

Preparation of particle-size-controlled SiC powder for single-crystal growth

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Abstract High-purity β -SiC powders for SiC single-crystal growth were synthesized by direct carbonization. The use of high-purity raw materials to improve the quality of a SiC single crystal is important. To grow SiC single crystals by the PVT method, both the particle size and the packing density of the SiC powder are crucial factors that determine the sublimation rate. In this study, we tried to produce high-purity β -SiC powder with large particle sizes and containing low silicon by introducing a milling step during the direct carbonization process. Controlled heating improved the purity of the β -SiC powders to more than 99% and increased the particle size to as much as $\sim 100\ \mu\text{m}$. The β -SiC powders were characterized by SEM, XRD, PSA, and chemical analysis to assess their purity. Then, we conducted single-crystal growth experiments, and the grown 4H-SiC crystals showed high structural perfection with a FWHM of about 25-48 arcsec.

Key words β -SiC powder, Direct carbonization, High purity

1. Introduction

Silicon carbide (SiC) is well known as a superior ceramic material with high thermal stability, high strength, good chemical resistance, and high hardness [1-3]. SiC single crystals have recently been considered as upcoming alternative semiconducting material that can substitute Si semiconductor owing to their wide band gap and good thermal stability [4-6].

Currently, the most useful method for growing a SiC crystal is a physical vapor transport (PVT) method. This method involves subliming a raw material in a high temperature region (source material) and growing a single crystal in a low temperature region (seed crystal) [7, 8]. The various defects of causing something can be generated in the growth. Defects nucleated in the substrates and SiC epilayers cause performance degradation of the device; these defects include micropipes, elementary screw dislocations, and stacking faults. In 1992, Koga et al. reported for the first time that p-n junctions exhibited a very low breakdown voltage in the presence of micropipe defects [9].

During the PVT growth process, SiC powder, which is used as the raw material, may have a direct impact

on the quality of the single crystal [10]. To obtain a high-performance SiC device, high-purity SiC powder with a large particle size is required. Commercially available SiC powder is usually synthesized by the Acheson method [11], which is suitable for obtaining α -SiC powder; however, it has limitations with regards to obtaining high purity SiC powders. Moreover, SiC powders can be produced by the direct reaction of silicon with amorphous carbon in a microwave [12] field and using plasma technique from CH_4 and SiH_4 gas mixtures [13].

Over last few years, in our lab, we have synthesized β -SiC powder by a carbothermal method using phenyl containing silica sol [14, 15]. It was confirmed that the purity of the synthesized source material affected the quality of the single crystal [16, 17]. However, the carbothermal method has disadvantages such as low yields and a complicated process. Direct carbonization, also known as combustion synthesis, is the most promising method, which is simple, generic, and low cost [18, 19]. However, it leaves behind significant amounts of unreacted silicon and other impurities.

In this study, we tried to produce high-purity β -SiC powder containing low silicon by incorporating a milling step during the direct carbonization process. To achieve a high-purity stoichiometric SiC from the synthetic powder, the purification process was also studied.

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2. Experimental Procedure

A carbon source (amorphous carbon black, particle size 0.5 μm , 99.9 % purity; (TIANJIN KIMWAN CARBON TECHNOLOGY & DEVELOPMENT CO., LTD) and Si source (particle size 4.5 μm , 99.999 % purity, SM-1565; Strategic Metal Investments Ltd.) were used as starting materials. To prevent trapped impurities in the synthesized SiC powder and to ensure that it reacts uniformly, ball milling was carried out on the mixture (1.2 : 1 ratio of carbon:silicon) for 90, 120, and 150 h with SiC balls of varying diameter (15 mm, 10 mm, 5 mm and 1 mm).

Then, the SiC powder was obtained by a two-step heat treatment at 1400°C for 4 h and at 1800°C for 2 h under Ar atmosphere. After the first heat treatment step, 0.2 mol of the carbon source was added, and ball milled was carried out to reduce the amount of free Si and SiO₂.

