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LETTER TO THE EDITOR

New type of defects in SiC grown by the PVT method

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Abstract

The quality of SiC crystals grown by the physical vapour transport (PVT) method was studied by means of optical microscopy and scanning electron microscopy (SEM) observations with the aid of etching by molten KOH. New types of defects were found, including triangular etching pits, shallow hexagonal etching pits and dendritic silicon inclusions in 4H-SiC. The triangular etching pits usually appear on the C face with a size comparable with the irregular dark etching pits due to the micropipes, while the shallow hexagonal etching pits were observed on the Si face with a size comparable with that due to the micropipes. The silicon inclusions exhibit dendritic shape up to several microns like those usually observed in metal alloys. In addition, 4H-SiC and 6H-SiC domains with different polarities in the growth surface were found to develop from the same seed. The interface of 4H-SiC and 6H-SiC was one of the sources for inducing the micropipes.

1. Introduction

Silicon carbide is an appropriate material for the fabrication of high temperature, high frequency and high power electronic devices, due to its wide bandgap (2.3–3.2 eV), high breakdown field ($>20 \times 10^{-5}$ V cm^{-1}), high thermal conductivity (5–7 W cm^{-1} K^{-1}), and high electron saturation drift velocity (2.0×10^{-7} cm s^{-1}) [1, 2]. SiC crystals of over 2 inches in diameter on a commercial scale have been produced with the PVT technique [3]. But the amount of defects needs reduction and the quality of the SiC wafer needs further improvement. Various kinds of defects have been known to exist in the grown SiC crystals [4–11] such as micropipes, dislocations, stacking faults, subgrain boundaries and inclusions. Among them, micropipes, hollow tubes with diameters from microns to tens of microns extending along the $\langle 0001 \rangle$ c-axis, are regarded as the killer defects for SiC high power and high voltage devices.

Usually, it is difficult to observe dislocation-related defects on the as-polished surfaces of SiC. Defect selective etching with molten KOH is a simple and quick method to reveal such

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defects [7, 8, 12–19]. In this paper, we report the defects on both the C faces and the Si faces of 4H-SiC etched by molten KOH. Besides the familiar micropipes and planar etching pits, we also found new defects, including triangular etching pits on the C faces, shallow hexagonal etching pits and dendritic silicon inclusions on the Si faces. The formation mechanism of dendritic Si inclusions is discussed. The interfaces of 4H-SiC and 6H-SiC were examined in the case of co-growth of 4H-SiC and 6H-SiC over the same seed.

2. Experimental procedure

SiC crystals are grown by the PVT method with the growth temperature range of 2200–2300 °C under the flow argon pressure of 1500–3000 Pa. The more detailed experimental description can be consulted elsewhere [20]. Under these conditions, we obtained SiC single crystals with a diameter up to 2 inches and a thickness up to 15 mm. The average growth rate was 0.5–0.8 mm h^{-1}.

Rectangular samples with a size of 5×5 mm^2 and a thickness of 1 mm were cut with the thickness direction parallel to the c-axis from the grown SiC boules. Then, they were mechanically polished with diamond slurries of different grain sizes from 40 μm to 1 μm before etching. Molten KOH was used to achieve preferential chemical etching of the wafers at 470 °C for 20 min. Since the stirring of the melt is very important for reproducible etching [12], the melting temperature was kept constant for more than 30 min before the etching process.

Raman spectra were used to identify the polytypes of SiC. Etching surfaces were observed by optical microscope and SEM (Hitachi, S-4200) with an energy dispersive x-ray spectrometer.

3. Results and discussion

As is well known, SiC shows two polarities in the $\{0001\}$ direction called the (0001) Si face and $(000\bar{1})$ C face. After etching, the two kinds of faces differ in light reflection. The C face is shinier and smoother than the Si face. This can be attributed to the different etching rates of the two faces in molten KOH. It has been estimated that the etching rate of the C face was about four times that of the Si face in molten KOH [12, 13] and a similar result was obtained when SiC was etched in KOH vapour [21]. The different etching rates of the C face and the Si face are due to the fact that the two faces have different surface free energies. Since the C face has a lower surface free energy, it exhibits a faster etching rate. Typical etching patterns on the C face and the Si face of 4H-SiC were shown in figure 1. The smoother C face of 4H-SiC shows smaller irregular dark etching pits due to the micropipes in figure 1(a) while the coarser Si face shows several larger hexagonal micropipes in figure 1(b). This is in conformity with the previous study [14]. The different etching patterns of the two faces are due to the fact that the C face and the Si face of SiC are attacked by KOH isotropically and preferentially, respectively.

