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A novel approach to the suppression of growth-induced polytype domains during the growth of large-size SiC single crystals

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The occurrence of polytype domains in the central region decreases the yield of wafers, when large diameter 6H-, 4H-silicon carbide(SiC) single crystals are grown by a sublimation method. Accordingly, the suppression of polytype domains is very important. Previous studies revealed that polytype domains occur in SiC crystals during the growth process and the domains were based on the root of micropipes and macro-defects. However, in spite of many studies and much development, the suppression of polytype domains has not been perfectly solved. In this study, we verified the systematic experimental results that the relationship between ΔT_{B-U} (vertical temperature gradient) and ΔT_{F-I} (the temperature difference between initial temperature and final temperature at bottom of crucible) has an important effect on the occurrence of polytype domains. It was found that the optimization of ΔT_{F-I} was more important than that of ΔT_{B-U} in order to reduce the macro-defects and polytype domains.

Key words: Silicon carbide, single crystal, polytype domain, sublimation, temperature gradient

Introduction

Crystalline silicon carbide (SiC) has been recognized as the most useful wide bandgap semiconductor for applications at high temperature, high frequency, and for high power devices because of its excellent chemical, physical and mechanical properties and receives attention as a substrate material for opto-electronic and telecommunication devices such as GaN-on-SiC for blue LEDs and microwaves [1]. For these device applications, the development of large diameter SiC crystals that have low defect densities has been proceeded [2,3]. However, in spite of many studies and much development, the occurrence of growth-induced defects such as micropipes, planar defects, dislocations and polytypes is still under discussion and is not perfectly understood [4]. However, it is well known that the growth-induced polytype domains still occur in the internal region of SiC crystals during the growth process. Previous studies [3] including our previous report [4] revealed that the misoriented-domains occur due to the accumulated micropipes and/or some particles based on carbon and silicon and the polytype domains are also based on the root of micropipes. While these reports [3, 4] established a view point of the microscopic approaches, where the micropipes affect the formation of domains, and a high temperature gradient between the seed and bottom of the crucible also affect the occurrence of domains.

However, the polytype domains can occur due to other factors for many growth conditions. Precisely, a novel view point on the process conditions is not enough to prevent the occurrence of domains from the micropipes and under a high vertical temperature gradient.

In this study, we will show systematic experimental results with regard to the evolution of growth-induced polytype domains from the view point of growth process factors.

Experimental

Silicon carbide (SiC) single crystals were grown by a sublimation method in this study. 6H-SiC single crystals were also grown on 6H- or 4H-SiC(0001) and 6H- or 4H-SiC(000-1) seeds without polytype domains to avoid the effect of polarity and the polytype of the seed.

The SiC source material was a high purity powder. All the components used in the process were cleaned and purified to prevent defect formation by particles or contaminants from the source and graphite. The distance between the seed surface and source surface was varied in the range of 40-55 mm.

The upper surface temperature (T_U) and bottom temperature (T_B) of the crucible were measured by an optical pyrometer. The growth temperature was precisely controlled in the range of 2000-2250 °C at T_U. Also the temperature difference between the upper surface and bottom of the crucible (e.g. vertical temperature gradient: ΔT_{B-U}) was varied in the range of 20-200 °C.

During the crystal growth, T_U was kept constant during a growth step and T_B has always to be higher than T_U. However, T_B was changed towards a higher temper-

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ature due to a graphitization phenomena of the SiC source. Accordingly, the temperature measured at T_B was varied during growth the process. In this report, the temperature variation between the initial and final stage of growth process is denoted as ΔT_{F-I}.

To confirm the effect of ΔT_{F-I} on the domain formation, not only high quality seeds but also low quality seeds with micropipes, planar defects and dislocations were used.

The growth pressure was controlled in the range of 0.66-4 Kpa under an Ar atmosphere. During heating and cooling, an Ar pressure in the range of 67-80 Kpa was maintained to avoid crystallization at a lower temperature, which would lead to the formation of undesired polytype domains formation [5]. The diameter of the SiC single crystals grown was 60-80 mm, and height was 20-30 mm. The growth rate was a maximum 0.7 mmh^{-1} and an average 0.26 mmh^{-1} in accordance with the growth parameters.