X-ray powder diffraction analysis was carried out using an X-ray diffractometer (P/MAX 2200V/PC, Rigaku Corp.) with a Cu target ($K\alpha = 1.54 \text{ \AA}$) to identify the crystalline phase of the SiC powder. The purification of β -SiC was carried out by thermal treatment as follows: the powder was placed in a graphite crucible. It was heated to 1850°C at a heating rate of 15°C/min and held for 15 min at that temperature under argon. Then, the temperature was increased up to 2000°C at a heating rate of 2°C/min and held at that temperature. It was cooled down to 1850°C, and then heated up to 2000°C again. This was repeated three times. Then, high purity and grown particle sized β -SiC powder was obtained. The shapes and sizes of the powders were observed by a scanning electron microscope (JSM-6700F, JEOL, Japan) and a particle size analyzer (Beckman Coulter, Model LS230). The purities of the β -SiC products were measured according to guidelines outlined in the Korean Industrial Standard (KS L 1612).

The single-crystal growth temperature was 1900°C, and the Ar pressure was 6~8 Torr during the growth process. Polymorphism of the grown crystals was assessed using X-ray diffraction (high-resolution X-ray diffraction, HRXRD).

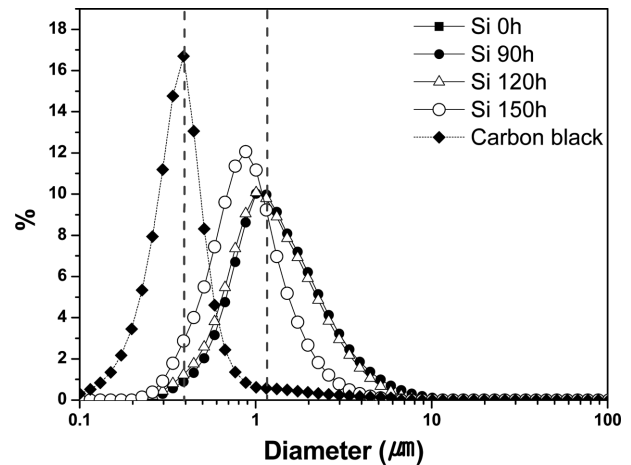


Fig. 1. Particle size distribution analysis results of the starting materials, carbon and silicon with ball milling time.

Table 1
Particle size analysis of starting materials with ball milling time

	Carbon black	Silicon			
		0 h	90 h	120 h	150 h
Mean size (μm)	0.425	4.562	1.509	1.376	0.947

3. Results and Discussion

The starting materials were carbon black and Si metal. To ensure a homogeneous reaction, we adjusted the particle size of the starting materials. The reaction is started from the silicon surface with carbon black. It should be adjusted similar to the size of the two materials. Fig. 1 shows the particle size distribution of the starting materials. The size of the Si particles was controlled to 0.95 μm through ball milling (Table 1).

Then, the mixed starting material was heat treated at 1400°C for 4 h and at 1800°C for 2 h under Ar atmosphere. Fig. 2 shows a schematic diagram of the synthesis of β -SiC. It can be seen that at temperatures below the melting point of Si (1412°C), a Si (solid) + C (solid) type reaction occurs. The direct reaction of the powdered mixture of Si and graphite under normal pressure begins slowly around 1150°C [20] and continues till temperatures of 1400°C over 4 h at the solid-solid contact areas via the following reaction: $\text{Si(s)} + \text{C(s)} \rightarrow \beta$ -

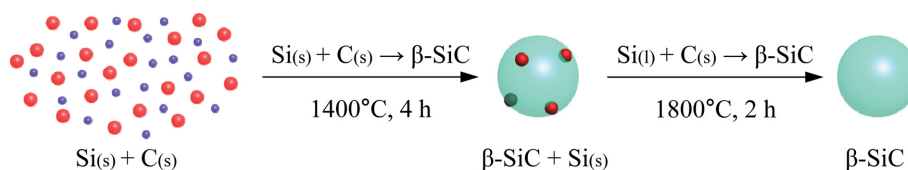


Fig. 2. Schematic diagram of the synthesis of β -SiC.

