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Methods for the reduction of the micropipe density in SiC single crystals

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Abstract Micropipes are very harmful for SiC devices. Even one micropipe in the active area can destroy a high-voltage SiC device. Therefore, it is necessary to reduce the density of micropipes in SiC single crystals. In the present paper, we proposed methods for reducing micropipes. Restriction of screw dislocations and decrease of inclusions are the key factors to reduce the number of micropipes. (0 0 0 1) Si-face, $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces acted as growth surface in different experiments. Active carbon was appended to act as carbon source. The crucible and active carbon were subjected to X-ray diffraction investigation before and after growth. The experimental results indicate that the activity of the graphite crucible was low, and it decreased with the progressing crystal growth, which increased the probability of micropipe formation. Appending active carbon can act as ample carbon source for crystal growth. The reduction of micropipes was achieved by the restrained formation of Si liquid phase. Using $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces as the growth surfaces the generation of micropipes was restricted, as no new micropipe generated on the $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces. At the same time, the density of edge dislocations is reduced considerably.

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Introduction

Silicon carbide (SiC) is a promising substrate material for making high frequency, high temperature and high power devices [1]. Most SiC substrates still contain various structural defects, such as micropipes, dislocations, inclusions and mosaic structures [2]. Micropipes are the most harmful defects in SiC devices. Even one micropipe in the active area of a high-voltage SiC device would destroy the device [3]. Hence, researches on micropipes never stop since they have been discovered. Heretofore, several models have been proposed to elucidate the formation mechanism of the micropipes [4–9]. Generally, there are two viewpoints for the formation mechanism of micropipes. One mechanism is based on the Frank's model of hollow core dislocations [10]. Other mechanisms are generalizing the cause as the second phase and impurities on the growth surface, which subsequently or almost simultaneously attract dislocations and become cores of dislocations, then micropipes generate along the dislocation lines [11].

Reducing the number of micropipes in SiC single crystal is the most concerned topic for researchers. Filip reported the micropipe healing in SiC wafers by liquid-phase epitaxy in Si–Ge melts [12]. Dmitriev used micropipe filling process to reduce the density of micropipes [3]. Kato used etch back process of seed crystal to restrict the generation of micropipes and dislocations [13]. Appending Si can reduce the occurrence of carbon inclusions, which can decrease the number of micropipes [14, 15]. Recently, Nakamura used 'repeated a-face growth' method, which reduced the number of dislocations in SiC single crystals by two to three orders of magnitude, and the density of micropipes were also reduced [16].

In this paper, we try to reduce the number of micropipes by restricting the conditions for micropipe formation.

Analysis

There are two ways a SiC single crystal can form micropipes—replicating from seed crystal or generating during growth process. Replicating of micropipe is unavoidable since micropipe is inherent from the seed crystal. So improving the quality of seed crystal is the only way to reduce the number of replicated micropipes. The formation of new micropipes during the growth process is closely related to growth conditions. These can be improved during the growing process. Therefore our investigation is mainly focusing on reducing the latter kind of micropipes.

Previously, several models are proposed to explain the formation mechanism of micropipe. However, a detailed understanding of the mechanism remains unclear. By analyzing those models, it can be found that the formation of micropipes is related to screw dislocations (SDs), stacking faults (SFs) and inclusions. SFs and inclusions are primarily necessary conditions for origination of micropipes, and SDs provide power to their subsequent growth.

Generally, SDs propagate along [0001] direction in SiC single crystal Burgers vectors parallel to *c*-axis [10]. SFs are created by the motion of partial dislocations [17–19], and spread perpendicular to *c*-axis [20].

