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Process Gas Control for High-Resistance HPSI-SiC Growth

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Abstract. In this study, we tried to grow SiC ingots with high resistivity and polytype stability with adoption hydrogen mixed gas flow to the PVT method. Three different types of growth atmosphere of N_2+Ar, H/Ar ratio:10% and 30% were employed. The polytype inclusion, crystal shape and transparency, and their resistivity were systematically investigated by UVF images, exposing backlighting, and high resistivity analysis using COREMA (Contactless Resistivity Mapper), respectively. The SiC ingot grown with adoption N_2+Ar exhibited a suppression of polytype inclusion, a convex shape and a lower resistivity. In contrast, the SiC ingot with more higher H/Ar ratio of 30% than that of 10% shows no polytype inclusion and highest resistivity of 1.7E11mΩ·cm. The growth atmosphere of relative higher H/Ar ratio in SiC crystal growth could be led the way to manufacture HPSI (high-purity semi-insulating)-SiC single crystal with polytype stability.

Introduction

The next generation of wireless infrastructure will depend on wide band gap semiconductors owing to their unique materials properties, including: their large bandgap, high thermal conductivity, and high breakdown field [1, 2]. To ensure the competitiveness of next generation of materials, it is essential to make SiC MESFET and GaN HEMT microwave devices more suitable for a wide range of applications. The application of high-resistivity HPSI 4H-SiC to microwave devices is absolutely indispensable. To ensure stable quality and high resistivity values of HPSI (high-purity semi-insulating)-SiC single crystal, it is necessary to suppress nitrogen incorporation during growth [3-5]. However, in the universal PVT method, nitrogen flow is essential for polytype stability. Therefore, we aim to obtain high-resistivity HPSI-SiC ingots while maintaining polytype stability without nitrogen flow by applying a new gas flow. To solve the problems caused by such nitrogen inclusion, we apply a hydrogen mixed gas atmosphere to the PVT method to obtain HPSI-SiC ingots with stabilized polytype and high resistivity characteristics [6]. The occurrence of polytype instability is caused by stacking defects resulting from the instability of the Si/C ratio due to the Si-rich vapor source sublimated from the raw material powder generated during PVT growth. In a previous study, hydrogen added to the ambient gas during the PVT process can easily diffuse through the graphite crucible walls. Since the reaction rate at typical PVT growth temperature is fast, hydrogen will reach equilibrium status with the graphite hot zone elements. This will result in an increased concentration of gaseous hydrocarbons, mostly C_2H_2, in the growth ambient, as compared to the case of growth in pure argon. Hydrogen will also interact with the SiC charges producing SiH and C_2H_2 via the reaction $2SiC+2H_2=2SiH+C_2H_2$. Through this chemical reaction, we aim to suppress the occurrence of stacking faults by increasing carbon-bearing species (C_2H_2) in the Si-rich atmosphere and controlling the Si/C ratio to 1:1 [7-9].

In addition, since the application of H_2 gas during growth gives rise to the effect toward etching impurities on the surface of the growth ingot, high-quality SiC ingots can be obtained [10, 11].

Experiments

As shown in Table 1, three types of PVT growth were performed. At a conventional nitrogen and inert gas Ar atmosphere (N_2+Ar), Method A with 10% H_2 gas (H/Ar) and Method B with 30% H_2 gas (H/Ar) were added. We tried to find out whether it is possible to achieve polytype stability while maintaining high resistivity during addition of hydrogen mixed gas without nitrogen and to find the optimal mixed gas ratio. Except for the gas flow condition, the hot zone design was identical. As shown in Fig. 1, growth conditions other than the gas atmosphere were the same. The SiC crystals were grown using a 4° off 4H-SiC seed as the seed crystal. Three SiC seed crystals were prepared by wafering process from the same ingot grown by under growth temperature of 2000 ~ 2400 ℃. The mixed inert gas of 1 ~ 40 torr was continuously supplied for 100hour. The axial thermal gradient of the SiC crystals during the growth is estimated at the range of 15~20 ℃/cm.