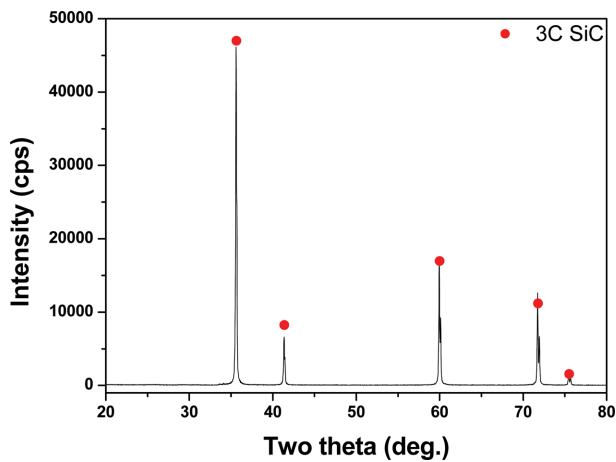


Fig. 3. X-ray diffraction spectra of the β -SiC powders as synthesized at 1800°C.

SiC(s). The sufficient reaction time of 4 h at 1400°C, which is lower than the melting point of Si, is to minimize the amount of Si trapped inside the β -SiC particles.

However, even after at the reaction 1400°C for 4 h, a small amount of unreacted Si was found to be trapped inside the β -SiC particles. To ensure completion of the reaction, the reaction temperature was increased to 1800°C and held for 2 h under an Ar atmosphere. On increasing the temperature to values higher than the melting point of Si (> 1400°C), the reaction of molten silicon Si(liquid) with C(s) basically follows this mechanism: $\text{Si}(l) + \text{C}(s) \rightarrow \beta\text{-SiC}(s)$. In this state, the liquid Si will penetrate or the Si atoms will diffuse through the pores and other paths of least resistance into the C(s), where the reaction then occurs to form β -SiC or dissolution of carbon in the molten silicon and transport to a (colder) deposition location, with SiC formation either

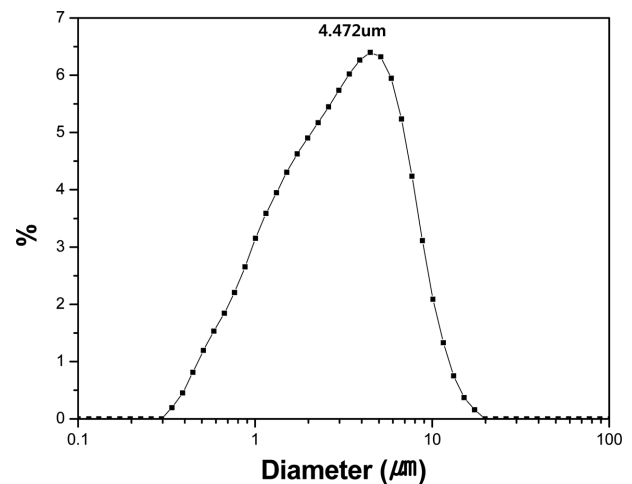


Fig. 4. Particle size distribution analysis results of β -SiC powders.

in solution or at the deposition site.

After the first heat treatment, X-ray diffraction was conducted to determine the crystallinity and phase of the SiC powder (Fig. 3). The pattern for the synthesized β -SiC powder mainly shows diffraction peaks around 35°, 60°, and 72° (JCPDS card number 73-1665), which indicates that the synthesized β -SiC powder did not contain free silicon or free carbon. The obtained SiC powders show a narrow particle size distribution, with a mean size of 3.53 μm (Fig. 4). SEM observations of the β -SiC particles (Fig. 5) show that the primary particles had a regular-angled shape with a size below 4 μm . From the results, we conclude that β -SiC powder with a purity over 97 % can be obtained. The major impurities were carbon (0.02 %) and silicon (2.48 %). For the removal of unreacted silicon, 0.2 mol of the carbon source was added, and the mixture was annealed for 12 h. In this