On the Si face of 4H-SiC, shallow etching pits with hexagonal shape are observed after etching as indicated by figure 2(a). They are comparable with the micropipes in shape and size, but they are not due to micropipes since they do not penetrate through the wafers. Instead, their depth is only a few microns. The inset of figure 2(a) showed that the hexagonal pits were coarse on the bottom. The hexagonal symmetry of the concaves appearing on the Si face indicates that it is related to the sixfold symmetry crystal structure of the 4H-SiC. On the C face of 4H-SiC, etching pits with triangular, round and shell-like shapes are revealed with the help of the transmission mode of optical microscopy as shown in figure 2(b). Shell-like and round etching pits have been reported in previous studies [14, 15, 18]. It is believed that shell etching

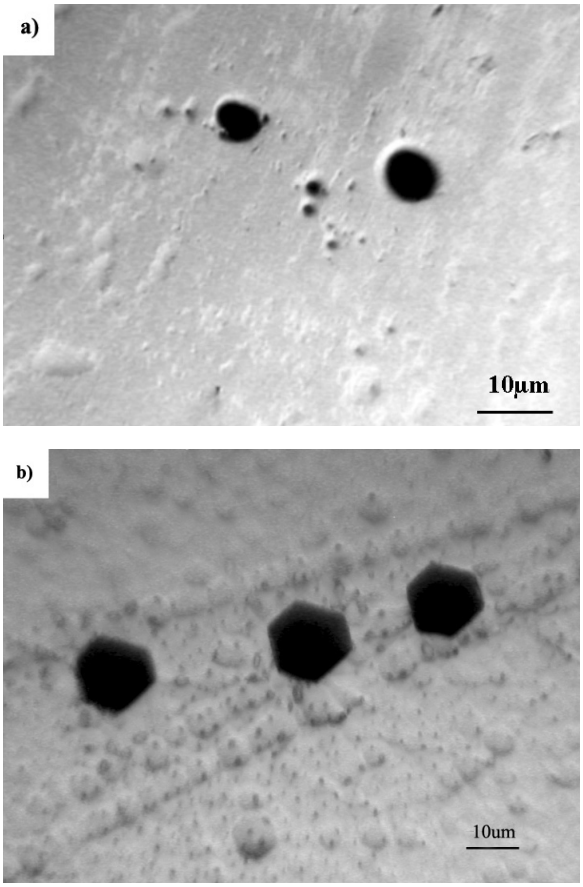

Figure 1. Typical micrographs of etching pattern on the C face (a) and the Si face (b) of 4H-SiC. The sample was etched by KOH at 470 °C for 20 min.

pits are due to the existence of threading edge dislocations [15, 18]. On the other hand, the triangular etching pits are new to 4H-SiC bulk crystals grown by the PVT method. Their sizes are comparable with the irregular dark etch pits in figure 1(a). They are believed to be related to dislocations. In previous studies, Nishiguchi *et al* observed similar triangular etching pits on the C face of 15R-SiC grown by the Acheson method [17], and with the help of TEM Okada *et al* found triangular defects with isosceles shape on the 4H-SiC epilayers which were related to the stacking fault on (0001) plane [22]. Yoo *et al* [16] have observed starfish-like etching pits on 6H-SiC.

Micropipes and polytypes are two most important defects in PVT growth of SiC. However, the origins of micropipes in SiC crystals are not clear to date and it is rather difficult to control SiC polytypes in PVT growth of SiC. The above-mentioned two new defects, i.e. triangular etching pits and the shallow hexagonal etching pits, might be possible sources of micropipe and polytype formation.

Another new type of defect found in our investigation concerns inclusions. The compositions of the inclusions have been tested by the energy dispersive x-ray spectrum. The results show that the inclusions are mainly composed of silicon, as indicated by the inset in figure 3, along with a little chlorine. Chlorine was not included into the crystal during the growth process because x-ray fluorescent spectrum analysis shows that no chlorine is present

