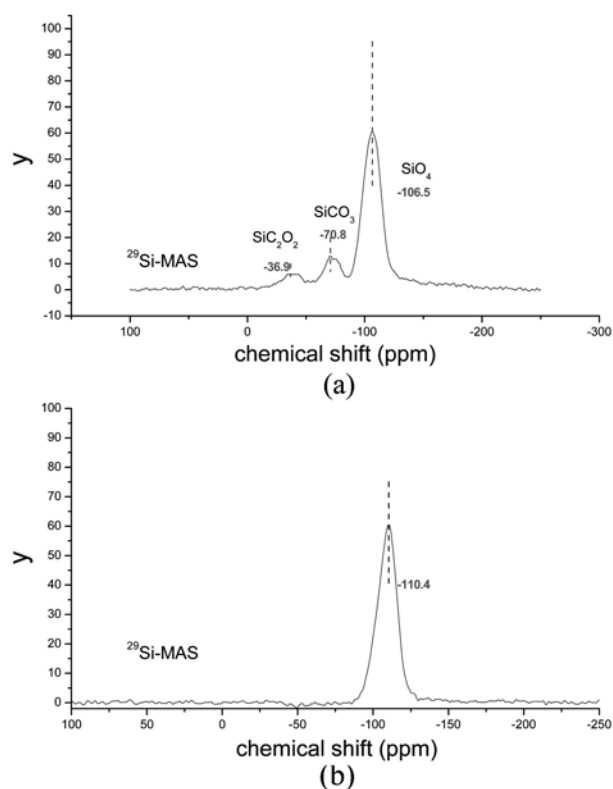


Fig. 2. ^{29}Si -NMR spectra of calcined (a) precursor-1 and (b) precursor-2.

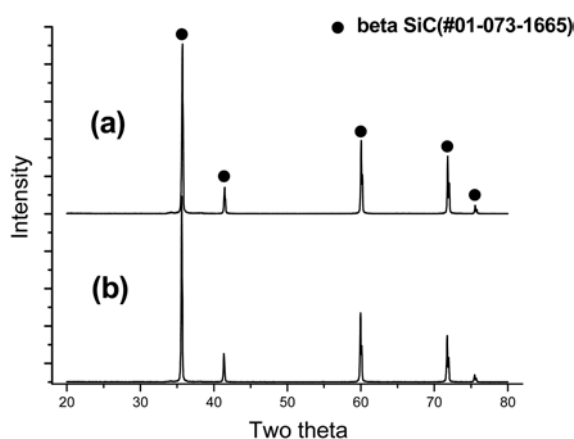
Table 1. Production yield and the chemical analysis of SiC.

Reactant	Heat treatment condition	Sample No.	Yield	Purity of β -SiC	Free-C	(wt%)	
						Silicon	
						SiO ₂	Free Si
Precursor-1 (TEOS + Phenyltrimethoxysilane)	Two-stage process	SiC-1	84.4	99.7	0.12	0.15	0.08
	Conventional process	SiC-2	62.0	99.7	0.08	0.10	0.06
Precursor-2 (TEOS + Phenolic Resin)	Two-stage process	SiC-3	67.0	99.7	0.10	0.08	0.07
	Conventional process	SiC-4	49.0	98.4	0.08	0.30	1.18

Table 2. GDMS analysis results of β -SiC prepared from Precursor-1 by a two-stage heating process.

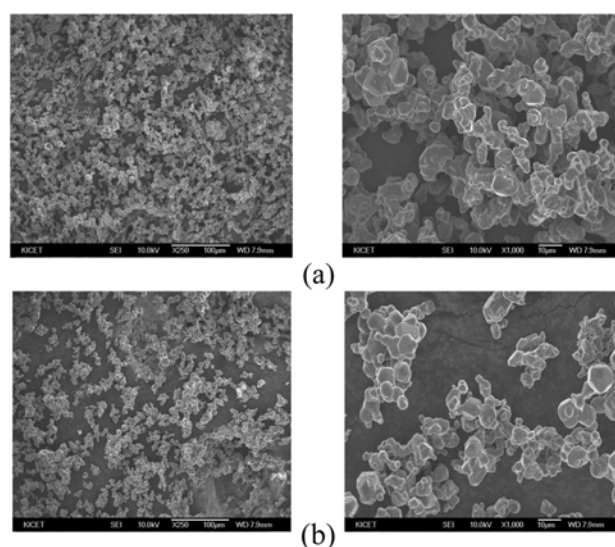
Element	Content (ppm, wt)	Element	Content (ppm, wt)
B	14	Ca	2.1
Na	0.06	Sc	< 0.01*
Mg	< 0.05*	Ti	1.7
Al	110	V	0.28
Y	< 0.05	Mn	< 0.05*
Zr	0.14	Fe	0.2
Cl	~ 2	Co	< 0.01*

*out of detection limit.