Silicon droplets and carbon particles are common inclusions in the SiC single crystals that are grown by physical vapor transport (PVT) method. Carbon particles form as a result of seed surface graphitization, and occur at the incipient stage of growth [15, 21]. The occurrence of silicon inclusions can be explained by the formation of Si drops on the surfaces of the SiC seeds. Drachev et al. have studied liquid silicon drops on the surfaces of seeds [22], and a brief thermodynamic analysis of the Si liquid phase development was carried out in the temperature range of 1,500–3,150 K. The fabrication of SiC single crystals is carried out at high temperature (>2,000 °C), and the crucible is a strong carbon source for crystal growth [8]. With the progress of the crystal growth, the activity of carbon of crucible decreases, which will degrade the reactions between the crucible wall and the gaseous species inside the crucible. In this case, the growth rate will decrease and the occurrence of silicon drops will increase [23]. So, maintaining activity of carbon source is important for reducing the silicon inclusions.

Reducing inclusions and avoiding SDs and SFs are explicit ways for the reduction of micropipes. In this paper, we discuss the ways for reducing the silicon inclusions in SiC single crystal. In order to avoid SDs and SFs, $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces will act as the growth surface. Active carbon (amorphous carbon) is appended for reducing of silicon inclusions.

Experimental procedure

6H–SiC single crystals were fabricated using PVT technique. The growth was carried out in an inductively heated graphite crucible. The seed temperature was set to 2,200 °C. The system pressure of the argon gas was 40 mbar and temperature gradient is about 20–30 °C/cm. The SiC seed crystals were 6H–SiC grown by the PVT technique. The (0 0 0 1) Si-face, $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces (cut from PVT crystal) acted as the growth surfaces. The source material was SiC powder of an average grain size of 120 μm. The distance between the seed crystal and the source was about 20 mm. Four different experiments (labeled with 1, 2, 3, 4) were done, and the grown crystals were labeled crystal 1, 2, 3 and 4 correspondingly. Table 1 shows the respective growth conditions.

The graphitization degree of the graphite crucible was measured by a Rigaku X-ray diffractometer, using high-purity silicon powder as calibrated standard material. Crystals 1 and 2 were cut parallel to the growth directions for investigation of defect formation at different stages of growth. Crystals 3 and 4 were cut perpendicular to growth directions for investigation of the number of micropipes and dislocations.

Results and discussion

Figure 1 shows the images of seed and grown crystals in experiments 3 and 4. The short lines are edge dislocations. The long black line in Fig. 1a is micropipes. It can be seen that the densities of edge dislocations decrease greatly after growth and no new micropipes appear along growth directions.

Figure 2 shows the images of the crystals which were cut parallel to the growth direction. Crystal 1 has more defects than 2, including inclusions, voids and micropipes. The defects in the crystal 2 mainly appear near the seed. With the progress of crystal growth, no new defect occurred in crystal 2; only the micropipe formed at first extends along growth direction. However, the defects in crystal 1 appear from the beginning to the end in crystal growth. With the progress of growth, new defects may form at any parts of the crystal.

Figure 3 shows the XRD results of the crucible and active carbon. After growth, the diffraction peaks of the crucible used in experiment 1 were sharp and had high intensities. That is to say, the graphitization of the crucible was increased. Active carbon has an amorphous structure before growth. After growth, graphitization occurs to a

Table 1 The condition for the experiments

Number of experiments	Source materials	Growth surface	Name of grown crystal
1	SiC	(0001)	Crystal 1
2	SiC + C	(0001)	Crystal 2
3	SiC	$(11\bar{2}0)$	Crystal 3
4	SiC	$(1\bar{1}00)$	Crystal 4

C in the experiment 2 is active carbon

certian extent, however, the graphitization degree is still low. The graphitization degree of crucibles can be calculated by the formula (1)

$$g = [(0.344 - d_{002})/0.0086] \times 100\% \quad (1)$$

where g is graphitization degree, d_{002} crystal plane distance of graphite (002) planes. d_{002} and the g values of the crucible are shown in Table 2.

Using crystal faces parallel to the [0001] direction as growth surface would not provide condition for micropipes. Thus, no new micropipe appears, as shown in Fig. 1. At the same time, the density of edge dislocations is reduced considerably. In Ref. [16], Daisuke Nakamura gave the reason for reduction of edge dislocations in detail.