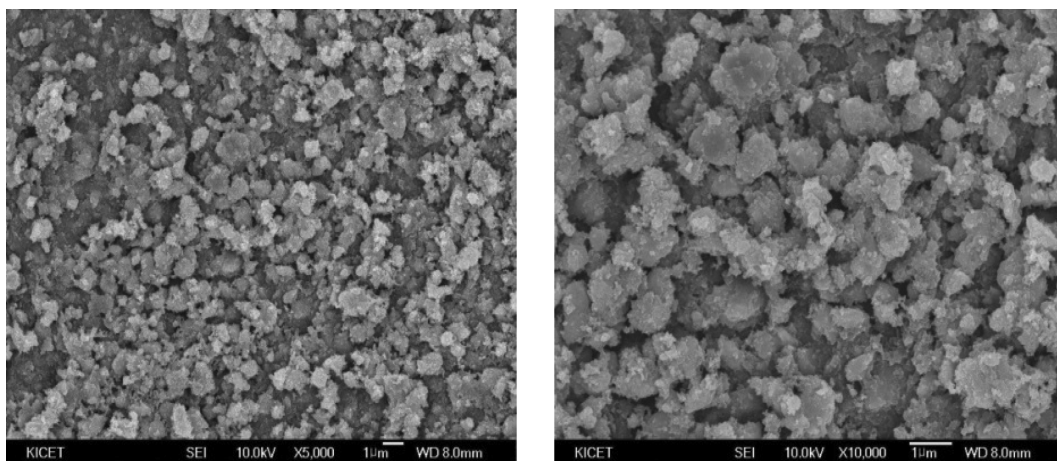


Fig. 5. SEM images of the β -SiC powders synthesized at 1800°C.

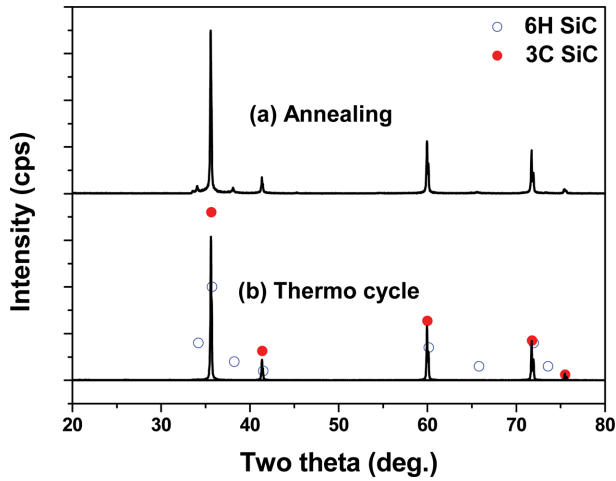


Fig. 6. X-ray diffraction spectra of the β -SiC powders as (a) annealing powder at 1800°C and (b) thermocycle powder.

study, we also carried out thermocyclic treatment with the annealed β -SiC powder. XRD analysis (Fig. 6) shows that the annealed β -phase powder underwent partial phase transition to the α -phase during the thermo-

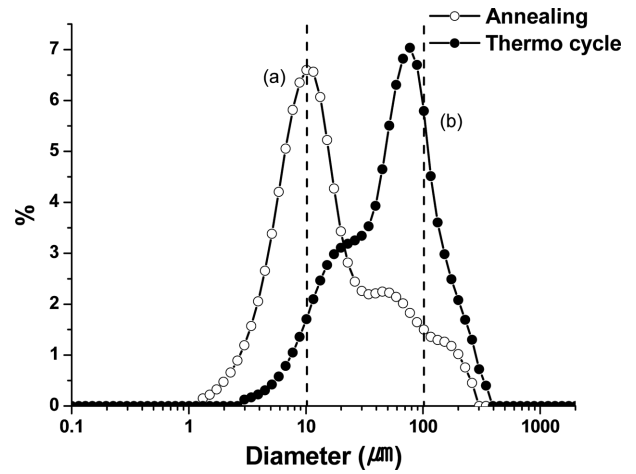


Fig. 7. Particle size distribution analysis results of the β -SiC powders (a) annealing powder at 1800°C and (b) thermocycle powder.

clitic treatment process. The particles in the β -SiC powder could grow up to sizes of 100 μm from the synthesized powders by the thermal growth method (Fig. 7 and 8).