The image of UVF (ultra-violet fluorescence) of the growth ingot was obtained to observe polytype inclusion and their transparency of the ingot was investigated to decide nitrogen incorporation concentration. Resistivity measurements conducted on the three SiC ingots grown after growth run by a Lehighton Resistivity Measurement system(1510EB). In addition, high resistivity measurements were also performed using COREMA (Contactless Resistivity Mapping).

Table 1. Gas flow condition for three different SiC crystal growth using by addition of different gas ratio.

	Conventional	Modified A	Modified B
Gas Flow	For power devices	H/Ar ratio 10%	H/Ar ratio 30%

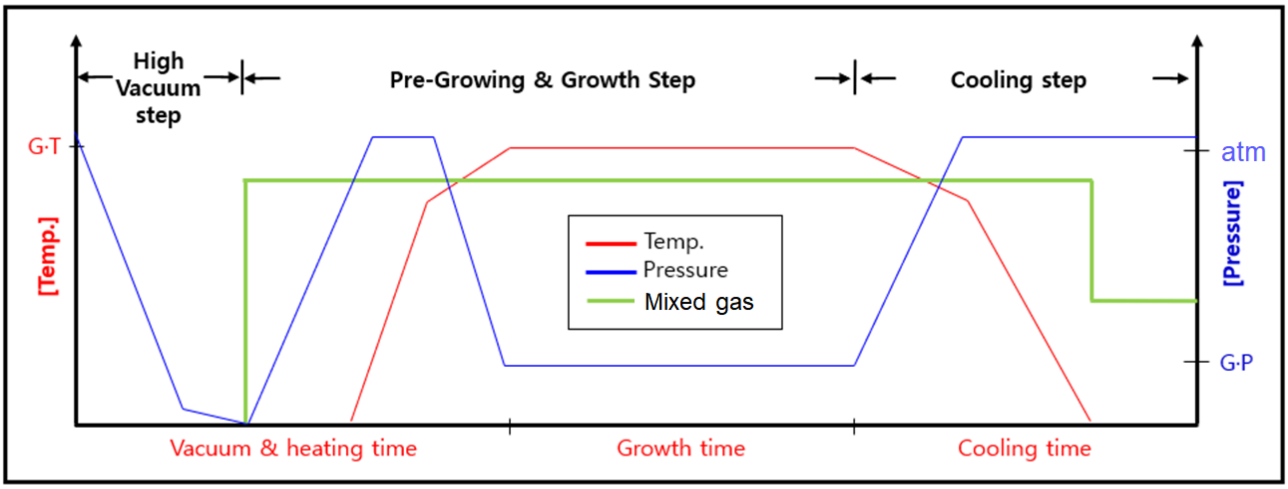


Fig. 1. The growth condition for SiC single crystal.

Results and Discussion

Grown ingot and polytype inclusion

To investigate the effect of hydrogen mixed gas application on polytype incorporation and resistivity characteristics, three PVT growths were performed under identical growth conditions excluding the gas atmosphere. The growth results of the three ingots are shown in Fig. 2. Here, upper and bottom blueish regions of SiC ingots shows illusion caused by interference. First, the UVF measurement results showed that polytype incorporation was suppressed in a nitrogen atmosphere at conventional growth resulting from the effect of suppression of polytype incorporation. In Method A, since the Si/C ratio was not optimized due to the absence of nitrogen and low hydrogen mixed gas ratio, polytype incorporation associated with orange color observed. However, in Method B, it was confirmed that the polytype was suppressed due to a relatively high hydrogen mixed gas ratio. This implies that the Si/C ratio is well controlled even under a hydrogen mixed gas atmosphere. Secondly, the shape of the ingot was investigated. The convex shape of ingot suppresses the formation of irregular terraces on the crystal surface. Therefore, it allows uniform diffusion of growth sources and high-quality SiC ingots can be obtained. In the conventional growth under nitrogen atmosphere, the optimized vertical and horizontal temperature gradients produce a convex shape ingot. When hydrogen mixed gas is added in the growth section, generation of a decrease in growth temperature and the stability of the crystal shape. This issue can be secured by controlling the growth power.

