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Stable and high-speed SiC bulk growth without dendrites by the HTCVD method

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ABSTRACT

We investigate growth conditions to obtain high-quality SiC bulk crystals by the High-Temperature Chemical Vapor Deposition (HTCVD) method. Formation of dendrite crystals, which sometimes occurs on the growth front and degrades the material quality, is raised as an issue. We find that a bulk crystal growth under a high vertical temperature gradient, where the temperature of the back side of the bulk crystal is much lower than that of the crystal surface, suppresses the formation of dendrite crystals. Under growth conditions with a high temperature gradient, a very high-speed growth of 2.4 mm/h is achieved without the formation of dendrite crystals. Growth of a thick 4H–SiC bulk crystal without the dendrites is demonstrated and the quality of a grown crystal is evaluated.

1. Introduction

Silicon Carbide (SiC) semiconductor power devices are a key technology for realizing a low carbon society since they have excellent electronic, optical and mechanical properties [1,2]. However, reducing the production cost and improving the quality of SiC wafers are still being requested for mass production of SiC devices. At present, a physical vapor transport (PVT) method is the most employed technique for producing 4H–SiC wafers [3,4]. In this method, SiC powders are mounted as source materials into a quasi-sealed crucible. The powders are sublimed at a high temperature of 2300–2400 °C. Sublimed SiC gas-species crystallize on the seed placed at a cooler position. One of the issues in this method is the limited supply of source materials due to the difficulty of adding source materials during the growth process. Moreover, the source materials tend to become C-rich as growth proceeds since saturated vapor pressures of Si and SiC compounds are different [5,6], while varying process conditions during growth can cause a worsening of the crystal quality. Because of these reasons, 4H–SiC bulk crystals grown by the PVT method are limited to a certain crystal length.

An HTCVD method has been proposed as an alternative to the PVT method to realize a high productivity in SiC bulk growth [7–11]. In this method, a SiC bulk crystal is grown in an opened vertical crucible made of graphite. The growth temperature is over 2100 °C, which is almost the same as the PVT method. The source materials are supplied as gases from outside of the reactor and this enables a continuous supply of source materials. Therefore, long-term growth, in other words, thick bulk crystal growth, can be realized. A higher controllability of process conditions is also one of the advantages in the HTCVD method. For example, the amount of supplied source materials, C/Si ratio and growth temperature, can be controlled independently. Since precise control of C/Si ratios is possible during a growth period, worsening the crystal quality by the variation of the C/Si ratio can be suppressed. These features will contribute to realizing the high-speed growth of high-quality SiC bulk crystals. Another advantage is that the purity of the gas source is much higher than that of the powder source for the PVT growth. Residual impurity densities of nitrogen and boron are reported in the mid of 10^{14} cm^{-3} in the HTCVD method [7], and producing semi-insulating wafers is easier thanks to this feature [12].

High supersaturation on a growing surface is desirable to obtain high growth rates. High supersaturation, however, can lead to homogeneous nucleation of Si and SiC clusters in the reactor when the partial pressure of the source gases exceeds a certain level [13,14]. The nucleation of clusters limits growth rates. Thus, accelerating the evaporation of clusters is required for high-speed

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growth. One solution is to increase the growth temperature. Single crystals growth with a high growth rate of 1.0 mm/h has been achieved by grown at 2370 °C in the HTCVD method [15]. Another solution is to add Cl to a gas system. The formation of Si clusters are suppressed by using a chlorinated precursor or adding HCl gas in the CVD methods [16–18]. The gas system with HCl was employed in the HTCVD method and a high growth rate of 1.4 mm/h was achieved at a relatively low temperature of 2200 °C [19,20].

Another issue in obtaining high growth rates is the formation of dendrite crystals (tree-like crystals) on the growth front, which sometimes arises in the HTCVD method and obstructs high-quality bulk SiC crystal growth. As described above, high-speed growth exceeding 1.0 mm/h has been achieved at short-duration growth. However, continuous long-duration growth with a high growth rate (> 1.0 mm/h) has not been reported. To realize continuous growth, it is necessary to establish a condition for stable growth without the formation of dendrites and to keep this condition over the growth duration.

In this paper, we investigate the conditions where dendrite crystals are suppressed in the HTCVD method. By employing an optimal growth condition, thick bulk 4H–SiC crystal growth without the formation of dendrites is demonstrated at a high growth rate.

2. Simulation and experiment

A schematic illustration of an HTCVD reactor is shown in Fig. 1. The hot zone of the reactor is heated using upper and lower induction coils. The coils are controlled independently. The source gases are supplied from the bottom of the reactor. The gases are introduced to the cracking zone whose temperature is very high, such as 2500 °C, and decomposed there. The decomposed gases are carried to a seed crystal held on a susceptor with a face-down configuration. The temperature of the seed crystal is slightly cooler than the gas-temperature and source materials crystallize on the seed crystal.