**Fig. 3.** X-ray diffraction spectra of β -SiC derived from (a) Precursor-1 and (b) Precursor-2 by two-stage heating process.

The β -SiC yields achieved with the two precursors and different heat-treatment conditions are presented in Table 1. This demonstrates firstly that the use of a two-step heat treatment can achieve a yield that is ~20% greater than that obtained with a conventional heat-treatment method, regardless of the precursor used. This is attributed to the lower temperature of the first stage, which reduces the loss of SiO and CO through explosive gasification.

The chemical structure of the precursor is also shown in Table 1 to have an effect on the yield, with the 62 and 84.4% obtained with Precursor-1 using conventional and two-stage heat treatment, respectively, being notably higher than the 49 and 67% obtained using Precursor-2.

**Fig. 4.** SEM images of β -SiC powder derived from (a) Precursor-1 and (b) Precursor-2 by two-stage heating process.

Since both precursors were prepared from TEOS, the only difference in their structure lies in the presence of Si-C bonds in Precursor-1. It is believed that these Si-C bonds help prevent the loss of silicon atoms, whereas the isolated carbon atoms in Precursor-2 cause SiO to more readily evaporate during carbonization. It is also worth noting that the use of either a two-stage process or Precursor-1 results in a higher purity (99.7%) final product with a metallic impurity content of 130 ppm (table 2), when compared to conventional treatment of Precursor-2 (98.5%).

In the X-ray diffraction patterns for the β -SiC products produced by two-step heat treatment of Precursor-1 and Precursor-2 shown in Figure 3, the only discernible diffraction peaks at approximately 35°, 60°, and 73° all correspond to the β -SiC phase (JCPDS card number 73-1665). This means that the difference in chemical structure between the two precursors has no effect on the crystal formation. Furthermore, SEM observation of the β -SiC particles (Figure 4) found no discernible difference in microstructure, though their mean particle size did differ slightly (Figure 5). However, these sizes are not considered to represent individual particles, but rather agglomerations of 10 μ m or smaller particles.

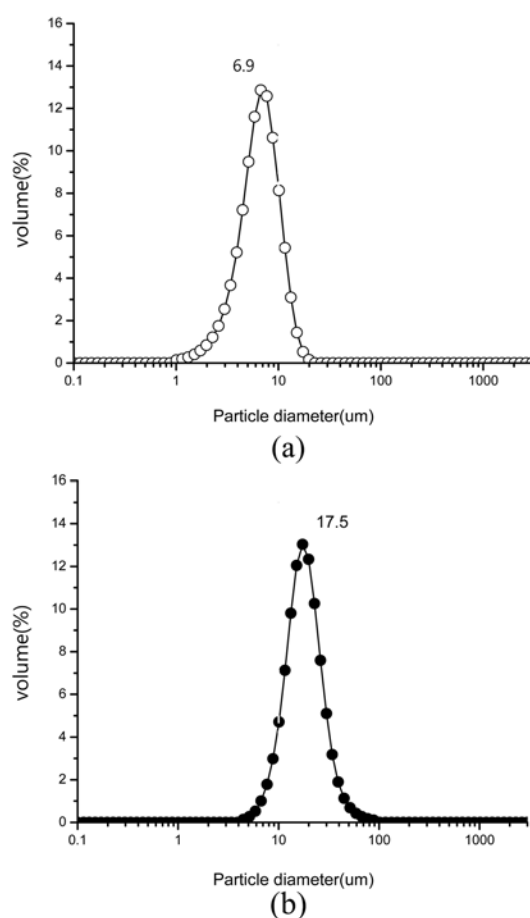


Fig. 5. Particle size distribution analysis results of β -SiC derived from (a) Precursor-1 and (b) Precursor-2 by two-stage heating process.

Conclusions

The synthesis of β -SiC was successfully achieved using different carbon sources, finding that the initial presence of a Si-C bond in the precursor used can improve the yield by preventing the loss of silicon atoms during the thermal process. Moreover, incorporating an intermediate step holding step at 1550 °C prior to heating to the 1800 °C needed for synthesis also leads to an improved production yield over a conventional single-stage heat-treatment process. This improvement in the synthesis of β -SiC powder is expected to provide the basis for producing single crystals of SiC with a reduced number of crystal defects, and on a scale more amenable to meeting the demands of practical application.

Acknowledgments

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