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## The SiC Single Crystal Growth from Nanomaterial Precursor

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### ABSTRACT

*Unlike the conventional layer by layer growth, three dimensional growth experiments of SiC single crystal by the Chemical Particle Deposition (CPD) method were carried out both on the polar and nonpolar plane of the SiC seed crystal. The comparison of the morphology of the grown crystals on both samples indicated that the electric field formed by the seed crystal strongly effected the diffusion of the supplied Si and C atoms and their compounds to grow the epitaxial crystal. In spite of the low ionicity of Si-C bonds, this remarkable effect of the electric field on the three dimensional crystal growth mechanism in the CPD method strongly suggested its contribution to the ordering of the stacked layers with its long working range, beyond the deformed boundary layers between the seed surface and the grown crystal.*

### INTRODUCTION:

The conventional SiC single crystals have been grown from the vapors or the solutions, including Si and C atoms and their compounds, since SiC does not have a liquid phase.

The crystal growth from lean source materials like the vapors and the solutions necessarily progresses through the layer by layer growth mechanism, and is dominated by spiral growth [1,2]. The high concentration screw dislocation caused the deterioration of the crystal quality. In order to solve this problem, The CPD method in which nanomaterials of SiO<sub>2</sub> and C were used as the raw materials, was proposed at ICSCRM2001[3]. In the CPD method, nanometer size raw materials are mixed and changed into micrometer size particles by the spray dry method. Such a micrometer size particle which consists of the ultrafine SiO<sub>2</sub> and C particles can be regarded as a droplet of the melt of SiC which reacts on or near the seed crystal surface to form the epitaxial SiC crystal and grows the SiC single crystal in three dimensions.

The continuous feed of the particle precursor in CPD method will be able to realize the continuous growth of SiC single crystal.

The SiC single crystals grown by the CPD method in many cases inherited the polytypes of the seed crystals [4,5]. In order to reveal the cause of this fact, the growth mechanism of the SiC single crystal in the CPD method was investigated through the crystal growth experiments by the CPD method on the seed surfaces with different electric characteristics, polar and nonpolar. Since SiC has polytype which has long periodic structure along its c-axis, like 4H, 6H and 15R, it is reasonable to consider the Coulomb's force as the dominating force affecting the stacking of SiC layers in the single crystal, with its long working range.

## EXPERIMENTAL DETAILS

The SiC growth experiments by the CPD method were carried out using the apparatus consisted of an electric furnace with graphite heaters, and a powder feeder just like the one developed by Bernoulli about 100 years ago (see figure 1.). The raw materials of the precursor for the CPD growth were, SiO<sub>2</sub> (fumed silica: 380m<sup>2</sup>g<sup>-1</sup>) and C (carbon black: 240m<sup>2</sup>g<sup>-1</sup>), both had the diameter of approximately 20nm. Although the liquid raw materials like TEOS (Si (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and phenolic resin with higher purity existed, they were not selected, considering the difficulties in the carbonize process. The fumed silica and the carbon black at 5:3 weight ratio, were mixed and ball milled as 7 wt. % aqueous slurry for 24h using nylon balls with iron core. The spray dry processing was carried out to turn that slurry into the precursor particles with 10-100μm diameter. The precursor particles were kept in the vacuum container to dehumidify for minimum of 24h. Before the start of CPD experiments, precursor powders were poured gently into the container of Bernoulli powder feeder which had 20-30 openings cm<sup>-1</sup> bottom mesh. The reactor chamber was evacuated to 0.4Pa, very slowly preventing the scattering of the precursor powders. Argon gas was introduced into the reactor chamber until it reached 10<sup>3</sup>Pa, after the leakage check for 1h.