The morphologies of SiC crystals and SiC seed surfaces were observed by an optical microscope with Normarski interference contrast (ME 600L, Nikon). Micro-Raman spectra were obtained at room temperature using a Renishaw micro-Raman spectrometer (Series 1000) in order to analyze the SiC polytype.

Results and discussion

When 6H-SiC single crystals of large diameter (above 63 mm) were grown, polytype domains of 4H-SiC were often formed in the central regions of 6H-SiC crystals as shown in Fig. 1. Fig. 1(b) shows a photograph of the axial-cut section of a polytype domain induced in a 6H-SiC crystal. The 4H-SiC polytype domain was confirmed by micro-Raman spectroscopy [6]. Also, this 4H-SiC polytype domain of a reverse triangular shape was enlarged during the growth process.

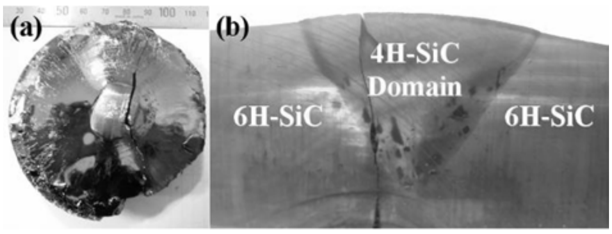

Fig. 1. Typical polytype domains existing in large size 6H-SiC crystals; (a) top view of grown crystal (80 mm in diameter) and (b) axial cut view.

The origin of polytype domains has been reported in many previous studies [7], where this domain occurs due to defects such as micropipes, hollow pipes and other defects.

However, in the present study, 6H-SiC crystals were grown on low-quality 6H-SiC seeds (micropipe density: 13,017/cm^2, macro-cavity defect density: 1,656/cm^2) which has many micropipes and planar defects as shown in Fig. 2(a) and (b). The growth conditions were a temperature of 2160 °C, a pressure 2.7 Kpa, and ΔT_{B-U} of 7.24 Kcm^{-1} (a relatively high vertical temperature gradient). As a result, a 6H-SiC crystal without polytype domains in the central region resulted as shown in Fig. 2(c). It was found that in this case, although the vertical temperature gradient (ΔT_{B-U}) was 7.24 Kcm^{-1} which is relatively high, comparied with a previous report [8], but the variation of the bottom temperature (ΔT_{F-I}) was 0.3 Kh^{-1} which is low.

Accordingly, it was confirmed that polytype domains occur due to the novel factor (ΔT_{F-I}) in addition to the effect from defects [6], a stress at the root of domains [9], and a high vertical temperature gradient [10]. In our study, it was found that the variation of the bottom temperature (ΔT_{F-I}) plays a role in the generation of polytype domains during the growth of large diameter crystals.

In the event, althougth the seed included many micropipes and hollow defects, a 6H-SiC crystal without polytpe domains could be obtained under a low variation of bottom temperature. Also although the vertical temperature gradient was too high, in our study, 6H-SiC crystals without polytype domain were grown. The vertical temperature gradient generally affects the crystal growth rate. So that, when the vertical gratient is high, the growth rate is also high. However, this phenomena can be explained for the growth of small diameter SiC crystals under 50 mm. During the crystal growth of a large diameter of over 75 mm, the vertical temperature gradient had no more effect on the variation of the growth rate because the radial temperature