Individual β -SiC particles aggregate and agglomerate

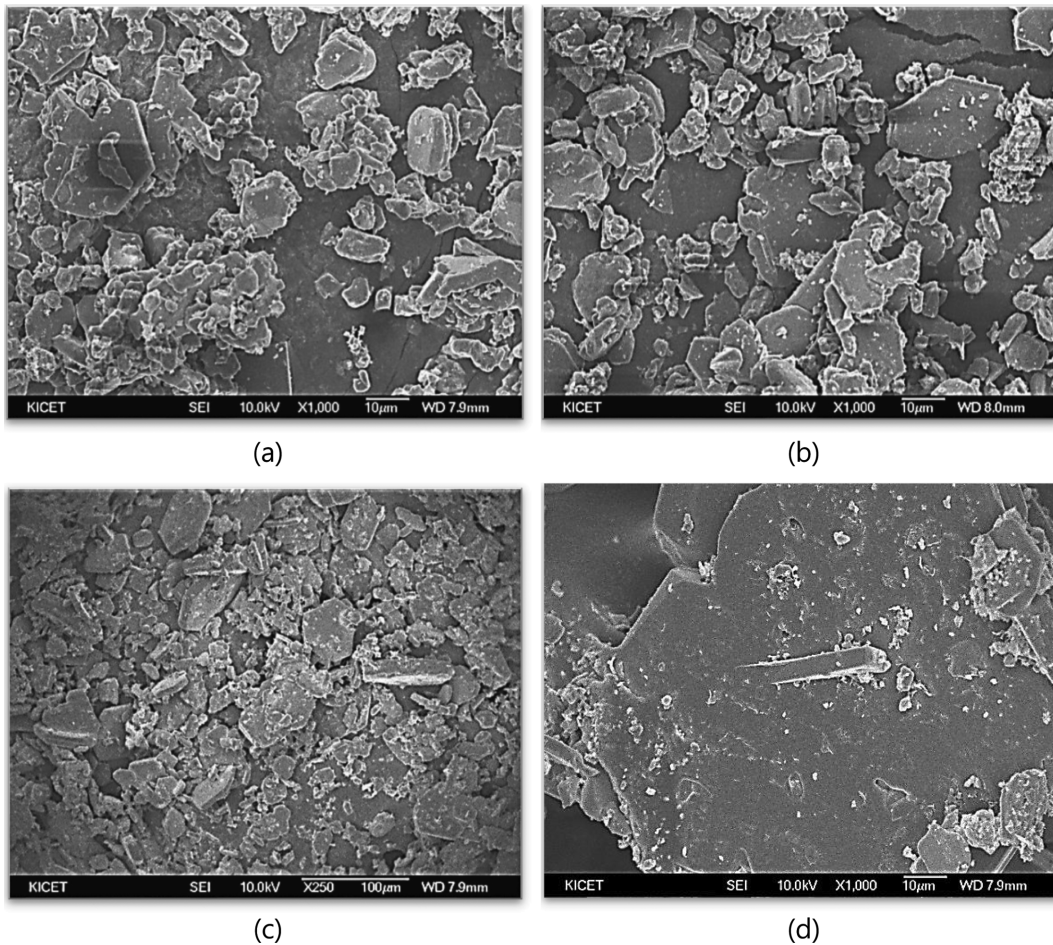


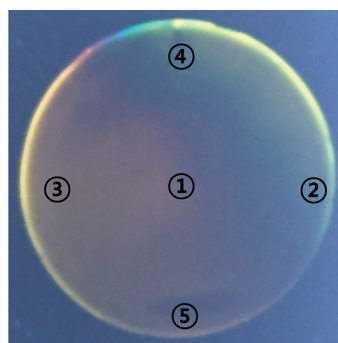
Fig. 8. SEM image of the synthesized β -SiC powders (a)–(b) after annealing, (c)–(d) after the thermocyclic process.

Table 2
Chemical analysis results of β -SiC powders as starting material which were obtained by Korean Industrial standard of KS L 1612