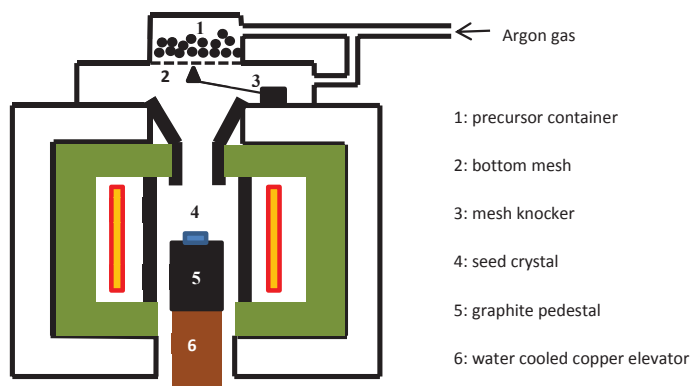
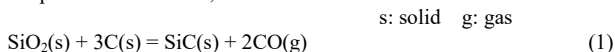
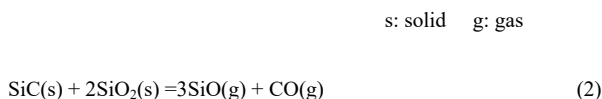


Figure 1. The schematic of the CPD experimental set up.

In order to determine the heating parameters a thermochemical review was conducted [6,7]. The reaction in the CPD process (carbothermal reduction of SiO<sub>2</sub> by C) is considered to proceed as follows,



Reaction (1) proceeds over 1745K, and after this reaction proceeded, C particle is wrapped up by the shell of SiC and reaction (1) is then retarded, since C atoms must diffuse through the SiC shell to react with SiO<sub>2</sub> or SiO. If C atoms were left, they may remain as “carbon inclusions” in the grown SiC single crystal. In order to complete the CPD process, the next reaction is needed.



Although Reaction (2) proceeds over 2021K, the setting of the furnace temperature must be carefully selected considering the results of the experiments, because the total reaction is heavily endothermic [4]. After the SiO<sub>2</sub> in the precursor is used up, epitaxial SiC crystal is left on the seed SiC crystal. This comprehensive reaction mechanism is schematically illustrated in figure 2. As shown in figure 2, the raw precursor particle, consist of the ultrafine fumed silica and the carbon black, reacts together with the surface SiC atoms and forms the epitaxial crystalline “hill” on it. At the moment of CO gas emission, the precursor particle turns to the fluid state and is stacked on the seed crystal under the effect of the electric field formed by the seed crystal. Such crystal growth in three dimensions under the effect of the electric field formed by the seed crystal is specific to the CPD growth and the melt growth.

In the experiments, stopped before the temperature of the reactor reached 2273K due to the malfunction of the Bernoulli powder feeder, some precursor particles leaked through the bottom mesh and reacted on the seed surface. Even in such cases, the single precursor particle inherited the structure of seed crystal (see figure 3. and figure 4.), although the reaction condition was not perfectly fitted.

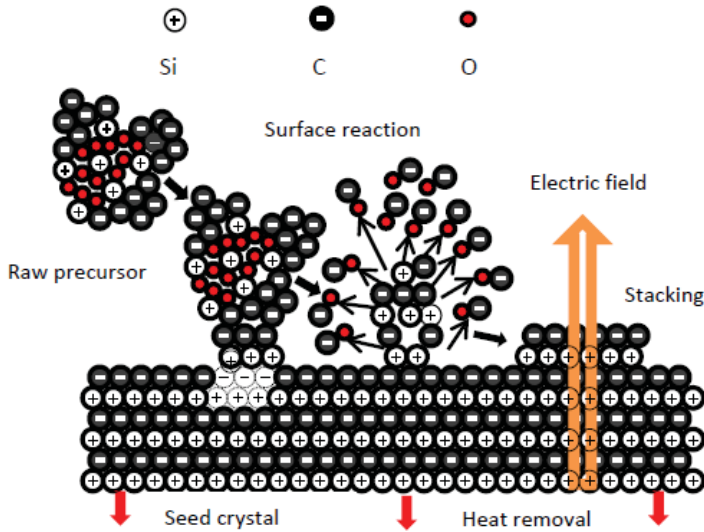


Figure 2. The schematic of CPD growth mechanism. The raw precursor reached on the seed crystal surface reacts together with the seed surface SiC atoms and forms epitaxial crystal under the effect of the electric field formed by the seed crystal.