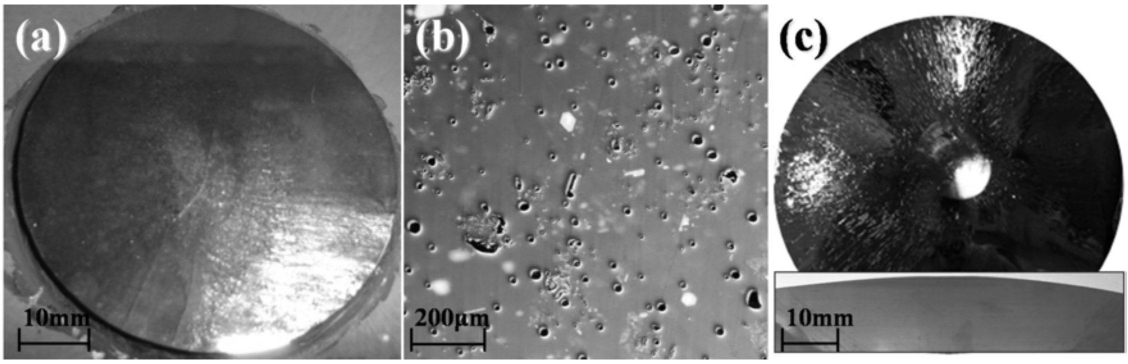

Fig. 2. Photographs of (a) a seed attached on a graphite lid, (b) Normarski microscopic image of the seed surface, and (c) as-grown 6H-SiC crystal without polytype domains. (growth temperature: 2160°C, ΔT_{B-U} : 7.24 Kcm^{-1} and ΔT_{F-I} : 0.3 Kh^{-1}).

difference between the periphery and center of the crucible was high. It should be noted that another important tendency or factor exists during the growth process of large diameter crystals. This means that the variation of the bottom temperature ($\Delta T_{F\text{-}I}$) corresponding to the graphitization rate of the SiC source is an important factor for the suppression of polytype domains.

Fig. 3 shows the important tendency for the formation of polytype domains as a relationship between $\Delta T_{B\text{-}U}$ (the vertical temperature gradient) and $\Delta T_{F\text{-}I}$ (the temperature difference between the initial and final stage at the bottom of the crucible). The first tendency (denoted as 'Δ' on fig. 3 and in table 1) shows the conditions of both high $\Delta T_{F\text{-}I}$ and high $\Delta T_{B\text{-}U}$. For example, polytype domains were found at a high $\Delta T_{B\text{-}U}$ (above 9 Kcm^{-1}) and high $\Delta T_{F\text{-}I}$ (1.2 Kh^{-1}). When $\Delta T_{F\text{-}I}$ was high (above 0.5 $Kh/^{-1}$), the graphitization of the SiC source should be rapidly accomplished, so that the amount of reaction gases (Si, Si_2C, SiC_2 and Si_2) at the surface of the seed should more than sufficient. As a result, the growth rate was high (the average growth rate : 0.45 mmh^{-1}) as shown in Fig. 3. During crystal growth, a high growth rate has an influence on the polytype instability in crystals due to the rapid supply of reaction gases. In this case, polytype domains were formed as shown in Fig. 1 and 4, when the temperature conditions were a high $\Delta T_{F\text{-}I}$ (above 0.5 Kh^{-1}) and high $\Delta T_{B\text{-}U}$ (above 4 Kcm^{-1}). Also, polytype domains occurred under the conditions of high $\Delta T_{F\text{-}I}$ (above 0.5 Kh^{-1}) and low $\Delta T_{B\text{-}U}$ (below 4 Kcm^{-1}).

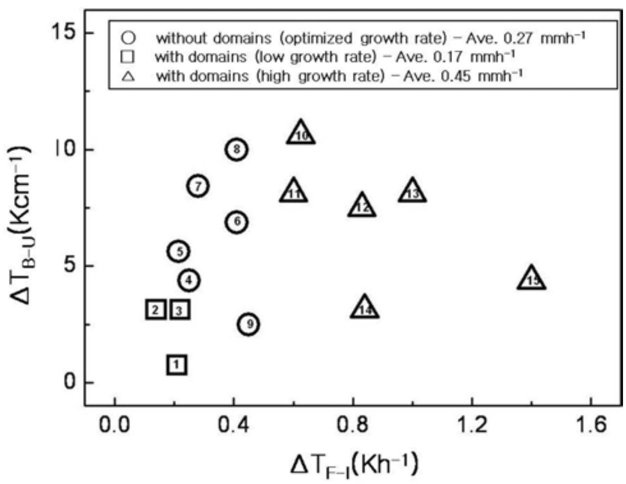

Fig. 3. The relationship between the vertical temperature gradient ($\Delta T_{B\text{-}U}$) and the temperature variation ($\Delta T_{F\text{-}I}$) between initial and final at the bottom of crucible in order to suppress the generation of polytype domain.