Finally, the transparency of the SiC ingots was evaluated. The transparency was conducted by exposing the backlight to the SiC ingot after outer diameter processing of SiC ingot itself. In the conventional growth, there is no polytype inclusion in the whole ingot, showing a single color. However, homogenous greened color of the ingot represents a nitrogen incorporation. In Method A, the greened color within SiC ingot is less than that of the conventional one, however, it is still mixed with nitrogen incorporation. In Method B, since growth under a high hydrogen mixed gas ratio, the transparent ingot with greatly suppressed nitrogen incorporation was grown. In order to find out the correlation between these transparency and resistivity, resistivity and high-resistivity measurements were conducted.

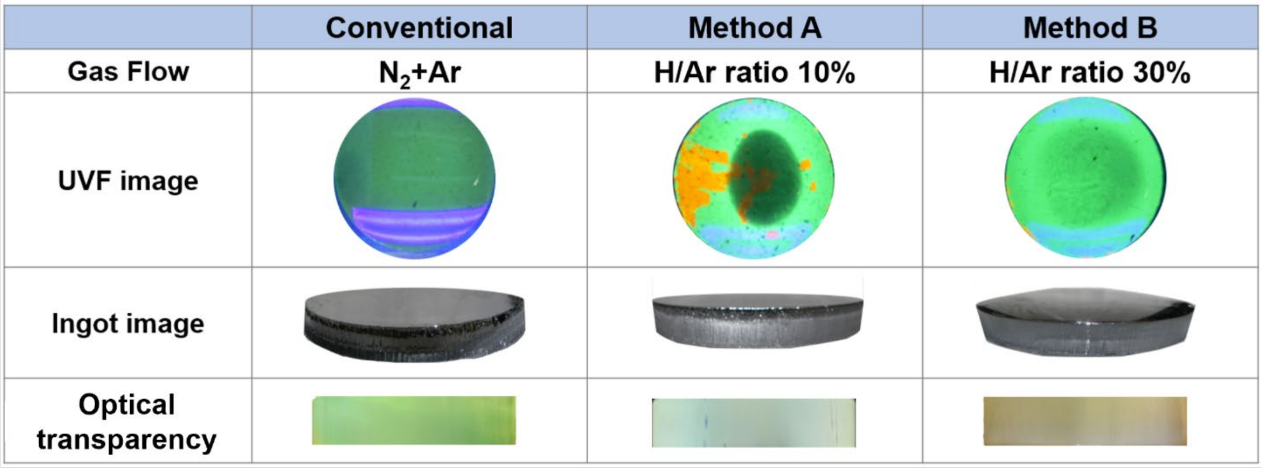
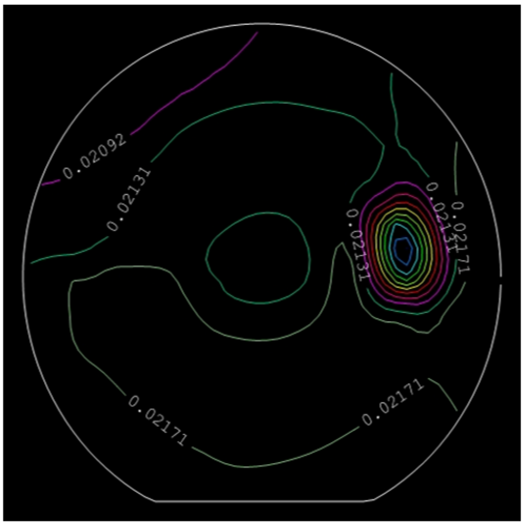


Fig. 2. UVF image of grown SiC ingot, cross-sectional image for SiC ingot and its transparency after growth run with adoption conventional N_2+Ar and H/Ar ratio.