The main vapor species for the SiC + C system at high temperatures are Si, SiC_2 and Si_2C [24]. The main reactions in growth occur as follows:

$$SiC_{(s)} = Si_{(g)} + C_{(s)} \quad (2)$$

$$2SiC_{(s)} = Si_{(g)} + SiC_{2(g)} \quad (3)$$

$$2SiC_{(s)} = C_{(s)} + Si_2C_{(g)} \quad (4)$$

$$2C_{(s)} + Si_{(g)} = SiC_{2(g)} \quad (5)$$

$$Si_{(g)} + SiC_{2(g)} = 2SiC_{(s)} \quad (6)$$

(2), (3) and (4) are the sublimation reactions of the source SiC powder, (5) is the reaction between graphite Si vapor and carbon source (crucible or appended active carbon), (6) is the reaction for SiC crystal growth. From these reactions, it can be seen that the SiC_2 vapor (p (SiC_2)) is formed from reaction (3) (p_1 (SiC_2)) and reaction (5) (p_2 (SiC_2), and the Si vapor (p (Si)) from reaction (2) (p_1 (Si)) and reaction (3) (p_2 (Si)).

During the growth process, the vapor pressure of Si is considerably larger than those of SiC_2 and Si2C, especially at low temperatures [15]. During heating-up and incipient stage of growth, the system is in a non-equilibrium state. In order to reach enough vapor pressure of Si for crystal growth, the seed crystal and source powder will provide Si according to reaction (2). Then additional carbon will be produced on the seed and it is easy to form carbon inclusions, which often lead to the generation of micropipes [21, 25]. As shown in Fig. 2c and d, there are inclusions and micropipes at the near seed part of crystals 1 and 2.

The study by Drachev [22] elucidated the condition for formation of a Si liquid phase as

$$p_{Si}(T_V) > p_{Si}^{sat}(T_S)$$

where T_V is the temperature of the sublimation point and T_S is the temperature of crystal surface, $p_{Si}(T_V)$ is the equilibrium partial pressure of free silicon in the vapor of SiC and $p_{Si}^{sat}(T_S)$ is the silicon saturation pressure at the temperature of crystallization T_S.

However, in the actual growth process, $p_{Si}(T_V)$ cannot represent the vapor pressure of Si because of the reaction between Si vapor and carbon source. So $p_{Si}^{R}(T_S)$ is used to represent the real pressure of Si vapor at the front of crystal. $p_{Si}^{R}(T_S) = p_{Si}(T_V) - p_{Si}^{E}(T_S)$ (where p_{Si}^{E} is the consumed vapor pressure of Si in reaction (5)). So $p_{Si}^{R}(T_S) > p_{Si}^{sat}(T_S)$ is the real condition for the formation of a Si liquid phase. It is obvious that the formation of a Si

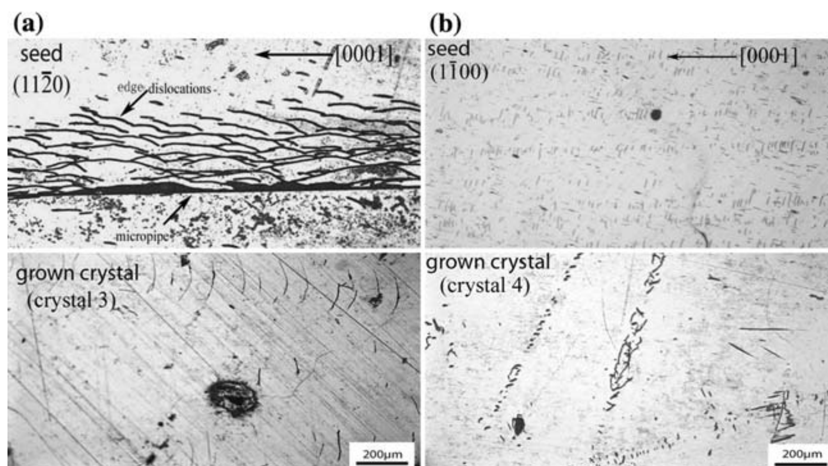


Fig. 1 Optical images of seed and grown crystals. These crystals were cut perpendicular to growth direction and etched with melt KOH (500 °C for 10 min) after polished. (**a**) Crystal 3, (**b**) crystal 4

