Sublimation growth and characterization of SiC single crystals

J. Takahashi, N. Ohtani, M. Katsuno, M. Kanaya and H. Yashiro
Advanced Technology Research Laboratories, Nippon Steel Corporation
5-10-1 Fuchinobe, Sagamihara, Kanagawa 229, Japan

1. Introduction

Silicon carbide (SiC) has excellent physical and electronic properties such as wide band gap (2.86eV for 6H, 3.09eV for 4H), high electric breakdown field (4×10^6V/cm) and large saturation electron drift velocity (2×10^7cm/s). In the 1960s and 70s, SiC research was intensively pursued [1] and some promising results for SiC devices for high power and high frequency applications were reported [2]. However, many research institutes halted the activities in the mid 1970s when they failed to grow large single crystal SiC.

Over the last decade, SiC bulk growth technology has shown significant progress [3,4]. In 1978, Tairov and Tsvetkov made a major step in the development of SiC, the use of a seeded sublimation growth technique for SiC bulk growth [5]. Since this pioneering work, considerable progress has been made, and SiC wafers of 30-35mm diameter are now commercially available. With the availability of large high quality substrates, SiC device research has accelerated [6]. In addition, there is a rapidly growing interest in SiC as a substrate material for GaN blue laser diodes. The similarity of the lattice structure between SiC and GaN is expected to improve structural and optoelectronic properties of GaN heterostructures [7]. In this paper, we briefly describe the seeded sublimation growth (modified-Lely) method and report on the results of growth and characterization of bulk SiC crystals.

2. Sublimation growth

SiC is so stable that it does not melt under any reasonably attainable pressure and rather sublimes at temperatures greater than 1800°C. Consequently, growth-from-melt techniques are not applicable, and a seeded sublimation growth technique, the so-called "modified-Lely method," is commonly employed for SiC bulk crystal growth. The main scheme of the method is as follows. The gas species, mainly Si, Si_2C and SiC_2 [8], sublimated from a solid powder source condense epitaxially on a seed crystal maintained at a lower temperature [5]. All these elemental processes occur at more than 2000°C and this uncommonly high temperature makes SiC crystal growth difficult.

Many of the technological problems in SiC crystal growth are caused by the polytypism phenomenon of SiC. The polytypism in SiC is described as different one-dimensional stacking sequences along the *c*-axis (*ABCB* for 4H, *ABCACB* for 6H). More than 200 polytypes have been reported, among which 6H, 4H and 15R are commonly observed in the sublimation growth process. The atomic arrangements of Si and C in 6H-, 4H- and 15R-SiC are shown in Fig. 1. A major problem in the seeded sublimation growth of SiC is simultaneous growth of more than two polytypes in one single SiC crystal even when a seed crystal of a desired polytype is used [3,9].

Figure 2 shows a schematic diagram of a crucible assembly used in the modified-Lely method. The assembly consists of a graphite crucible and heat insulators made of graphite felt. The SiC source powder and seed crystal are placed in the graphite crucible. The crucible is heated up to more than 2200°C by RF induction heating. To control the SiC gas flux, Ar gas is introduced into the reaction chamber. Typical growth conditions are combinations of the seed temperature of 2200-2300°C, the source temperature of 2300-2400°C, and the Ar pressure in the reaction chamber of 10-40Torr. The seed crystal is usually a mirror-polished (0001)Si (Si-face) or $(000\bar{1})$C (C-face) wafer. We also use $(1\bar{1}00)$ and $(11\bar{2}0)$ wafers as the seed crystal.

3. Growth in <0001> directions

Polytype

Several growth parameters such as the face polarity of seed crystal, growth temperature and impurities are believed to influence the polytype of grown crystal. The 4H polytype never occurs on the Si-face and can be grown on the C-face [10]. On the other hand, the 6H and 15R polytypes grow on both the Si-face and the C-face. We have tried to formulate growth conditions under which 4H- or 6H-SiC can be preferentially grown on the C-face, and examined several combinations of the seed and source temperatures and the Ar pressure [11]. It was also revealed that control of the growth front shape during growth is of great importance to obtaining single polytypic crystals. By optimizing the growth conditions, single polytypic SiC ingots of up to 2 inch diameter have been produced [12]. Figure 3 shows 1.5 inch 6H-SiC ingot and wafer fabricated in our laboratory.

