Effect of Growth Gas Flow Rate on the Defects Density of SiC Single Crystal*

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Abstract: A method for estimating the defects density in SiC bulk crystals by defect-selective etching in molten KOH has already been successfully demonstrated. In this paper, the results of applying this technique to bulk SiC crystals are reported. Etching produced hexagonal pits on the Si-polar (0001) plane, while round pits formed on the C face. The etching rate and the nature of etch pits for SiC depends on the growth process. For SiC crystals grown by the PVT process with high growth gas flow rate, the edge and screw dislocation density and the MP density are about 2.82×10^5, 94, and $38cm^{-2}$, respectively. For SiC crystals grown by the PVT process with low growth gas flow rate, those defects densities are about 9.34×10^5, 2, and $29cm^{-2}$, respectively. The results indicate that as the growth gas flow rate increases, the edge dislocation density decreases to avoid N_2 impurity.

Key words: SiC; defect; etching; PVT
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1 Introduction

Silicon carbide (SiC) is an attractive material for semiconductor devices operating under extreme conditions such as high temperature, high voltage, high frequency, and high power. SiC exhibits extraordinary physical properties, including a high electrical break down field, high thermal conductivity, and high saturation drift velocity[1~3]. Despite the potential of this material, SiC technology shows limitations and requires further study in order to obtain electronic devices with the same quality standards as Si technology. Indeed, the reliability of SiC-based devices is strictly correlated to the defects presented in the crystalline structure[4]. The presence of dislocations in the material kills electronic device performance and limits their lifetime. This has also driven the need for reliable techniques for quantifying the dislocation density in SiC. Transmission electron microscopy (TEM) and atomic force microscopy (AFM)[5] are the established methods for determining the dislocation density in single crystalline materials. However, TEM requires arduous sample preparation and AFM requires a relatively small and smooth sample surface.

Defect-selective wet etching in molten KOH also is a frequently applied technique to estimate the defects density in bulk SiC crystal. The etching processes have been reported in several papers[6~8]. For SiC, hexagonal shape pits form on Si-polar surfaces after 1～30min etching in a temperature range of 500～600℃. To overcome the difficulty of high-temperature etching, Siche *et al*.[7] added K_2CO_3 in the molten KOH. K_2CO_3 offers a surface oxidation, and the oxide is continuously removed by the KOH melt.

Previously, we inferred that the KOH defect etching optimum parameters of SiC samples grown by our research group are 430～450℃/10～40min. The composition of the etchant is K_2CO_3 : KOH = 5g : 200g. In favorable conditions, the hexagonal etch pits are well separated in space and can be clearly distinguished in their shape.

In this paper, we will present our etching study of SiC single crystals in molten mixtures of KOH and K_2CO_3. The crystals were produced by different physical vapor transport (PVT) growth processes: high growth gas flow rate and low growth gas flow rate. The goals were to estimate the defects density by calculation from the etch pit density and to gain a better understanding of the defects density for both high gas flow rate and low gas flow rate growth processes to further improve the crystal quality.

2 Experimental procedures

6H-SiC crystals in the {0001} direction were

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grown with the PVT technique. Both the Si and C terminated faces of 6H-SiC crystals were examined. Since the revealing of structural defects via preferential chemical etching demands flat and smooth surfaces, prior to etching the samples were mechanically polished with diamond slurries of different grain size from 15 to 0.5μm. The etching was carried out in a conventional etching furnace with resistance heating. Nickel was the crucible material for the KOH bath. Ni is chemically inert and shows no reaction with hot molten KOH. The molten mixtures of KOH (200g) and K_2CO_3 (5g) was used as the etchant. The wafer was fixed in a Ni-wire-cage and suspended into the etchant. The optimized etching condition for bulk SiC crystals grown by PVT process with high growth gas flow rate (sample A) was 440℃ for 30min, while for bulk SiC crystals grown by PVT process with low gas flow rate (sample B) was 440℃ for 20min. The temperature was measured by a sensor in the vicinity of the crucible placed in the furnace.

The investigations of the samples were performed by optical microscopy with a CCD camera, scanning electron microscopy (SEM JSM-6700F), and transmission electron microscopy (TEM JEM3010).

3 Results and discussion

During etching, bubbles (on the sample surface) formed. The color of the etchant changed from yellowish to gray.

3.1 Defects etching patterns

Typical etching patterns on the C face and Si face of 6H-SiC are shown in Fig. 1. The smoother C face shows round etching pits due to defects in Fig. 1 (a). However, all kinds of regular etch pits with different sizes and shapes appeared on the coarser Si face. Figure 1 (b) shows that the slight scratches were enlarged due to anisotropic etching. Thus, etching can be used to identify the polarities of SiC in the {0001} direction. In another words, the C face and the Si face of SiC are attacked by KOH isotropically and preferentially, respectively.