Temperature distributions inside the reactor in the initial stage of growth process were simulated computationally using VR-CVD SiC software. The simulation was made for a 2 in. diameter crystal. The heating power for the upper and lower induction coils was varied to create different vertical temperature gradients inside the crystal. Heat generation was assigned to the growing crystal surface as latent heat of crystallization.

Growth experiments were carried out to investigate the conditions that suppress the dendrite crystals. As seed crystals, 4H–SiC C-face substrates with a 4° off-angle were prepared. The diameters were 2 or 3 in. Temperatures were monitored for the crystal surface and the back side of the susceptor. The temperature of the crystal surface was measured by infrared thermography, while that of the back side of the susceptor was measured by a pyrometer. The C/Si ratio of the input source gases was kept at 0.9. The partial pressure of the source gases at the inlet P_{Source} was varied according to

$$P_{Source} = P_{all} \cdot \frac{f_{SiH_4} + f_{C_3H_8}}{f_{SiH_4} + f_{C_3H_8} + f_{H_2}}, \tag{1}$$

where P_{all} is the system pressure and f_{Gas} is the flow rate of each gas. After crystal growth, we visually confirmed if dendrite crystals emerged or not. Grown thickness was measured by cross sectional optical observation. Growth rate was evaluated from crystal thickness grown for 1 h.

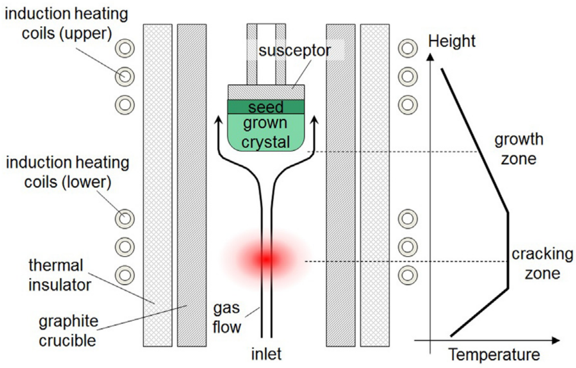

Fig. 1. Schematic illustrations of an HTCVD reactor and vertical temperature distribution.

We also performed a long-duration crystal growth to obtain a thick-bulk SiC crystal, maintaining a partial pressure of source gases at 11.9 kPa. Growth temperature was 2450 °C. A growing crystal was pulled up as the growth proceed to keep the position of the growth front and the growth temperature.

An obtained grown crystal was sliced into {0001} wafers 4° off-oriented toward [11–20] to evaluate the crystal quality. The wafer surface was mechano-chemically polished. Dislocation densities in the wafer were investigated by synchrotron X-ray topography (11-28 diffraction) and melton KN etching (480 °C, 1.5 min) [21,22].

3. Results and discussion

3.1. Simulation of temperature distribution

Fig. 2 shows simulated temperature distributions near the gas–crystal interface as a function of growth rate. Here r, z and T represent the radial distance from the center of the crystal, the vertical distance from the crystal surface and the temperature, respectively. The direction of z is downward. Thus, the gas phase is positioned at $z > 0$ and the interface is at $z=0$. The simulated temperature distribution for the growth rate of 0 mm/h, 0.5 mm/h and 2.0 mm/h are shown in Fig. 2(a)–(c), respectively. The temperature at the crystal surface rises as the growth rate is increased. For instance, that at the center of the surface ($r=0$ mm, $z=0$ mm) is 2300 °C (0 mm/h), 2302 °C (0.5 mm/h) and 2308 °C (2.0 mm/h). Note that the temperature variations are attributed to the generated heat by crystallization since the heating power for the coils are exactly the same in all of the calculations (not adjusting the power for the surface temperature). The temperature distribution in the gas phase is also varied by increasing the growth rate. The isothermal lines vary from nearly horizontal to nearly vertical as the growth rate becomes higher. This indicates that the heat flows radially in an outward direction especially at the high growth rate. The gas temperatures at the center ($r=0$ mm) for the growth rate of 0 mm/h, 0.5 mm/h and 2.0 mm/h are shown in Fig. 2(d)–(f), respectively. As shown in Fig. 2 (d) and (e), the gas temperature T becomes higher as the distance z increases ($dT/dz > 0$) when the growth rate is not so high. This is convincing because the temperature at the cracking zone is the highest in the reactor as shown in Fig. 1. In contrast, as shown in Fig. 2(f), a peculiar temperature distribution is created when the growth rate is 2.0 mm/h. The temperature local minimum point A is formed in the gas phase, which is located at $z=1.07$ mm. The gas temperature T becomes lower as the distance z increases in the vicinity of the surface ($z < 1.07$ mm). In other words, the vertical temperature gradient is locally reversed and is negative ($dT/dz < 0$) just under the surface. For instance, the gradient dT/dz is evaluated as −1.15 °C/cm at $z=0.01$ mm. At the reversed temperature gradient ($dT/dz < 0$), heat is released to the local minimal point from the growing crystal surface. The released