Resistivity Control

Resistivity control is an essential condition for industrial applications of SiC. We have succeeded in controlling resistivity over a wide range by *in-situ* nitrogen doping of SiC crystals [10,13]. The doping of grown crystals with nitrogen, a well-known donor in SiC, is easily performed by adding gaseous nitrogen to the growth chamber.

Figure 4 shows the dependence of the carrier concentration on the N_2 flow rate for nitrogen-doped 6H-SiC crystals grown on the C-face and the Si-face. The crystals grown on the C-face always showed higher carrier concentrations than those grown on the Si-face. The undoped crystal grown on the C-face was *n*-type with a carrier concentration of around $1.4\times10^{17}\text{cm}^{-3}$ and a resistivity of 0.34Ωcm. On the other hand, the undoped crystal grown on the Si-face exhibited a markedly different behavior. The crystal showed *p*-type conduction with a hole concentration of $1.1\times10^{14}\text{cm}^{-3}$ and the resistivity was as high as 1300Ωcm. This face polarity effect has been attributed to the preferential incorporation of donor (nitrogen) and acceptor (aluminium and boron) impurities [10]. The crystals grown on the C-face preferentially incorporate nitrogen while the crystals grown on the Si-face preferentially incorporate boron and aluminium during sublimation growth. Using this face polarity effect, the resistivity of SiC crystals can be controlled from 0.01Ωcm to 1000Ωcm.

Crystallinity

Molten KOH etching is commonly employed for defect characterization in SiC. Figure 5 shows a micrograph of the etched vicinal (0001)Si surface of a 6H-SiC $[000\bar{1}]$ grown crystal. A large dark hexagonal etch pit can be observed, which corresponds to an empty tube defect, "micropipe," penetrating the crystal along the *c*-axis. Large hexagonal etch pits are often located at the center of growth spirals [14], and thus micropipes are assumed to be hollow core screw dislocations with a large Burgers vector [15]. Sea-shell shaped etch pits (indicated by arrows), called "shell pits," are also revealed in the figure, which correspond to basal plane dislocations. Small etch pit rows, aligned almost in $\langle 1\bar{1}00\rangle$ directions, also often appear on the etched surface. They correspond to edge dislocation walls having a $\frac{1}{3}\langle 11\bar{2}0\rangle$ Burgers vector. The crystal comprises misoriented subgrains bordered by small angle tilt and twist boundaries [16,17].

Modified-Lely grown SiC crystals contain micropipe defects of typically 10^2-10^3cm^{-2}. While

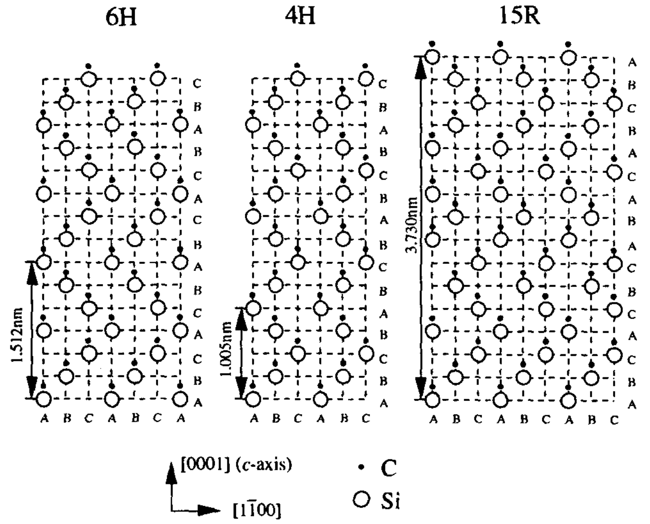

Fig. 1. Crystal structures of 6H-, 4H- and 15R-SiC seen from [$\bar{1}\bar{1}20$].

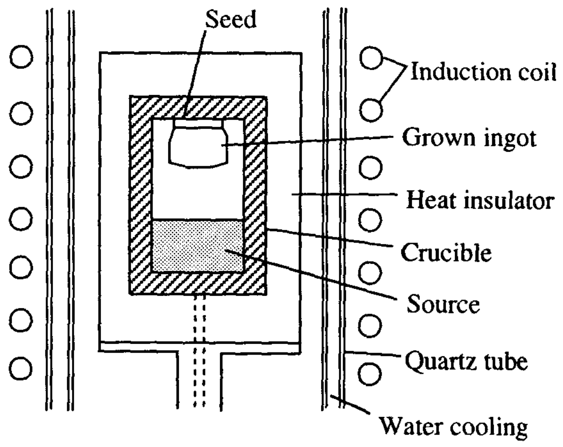

Fig. 2. Schematic diagram of a crucible assembly used in the modified-Lely method.