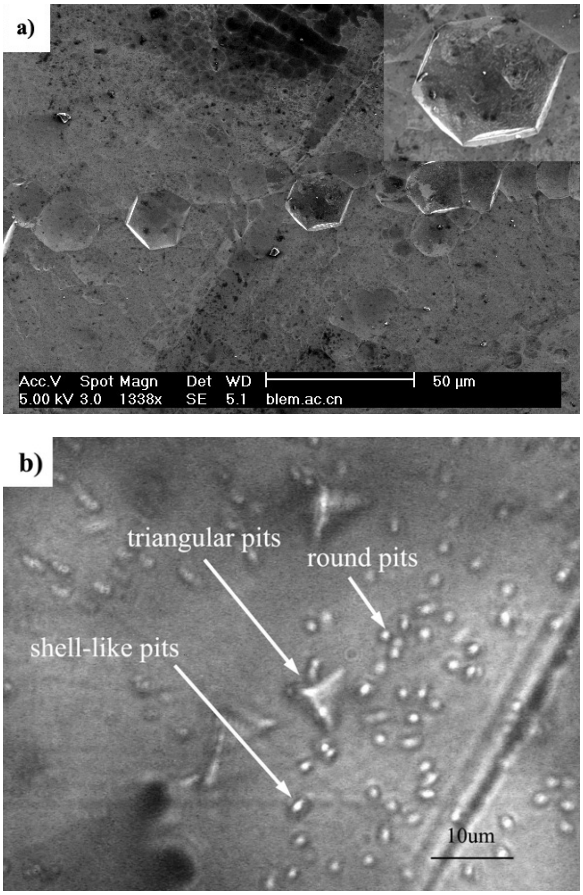

Figure 2. Hexagonal pits on the Si face (a) and triangular, round and shell-like pits on the C face (b) of 4H-SiC. The sample was etched by KOH at 470 °C for 20 min.

in both the graphite crucible and the SiC powder source. The presence of chlorine is due to the etching process. One main possibility is from KOH. It is interesting to note that the inclusions had regular dendritic shapes with a length of several microns, as shown in figure 3, which has not been reported before. Hirose *et al* [23] have reported the dendritic inclusions of the carbide of titanium and vanadium which were formed during SiC growth. Besides dendrite silicon, small dispersive silicon particles with a size of less than 200 nm were found near the dendrite silicon, as shown in the inset in figure 4. The origin of dendritic silicon inclusions is discussed as follows.

As we know, the vapour pressure of Si-rich species is significantly higher than that of C-rich species within the crucible for PVT growth of SiC, especially at higher growth temperatures. Si enrichment in the vapour can lead to Si droplet formation on the growing surface [9, 24, 25]. An inappropriate temperature gradient will accelerate the formation of Si droplets on the growing surface [26–28]. The temperature difference, ΔT, between the growing surface and the surface of the powder source defines the temperature gradient. The critical value of the temperature difference, ΔT_{C}, required for liquid silicon formation was found to be a function of the evaporation temperature of the powder source as described in [26]. It will decrease with the increase of the evaporation temperature, especially above 2875 K. If screw dislocations

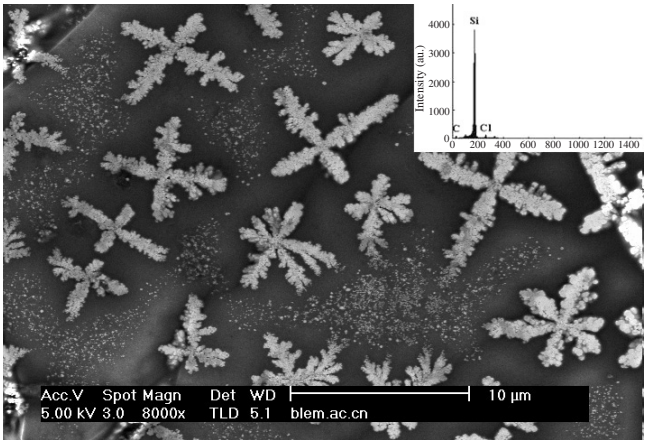

Figure 3. SEM image and EDX result of the inclusions existing on the Si face of 4H-SiC after KOH etching at 470 °C for 20 min.

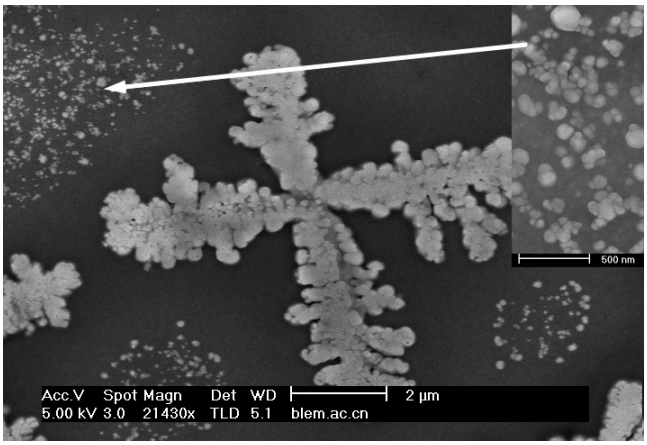

Figure 4. SEM image showing two different kinds of silicon: dendrite and particles. Dimensions of silicon particles are not over 200 nm and dendritic silicon has the size of 5–15 μm.