These results can be attributed to 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[7]. The different etching rates of the two faces are due to the different surface free energies. In single crystal materials, areas with structural imperfections have higher strain energies than perfect single crystal regions. Because of a higher chemical potential, strained areas of single crystals are more liable to

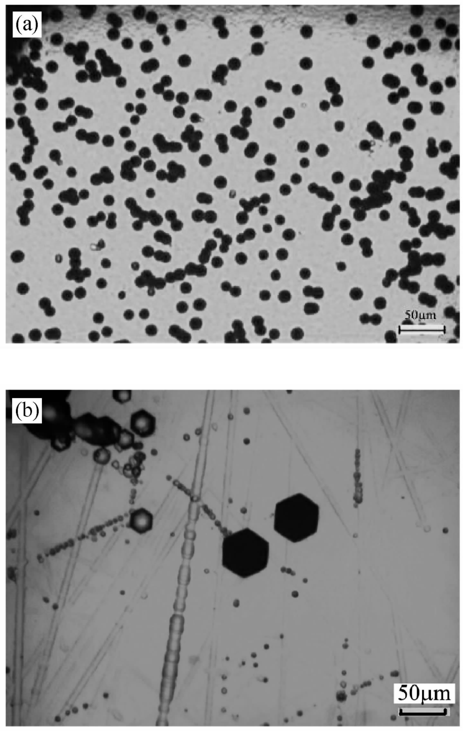

Fig. 1 Typical micrographs of etching pattern on the C face (a) and the Si face (b) of 6H-SiC

chemical attack than non-strained areas. Consequently, at optimum conditions the strained areas due to defects such as dislocations, micropipes, etc. are preferentially etched to produce etch pits. This is a defect-selective etching process. KOH is an anisotropic etchant, so after etching, regular hexagonal pits can be observed on the Si face. However, the etching rate is too fast on the C face, so the etch pits are round, which resemble isotropic etching.

The sizes and shapes of the etch pits are vital in evaluating defect statistics of the material and in distinguishing them clearly. Figure 2 shows the etch morphologies corresponding to MPs, screw dislocations (SDs), edge dislocations (EDs) and basal plane dislocations (BPDs). Figures 2 (a) and (b) represent the optical microscope images of sample A and sample B on the (0001) Si face, respectively. Sample A was grown in a high growth gas flow rate environment, while sample B was grown in a low growth gas flow rate environment. The nature of the etch pits and the defects density are remarkably different between Figs. 2 (a) and 2 (b) and will be discussed in detail in the next paragraph. According to Refs. [5,9], large hexagonal etch pits without bottoms represent micropipes, as shown in Fig. 3(a). Mid-sized hexagonal etch pits with bottoms represent screw dislocations, as shown in Fig. 3(b). Meanwhile small hexagonal etch pits with bottoms represent edge dislocations, as shown in Fig. 3(c). Shell-shaped etch features with

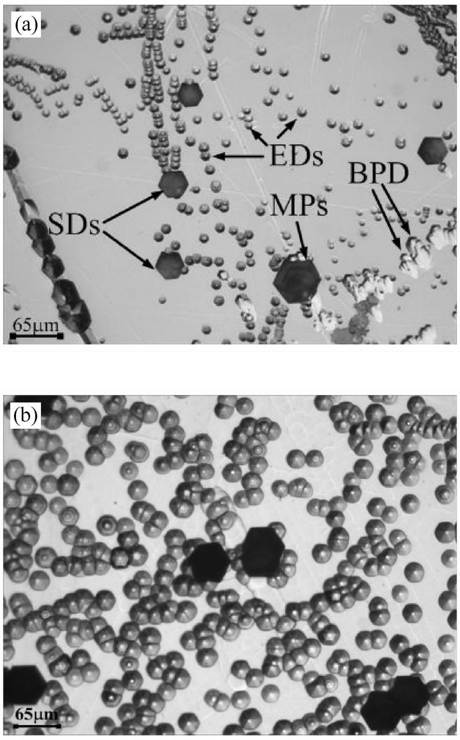

Fig.2 Optical microscope images of sample A (a), sample B (b) on (0001) Si face

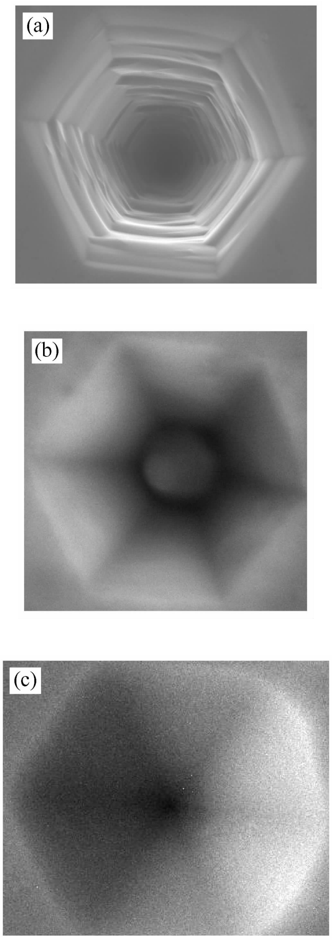

Fig.3 SEM images of KOH etched SiC crystal surface (a) MP; (b) SD etch pit; (c) ED etch pit