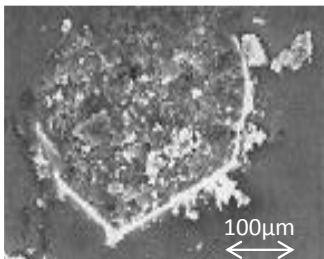


Figure 3. The image of the single precursor particle reacted on c-plane off-cut in a-axis of the seed crystal.

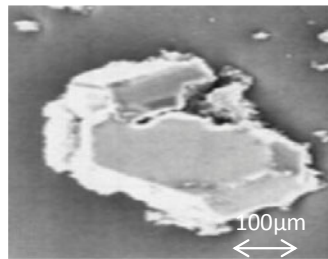


Figure 4. The image of the single precursor particle reacted on well-oriented c-plane of the seed crystal.

## RESULTS AND DISCUSSION

In the successful experiment, after 1 h of precursor feeding, about 200 μm SiC single crystal was grown on (000-1) plane of the seed crystal (see figure 5. and figure 6.).

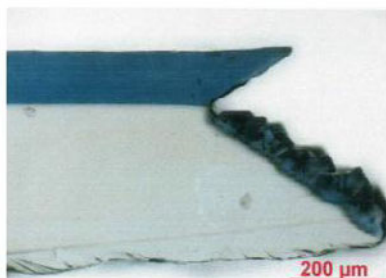


Figure 5. Sectional view of CPD grown single crystal layer.  $N_2$  gas was incorporated by air leakage.

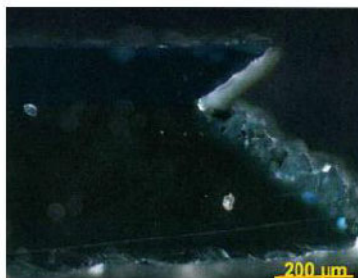


Figure 6. Polarized light image of figure 5. Only the polycrystalline part is bright.

### The effect of electric field in CPD method

In order to investigate the growth mechanism of SiC single crystal in the CPD method, growth on (000-1) plane (polar surface) and (1-100) plane (nonpolar surface) were conducted. The seed substrates for each experiment were cut out from a PVT grown SiC boule. Although the experiments were carried out following to the same program, the morphology of the grown sample were quite different from each other (compare figure 7 (a and b), and figure 8 (a and b)). The surface of the CPD grown crystal on (000-1) polar surface of the seed crystal formed the gentle “hills” with (000-1) plane on the top, as shown in figure 7(a), which indicated an almost isotropic spread of the Si and C atoms and their compounds supplied by the precursor particles. On the other hand, the morphology of the grown crystal on (1-100) nonpolar surface showed the rows with periodic peaks, parallel to c-axis and interrupted in a-axis, as shown in figure 7(b). This morphology corresponds to the electric field over (1-100) nonpolar surface of the seed crystal on which periodic electric field parallel to c-axis exists but electric field in a-axis lacks. Besides, the cross section of this sample included many pores and crevices, as shown in figure 8(b), contrary to the cross section of the grown crystal on (000-1) polar surface (see figure 8(a)), because of the weaker vertical electric field on (1-100) nonpolar surface compared to the one on (000-1) polar surface.

On the (000-1) polar surface, the strong vertical electric field attracts Si and C atoms and their compounds contained in precursor particles to the seed surface, assisting the thermal diffusion to grow the epitaxial SiC single crystal. As illustrated in figure 9., on the (1-100) nonpolar plane, the intensity of the vertical electric field is so weak that the atoms and the molecules in the reacted precursor particles could not sufficiently diffuse to form the uniform epitaxial SiC crystal, as shown in figure 7(b) and figure 8(b). This remarkable effect of the electric field over the seed surface, clearly supports that the electric field formed in the reacting precursor particle by the seed crystal, strongly effected the three dimensional structure of the grown SiC single crystal, inherited from the seed crystal. Such three dimensional stacking effect caused by the electrostatic field formed by the seed crystal, gave the exact epitaxy to the SiC single crystal grown by the CPD method.