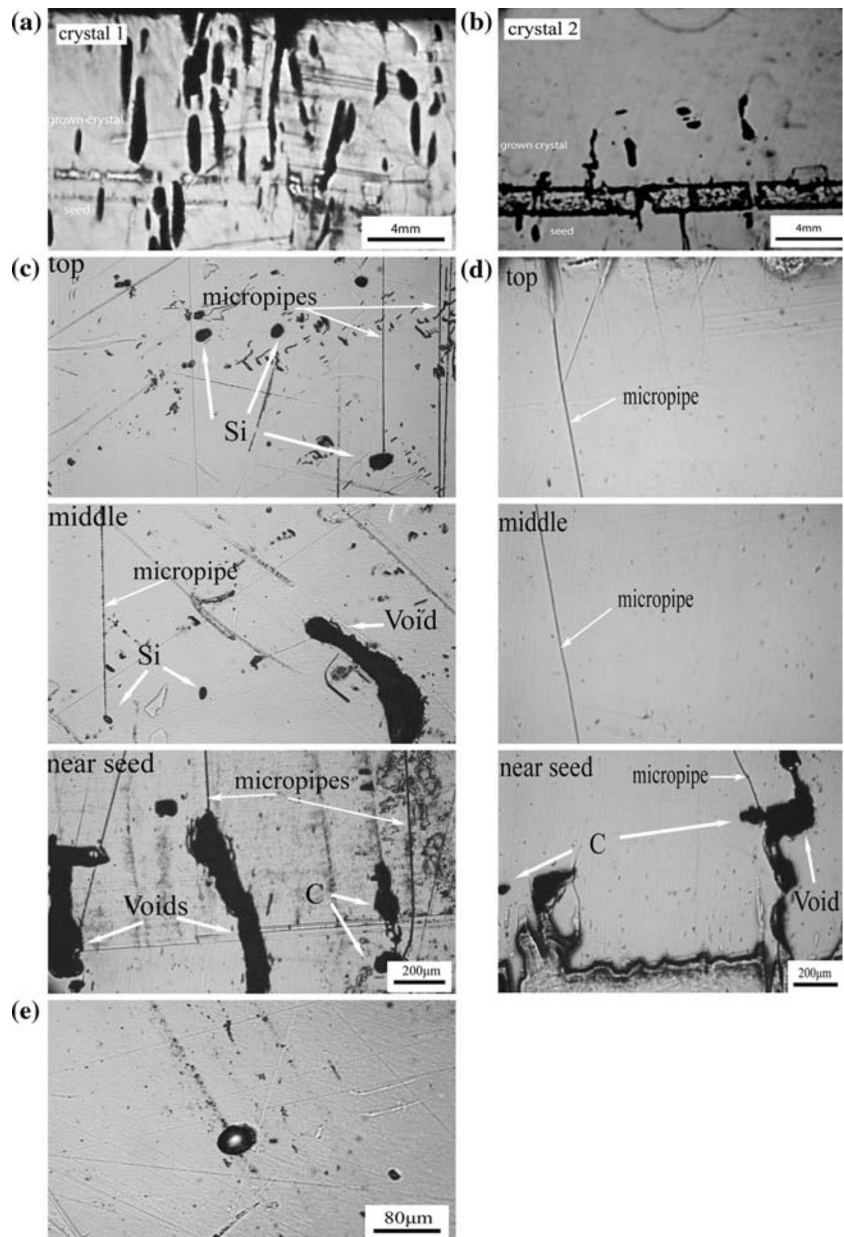
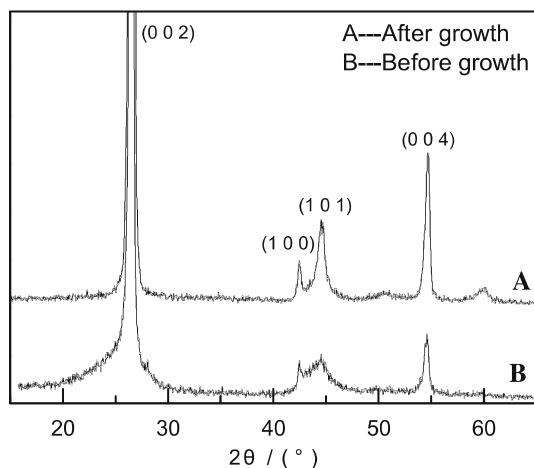