In the conditions of high $\Delta T_{F\text{-}I}$ and of either low $\Delta T_{B\text{-}U}$ or high $\Delta T_{B\text{-}U}$, the probability of 4H-SiC domain generation is increased under the condition of a high $\Delta T_{F\text{-}I}$ which corresponds with a low Si/C ratio and a C-rich atmosphere.

The second tendency (denoted as ' □ ' in Fig. 3 and table 1) was a low $\Delta T_{B\text{-}U}$ (< 4 Kcm^{-1}) and low $\Delta T_{F\text{-}I}$ (< 0.2 Kh^{-1}). In this case, the reaction gases were not sufficient to supply from the source to the seed surface, so that the growth rate was very low (the average growth rate : 0.17 mmh^{-1}). Also, in the case of a low $\Delta T_{B\text{-}U}$ and low $\Delta T_{F\text{-}I}$, the graphitization phenomena of the source should be properly accomplished and the amount of reaction gases (Si, Si_2C, SiC_2 and Si_2) should be sufficient. But, the reaction gases were not transported from the source to seed because the driving force for reaction gas transport was very low, which corresponds with a low vertical temperature gradient. As a result, the growth rate was low, below 0.2 mmh^{-1}. In addition, as $\Delta T_{B\text{-}U}$ was low, reverse-sublimation occurred at the seed surface, so that the seed surface was graphitized. If serious graphitization occurs on the seed surface prior to growth, a detrimental effect of the seed on the growth is that carbon layers on the seed surface can easily generate macro-defects such as micropipes, hollow pipes and planar defects. Then it is well known that the possibility of formation of polytype domains from these micropipes is high. It should be noted that the polytype domains were generated from macro-defects.

However, although $\Delta T_{B\text{-}U}$ was very low (2.5 Kcm^{-1}), a 6H-SiC crystal without polytype domain was successfully grown under an optimized $\Delta T_{F\text{-}I}$ (0.45 Kh^{-1}). It should be noted that the supply of reaction gases was sufficient under the optimized $\Delta T_{F\text{-}I}$.

The third tendency (denotes as 'O' on fig. 3 and in Table 1) show the optimized $\Delta T_{F\text{-}I}$. The optimized $\Delta T_{F\text{-}I}$ means that the graphitization of the source and the amount of reaction gases supplied was sufficient. As a result, the growth rate was optimized at 0.2-0.4 mmh^{-1} (the average

Table 1. The growth rate at each point versus $\Delta T_{F\text{-}I}$ as shown in Fig. 3.

□ Group ($\Delta T_{F\text{-}I} < 0.2\ Kh^{-1}$)	Growth Rate (mmh^{-1})	O Group ($0.2 Kh^{-1} < \Delta T_{F\text{-}I} < 0.5\ Kh^{-1}$)	Growth Rate (mmh^{-1})	Δ Group ($\Delta T_{F\text{-}I} > 0.5 Kh^{-1}$)	Growth Rate (mmh^{-1})
1	0.235	4	0.24	10	0.48
2	**0.13**	5	0.32	11	0.375
3	**0.14**	**6**	**0.18**	12	0.458
		7	**0.45**	13	0.33
		8	0.21	14	0.63
		9	0.246	**15**	**0.45**

(□ Group : low growth rate, O Group : optimized growth rate, Δ Group: high growth rate)