were absent near Si droplets, lateral growth of the SiC crystal can cover Si droplets [29] and keep them within the crystals. During the cooling down period of crystal growth, the temperature of the as-grown crystals can fall into a range corresponding to the crystallization of silicon, i.e. below 1687 K, and Si droplets crystallize. Since different crystal faces had different surface energies, the silicon crystal will develop to be a polyhedron whose surfaces had lower free energies. The temperature fluctuation during the cooling down period can break down the equilibrium near the crystallization front. Since the edges and vertexes of polyhedral Si had higher interfacial energies than the faces, liquid silicon near the edges and vertexes had a larger diffusion velocity. As a result, the crystallization rate of silicon on the edges and vertexes was higher. The silicon crystal gradually turned from a polyhedron to the urchin-like shape. Subsequently, the bulge of the urchin-like silicon can ramify and a dendritic shape was formed.

Silicon inclusions in SiC can induce the formation of the other defects such as micropipes, screw dislocations, planar precipitates and misoriented regions [28–30]. Two schemes can be

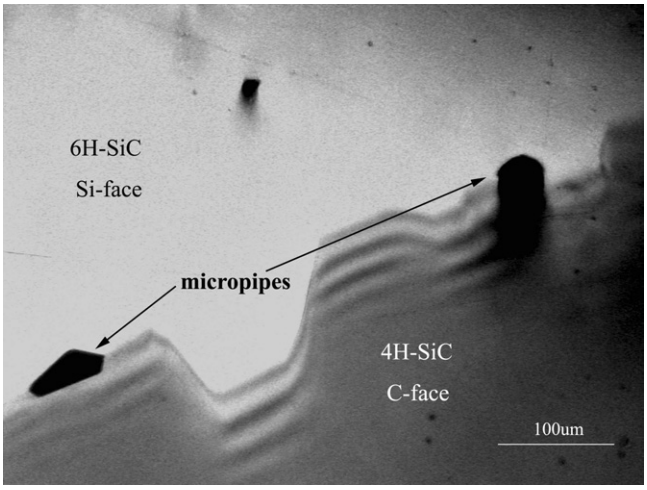

Figure 5. SEM image of interface between 4H-SiC and 6H-SiC.

adopted in order to avoid the formation of dendritic silicon inclusion. Firstly, since the number of Si atoms minus that of carbon atoms in equilibrium for the system of SiC + C increases with temperature [20], a lower growth temperature can be used. Secondly, it is suggested to maintain a lower temperature gradient between the growing surface and the surface of the powder source.

In our experiments, 6H-SiC growth can occur together with the growth of 4H-SiC over the same seed under certain conditions. We examined such a sample composed of both 6H-SiC and 4H-SiC. With the help of KOH etching, we found that the polished surface of the sample showed different polarities for 6H-SiC and 4H-SiC, as indicated by figure 5. Since the etching rate of the C face was larger than that of the Si face, the interface between 6H-SiC and 4H-SiC can be revealed. The interface showed clear regular boundary which had flat terraces and sharp edges. The terraces and edges were in fact the growth steps. The appearances of the growth steps showed that the crystal was grown by a step flow mode. Some micropipes were induced to form at the interface of 4H-SiC and 6H-SiC, as shown in figure 5. One cause for their origin may be the stress field due to the difference of crystal structure between 4H-SiC and 6H-SiC. Another cause, described by Takahashi *et al* [31], may be the enhanced dislocation generation at the interface of 4H-SiC and 6H-SiC in the growth process. As the interface between two SiC polytypes will act as an origin of micropipes, the formation of another SiC polytype when a certain SiC polytype is grown must be avoided. The growth temperature, supersaturation, impurities, Si/C ratio near the growing surface and the seed polarity should be carefully arranged for such a purpose.

4. Conclusions

New types of SiC defects, including shallow hexagonal etching pits, triangular etching pits and dendritic silicon inclusions, were revealed by molten KOH in 4H-SiC. Such a new type of SiC defects reflects the turbulences of the crystal growth conditions, such as growth temperature, temperature gradient and inert gas pressure. The first two defects might be possible origins of micropipes and polytypes, which needs further study. Triangular etching pits were related to dislocations. The origin of dendritic silicon inclusions can be explained by the theory of

solidification. A lower growth temperature and a lower temperature gradient can decrease the formation of dendritic silicon inclusions. The interface between 4H-SiC and 6H-SiC was examined in the case of co-growth of 4H-SiC and 6H-SiC over the same seed. The appearance of the regular growth steps at the interface indicated that the crystal was grown by a step flow mode. The existence of micropipes at the interface may be related to the stress field and the enhanced formation of dislocations at the interface. Further study on semiconductor properties of SiC bulk crystal which may be affected by the existence of polytypic interfaces and dendritic silicon inclusions is underway.

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