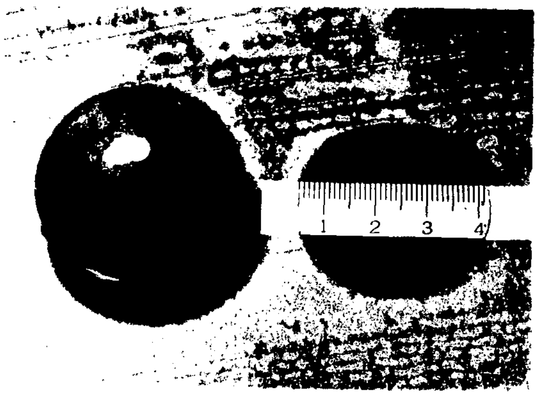

Fig. 3. 6H-SiC single crystalline ingot and {0001} wafer of 1.5 inch diameter.

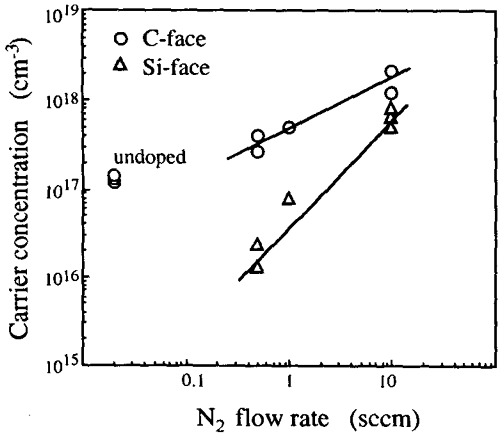

Fig. 4. Dependence of the carrier concentration on the N_2 flow rate for nitrogen-doped 6H-SiC crystals grown on the C-face and the Si-face.

Fig. 5. Micrograph of the etched vicinal (0001)Si surface of a 6H-SiC [000$\bar{1}$] grown crystal.

Fig. 6. Micrograph of the etched vicinal (0001)Si surface of a 6H-SiC [1$\bar{1}$00] grown crystal.

it is intuitive that micropipes would be harmful for devices, especially at high voltages, it has recently been shown that the failure of high voltage SiC diodes in reverse bias was caused by microplasmas generated in micropipes [18]. The mechanism of micropipe formation is at present poorly understood. Spiral growth, which is a dominant growth mode in the <0001> growth, is suggested to play an important role in hollow core formation [17].

4. Growth in the directions perpendicular to <0001>

One approach to growing SiC crystals free of micropipes is growth in the directions perpendicular to the *c*-axis [14]. Figure 6 shows a micrograph of the etched vicinal (0001)Si surface of a 6H-SiC crystal grown in the $[1\bar{1}00]$ direction, where no dark hexagonal etch pits associated with micropipes can be observed. It was also found that, for the $[1\bar{1}00]$ and the $[11\bar{2}0]$ growth, there occurs no spiral growth originating from micropipes or screw dislocations. In addition, the polytype of grown crystal perfectly inherited that of the seed crystal [14]. For the $[1\bar{1}00]$ and $[11\bar{2}0]$ grown crystals, a number of stacking faults on the basal plane were detected, whose density varies from 10^2 to 10^4cm^{-1} depending on the polytype and the growth direction [19].

All these results combine to suggest that the defect formation process in SiC depends on the crystal growth direction and is largely different between the directions along the *c*-axis and perpendicular to the *c*-axis [17].

5. Conclusions

We have demonstrated SiC single crystal growth by the modified-Lely method and produced SiC single crystals of more than 30mm diameter. Furthermore, growth in the directions perpendicular to the *c*-axis yields SiC crystals free of micropipes, which are greatly advantageous to SiC devices. Nevertheless, many aspects of the crystals and material quality are yet to be addressed, and further improvements are necessary before ideal SiC devices can be fabricated.

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