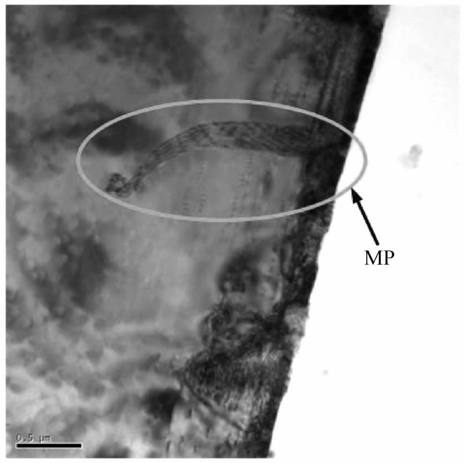

Fig.4 Cross sectional TEM image of an MP

bottoms not centered in the etch pit represent basal plane dislocations. The differences in etch pit sizes are due to differences in the strain energies and surface energies of the various kinds of dislocations and, hence, different etching rates. The strain energy of a dislocation is proportional to the square of the burgers vector[9], likewise the surface energy at the point where a dislocation intersects a surface. The sequence in the sizes of burgers vectors of an MP, SD, and ED is as follows: MP > SD > ED. The surface energy and etching rate follow the same sequence. Consequently, etch pits corresponding to MPs are large, those corresponding to SDs are medium, and those corresponding to EDs are small. However, the etch pit sizes of SDs can vary significantly because the burgers vector can vary. This is also true for MPs. The burgers vectors of SDs are usually $1c$, $2c$, and $3c$, where c is the unit c lattice parameter. Above $3c$, the critical burgers vector is exceeded and it becomes energetically more favorable for the dislocation to have a hollow core, i.e., form an MP. MPs usually have burgers vectors greater than $3c$[9].

The cross sectional TEM observation in Fig. 4 shows a profile image of an MP. This profile confirms that the MP is a hollow-core defect propagating along the growth direction of the SiC crystals.

3.2 Defects density

The etching rate depends on the growth process. The optimized etching condition for sample A grown by the PVT process with a high gas flow rate is 440℃ for 30min, which is typically 10min longer than that for sample B grown by the PVT process with a low gas flow rate. This indicates the higher stability of SiC grown by the PVT process with a high gas flow rate. In another words, the etching rate of sample A is slower than sample B.

For sample A (Fig. 2(a)), the calculated edge and screw dislocation density and the MP density are about 2.82×10^5, 94, and $38cm^{-2}$, respectively. For sample B (Fig. 2(b)), those defects densities are about 9.34×10^5, 2, and $29cm^{-2}$, respectively. The difference in defects density depends on the growth process. If the gas flow rate is low in the growth environment, for example sample B, N_2 can become the main impurity. Thus, sample B became n type doped SiC with high concentration. However, high doping concentration implied that too much impurity would release stress through dislocation. Due to the high gas flow rate for sample A, the effect of N_2 can be reduced. Therefore, the edge dislocation density of sample A is lower than that of sample B.

Another remarkable difference between sample A and sample B is the nature of the etch pits. While the etch pits of sample B become slightly round by nitrogen doping (Fig. 2(b)), those of sample A show a more profound hexagonal shape (see Fig. 2(a)). Theoretically, the etch pits of p-type material show a regular hexagonal shape[9]. Increasing the MPs and SDs density for sample A may be correlated with some impurities or thermal stress.

4 Conclusion

Hexagonal pits form on the Si face SiC (0001) crystals after etching in the molten mixture of KOH/K_2CO_3. SiC crystals with C face form round pits after etching. The optimal etching parameters depend on polarity, defect type, density, and distribution. The etching condition for sample A grown in a high growth gas flow rate atmosphere is 440℃/30min, which is typically 10min longer than that for sample B grown in a low growth gas flow rate atmosphere, indicating the higher stability of sample A. Moreover, for sample A the etch pits show a more profound hexagonal shape; for sample B the etch pits become slightly round by nitrogen doping. Thus, the etching rate and the nature of the etch pits depends on growth process. From the defects density data calculated from analyzed samples, we concluded that as the gas flow rate of PVT process increases, the edge dislocation density is reduced because of N_2 impurity reduced. Increasing the MPs and SDs density for sample A may have some relationship with impurities or thermal stress.

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生长气体流量对 SiC 单晶缺陷的影响*

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摘要： 实现了熔融 KOH 进行 SiC 体单晶择优腐蚀估测缺陷密度的方法.本文报道了采用该技术对体 SiC 单晶缺陷密度估测的结果.腐蚀会在 Si 面形成六边形腐蚀坑，在 C 面形成圆形腐蚀坑.腐蚀速率和蚀坑形状与 SiC 生长工艺有关.对在高生长气流量下用 PVT 工艺制备的 SiC 样品，其刃位错、螺位错与微管密度分别为 2.82×10^5，94 和 $38cm^{-2}$；对在低生长气流量下用 PVT 工艺制备的 SiC 样品，其上述缺陷密度分别为 9.34×10^5，2 和 $29cm^{-2}$.结果表明：随着生长气体流量的增加，由于避免了 N_2 掺杂，刃位错密度下降.

关键词： SiC；缺陷；腐蚀；PVT

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