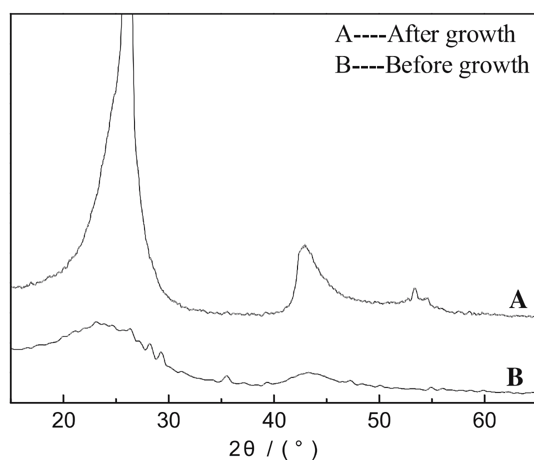
Fig. 2 Optical images of crystals cut parallel to growth directions. The exposed surfaces were etched with melt KOH (500 °C for 10 min) after a polish. (**a**) Crystal 1, (**b**) crystal 2, (**c**) different parts of crystal 1, (**d**) different parts of crystal 2, (**e**) amplificatory Si inclusions of (**c**)

liquid phase is related to reaction (5). As temperature and total pressure keep constant, reaction (5) is the main factor for the formation of Si liquid phase.

In experiment 1, the carbon activity is low due to the high graphitization degree of the crucible [26], and the graphitization degree is increased during the crystal growth, as shown in Fig. 3a and Table 2. That is to say, reaction (5) becomes difficult with the progress of crystal growth, which was controlled by the graphitization degree of the crucible. Then $p_{\mathrm{Si}}^{\mathrm{E}}$ turns low and $p_{\mathrm{Si}}^{\mathrm{R}}(T_{\mathrm{S}})$ becomes high. The probability of formation of Si liquid phase increases, which results in the increase in the probability of formation of the defects. As shown in Fig. 2c, the new defects occur in the middle and end parts. In experiment 2, the main carbon source is active carbon with a high activity even after growth. So it has enough activity to react with the Si vapor from the beginning to the end of growth. As temperature controls reaction (5), $p_{\mathrm{Si}}^{\mathrm{E}}$ keeps constant during growth process. Compared with experiment 1, $p_{\mathrm{Si}}^{\mathrm{E}}$ is high and $p_{\mathrm{Si}}^{\mathrm{R}}(T_{\mathrm{S}})$ is low. The probability of formation of Si liquid phase decreases, even to zero. As shown in Fig. 2d, no new defect occurred in crystal 2, although only one micropipe formed at first extends along growth direction.



(a) Crucible used in experiment 1



(b) Active carbon used in experiment 2

Fig. 3 XRD results: (**a**) crucible used in experiment 1, (**b**) active carbon used in experiment

Table 2 d_{002} and g values of crucible

Crucible condition	d_{002} (nm)	g (%)
Before growth	0.3371	80.2
After growth	0.3364	88.4

Conclusions

By appending active carbon to compensate the low activity of the graphite crucible or using, $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces as growth surfaces, we obtain single SiC crystal with considerable decreased micropipe density. When using the crucible as the only carbon source, the probability of micropipe formation increases, due to the activity of the graphite crucible decreasing in the progress of crystal growth. Appending active carbon can provide ample carbon for crystal growth and restrain the formation of a Si liquid phase, consequently reduce the occurrence of micropipes. Using $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces as the growth surfaces, the generation of micropipes was restricted, as no new micropipe generated on $(11\bar{2}0)$ and $(1\bar{1}00)$ crystal faces. At the same time, the density of edge dislocations is reduced considerably.

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