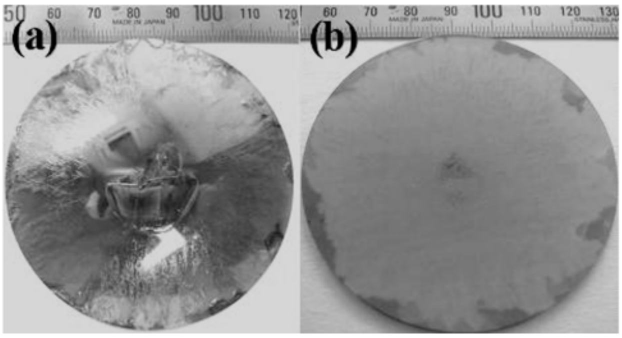

Fig. 4. (a) Top view of crystal grown under $\Delta T_{B\text{-}U}$: 9 Kcm^{-1} and $\Delta T_{F\text{-}I}$: 1.2 Kh^{-1}, and (b) lateral cut view.

growth rate : 0.27 mmh^{-1}) and high quality crystals without polytype domains were obtained as shown in Fig. 5.

From these results, it could be summarized that better crystals without polytype domains could be grown when the growth rate was optimized by the control of $\Delta T_{F\text{-}I}$.

In addition, it was found that although the growth rate was relatively high(No.7 and 15) or low(No.2, 3, and 6) (see Fig. 3 and table 1), if the $\Delta T_{F\text{-}I}$ was optimized in the range of 0.2-0.5 Kh^{-1}, good crystals without domains can be grown as shown in Table 1. This means that the $\Delta T_{F\text{-}I}$ will be a more important factor than the growth rate control for growing crystals of large diameter.

Finally, if $\Delta T_{F\text{-}I}$ is artificially controlled, high quality crystals without polytype domains can be obtained as shown in Fig. 5. But, if the $\Delta T_{F\text{-}I}$ condition is not optimized, there are three additional methods to optimize the control of $\Delta T_{F\text{-}I}$ as follows;

(i) Controlling $\Delta T_{F\text{-}I}$ by a higher growth pressure (The pressure can suppress the mass transport in the source)

(ii) Controlling $\Delta T_{F\text{-}I}$ by the presence of an insulator at the bottom of the crucible or by the modification of the bottom of graphite crucible

(iii) Controlling of $\Delta T_{F\text{-}I}$ by controlling the distance between the heating coil and top of the crucible

Conclusions

Many previous studies have reported and verified that the occurrence of polytype domains depends on defects such as micropipes, hollow pipes, planar defects and internal stresses. However, in our study, although the quality of the seeds used was very poor, an optimized $\Delta T_{F\text{-}I}$ condition prevents the occurrence of polytype domains. For this view-point, if the vertical temperature gradient ($\Delta T_{B\text{-}U}$) is optimized and the temperature difference ($\Delta T_{F\text{-}I}$) between the initial temperature and final temperature at the bottom of the crucible is not optimized, high quality SiC crystals without polytype domains can not be obtained. It is found that $\Delta T_{F\text{-}I}$ is more important than $\Delta T_{B\text{-}U}$ which is related to the generation of macro-defects, during sublimation growth.

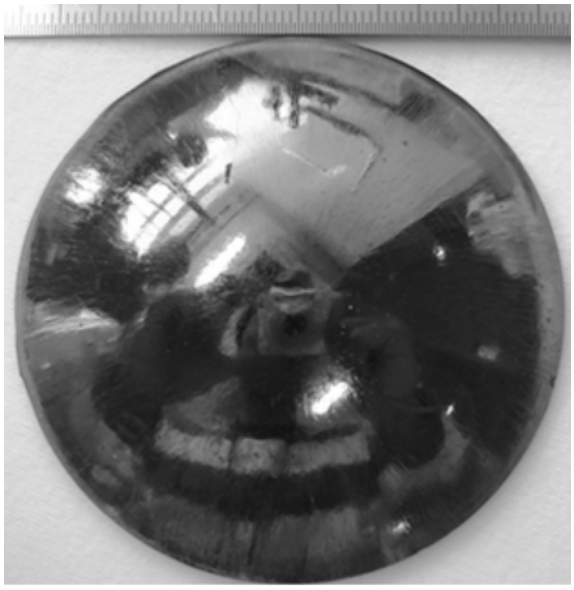

Fig. 5. Grown 6H-SiC crystal at the optimized $\Delta T_{F\text{-}I}$ temperature conditions.

In this study, we suggest a novel process factor in order to suppress the generation of polytype domains.

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