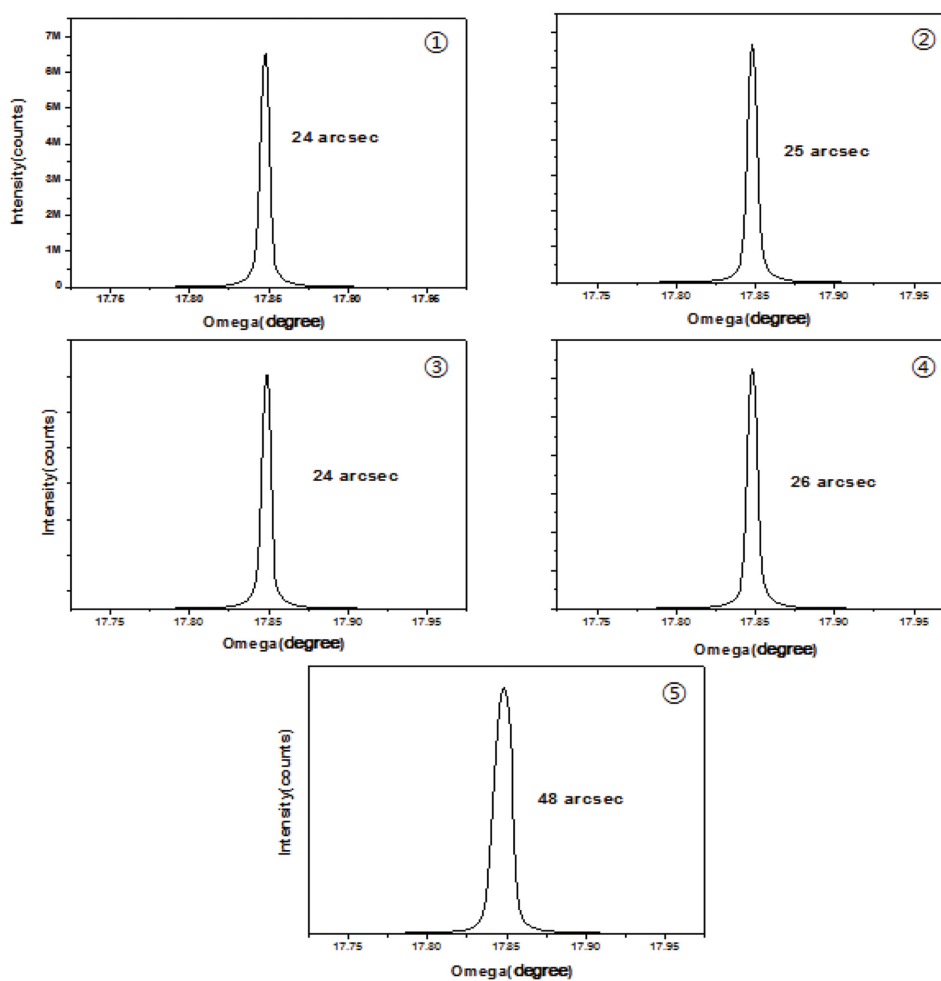
Component analysis (wt%)			
SiC	Free-C	Silicon	
		SiO ₂	Free Si
97.35	0.02	1.60	0.88

Table 3
Chemical analysis results of the β -SiC powders obtained by Korean Industrial standard of KS L 1612

Sample	Component analysis (wt%)			
	SiC	Free-C	Silicon	
			SiO ₂	Free Si
Annealing	95.9	3.97	0.06	0.02
Thermocycling	99.59	0.25	0.03	0.009



(a)



(b)

Fig. 9. 4-inch 4-H SiC wafer (a) image and (b) crystallinity analysis with FWHM of HRXRD.

by surface diffusion, which results in changes in particle size and morphology [21]. This growth takes place during annealing, but we were able to maximize the number of grains growing uniformly by an evaporation - recrystallization process through thermocyclic treatment. It can be confirmed by PSA and SEM results (Fig. 7 and 8).

The results of the chemical analyses (KS L 1612) of the SiC content in the annealed powder and thermocyclic powder are listed in Table 3. After the thermocyclic process, the purity of the purified β -SiC powder increased from 95.9 % to 99.59 %. In addition, the concentration of free silicon impurities was reduced from 2.48 % to 0.039 %. These results confirmed that thermal purification was effective in decreasing the silicon impurity in β -SiC powder.

Also, 4-inch 4-H SiC single crystals were grown using the PVT method. Crystallinity analysis of these samples was carried out using high-resolution XRD. The X-ray FWHM values of the substrate peak were in the range of 25-50 arcsec (Fig. 9), which confirms that the synthesized SiC powder was good for crystal growth.

4. Conclusions

In this study, we determine the feasibility of synthesizing highly pure SiC powder with low free silicon by direct carbonization. To reduce the amount of free silicon, we carried out ball milling with SiC balls. Since the direct reaction of a powdered mixture of silicon and graphite under normal pressure begins slowly around 1150°C [20], we inserted a holding step at 1400°C for 4 h, to minimize the amount of Si trapped inside the β -SiC particles. As a result, we obtained SiC powder with a purity of 99 % and a size of 100 μm . Using a beta SiC source, high quality 4H-SiC crystals were grown and they were found to show uniformly good crystallinity.

In conclusion, we confirmed that the β -SiC powder synthesized through a purification process is good to be used as a starting material for single-crystal growth.

Acknowledgements

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