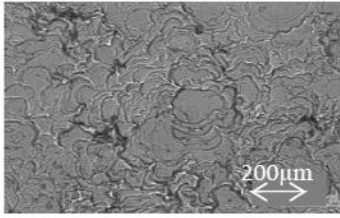


Figure 7(a). CPD grown surface on (000-1) seed surface.

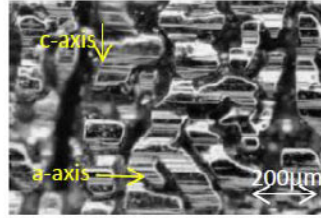


Figure 7(b). CPD grown surface on (1-100) seed surface.

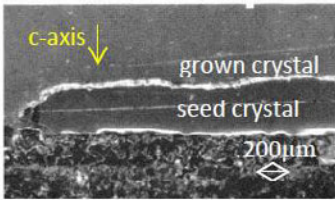


Figure 8(a). Cross section of figure 7(a) sample.

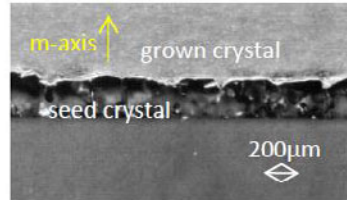


Figure 8(b). Cross section of figure 7(b) sample.

### (000-1) Polar plane

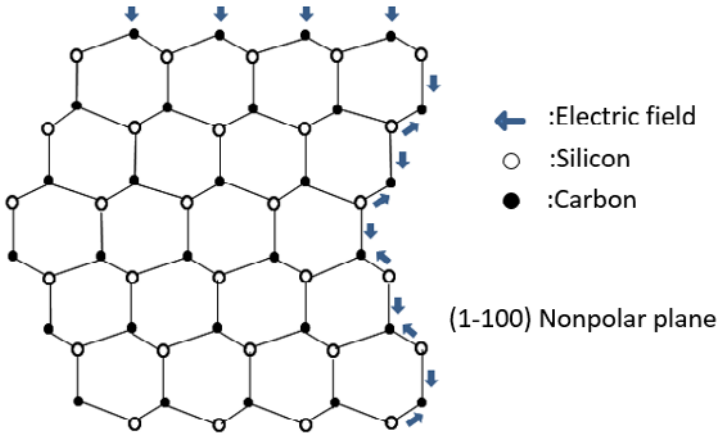


Figure 9. The schematic of the electric field over (000-1) and (1-100) planes.

## CONCLUSION

This study for the first time shows that the electric field over the SiC seed crystal strongly effects the diffusion and the stacking of the Si and C atoms and their compounds in the growth process by the CPD method. Although the SiC single crystal growth on the polar plane proceeds isotropically, the growth on the nonpolar plane proceeds anisotropically, reflecting the intensity and the direction of the electric field over the seed crystal surface.

## ACKNOWLEDGMENTS

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## REFERENCES

1. F.C.Frank, *Disc. Faraday, So.*, **5**, 48-54.
2. W.K.Burton, N.Cabrera and F.C.Frank, *Phil. Royal. Soc., London*, **243**, 299-358 (1951).
3. Y.Yamada and K.Sagawa, *Material Science Forum*, **389-393**, 159-162 (2002).
4. Y.Yamada, S.Nishizawa and S.Nakashima, *Material Science Forum*, **433-436**, 78-82(2003).
5. Y.Yamada, S.Nishizawa, S.Nakashima and K.Arai, *Material Science Forum*, **457-460**, 78-82(2004).
6. NIST-JANAF Thermochemical Tables Fourth Edition. Part1, 550, 641, 649
7. NIST-JANAF Thermochemical Tables Fourth Edition. Part2, 1728, 1753, 1882.