Resistivity measurements

In order to investigate the correlation between suppression of nitrogen inclusion and resistivity, resistivity measurement was conducted. The resistivity of the SiC ingot obtained from the conventional method using N_2+Ar atmosphere was confirmed to be 21–22 mΩ·cm as shown in Fig. 3 (a). In Method A added with a 10% hydrogen mixed gas ratio, the resistivity was relatively higher as 5.7E2–6E2 mΩ·cm as shown in Fig. 3 (b). It reveals that nitrogen incorporation was well inhibited and the resistivity characteristics increases as hydrogen mixture gas is added. However, this value is not an appropriate resistivity to be applied to HPSI-SiC. In contrast, Method B added with a higher hydrogen mixture ratio, it was confirmed to be unmeasurable as shown in Fig. 3 (c). This shows direct evidence for grown HPSI-SiC ingot in this growth condition. High resistivity measurement was additionally conducted toward SiC ingot grown by Method B.

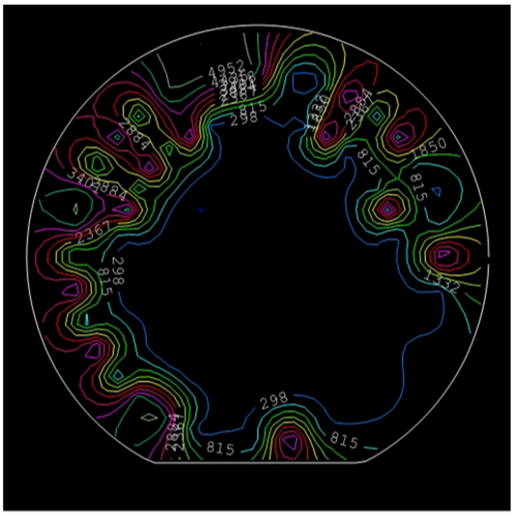


Statistical Summary

Number of Test Points	145
Average Value	0.02146
Maximum Value	0.02206
Minimum Value	0.01750
Sample Spread(%)	21.22
Std Dev Value	0.00058
Wafer Uniformity Value(%)	2.7
Contour Interval Value	0.0

Resistivity
21~22 mΩ·cm

(a) Conventional method with adoption N_2+Ar



Statistical Summary

Number of Test Points	145
Average Value	756.
Maximum Value	4902.
Minimum Value	4.
Sample Spread(%)	647.55
Std Dev Value	1671.
Wafer Uniformity Value(%)	220.87
Contour Interval Value	517.122

Resistivity
5.7E2~6E2 mΩ·cm

(b) Method A with adoption H/Ar of 10%

Statistical Summary

Number of Test Points	145
Average Value	3325.
Maximum Value	7442.
Minimum Value	95.
Sample Spread(%)	220.97
Std Dev Value	3477.
Wafer Uniformity Value(%)	104.58
Contour Interval Value	905.745

Resistivity
N/A

(c) Method B with adoption H/Ar of 30%

Fig. 3. Resistivity measurement results for three different SiC crystal substrates measured by a Lehighton Resistivity Measurement system (1510EB).

High resistivity measurement results by Contactless Resistivity Mapper

The SiC substrate grown by method B was subjected to high resistivity analysis using COREMA (contactless resistivity mapper) as shown in Fig. 4. The SiC wafers grown by the conventional and Method A could not be measured due to their lowest resistivity about ~E5 Ω·cm in COREMA measurement. The SiC wafer grown by Method B was properly measured to be 1.6E11~1.7E11 Ω·cm. This value is applicable to HPSI-SiC and shows a tendency consistent with the previous transparency evaluation.

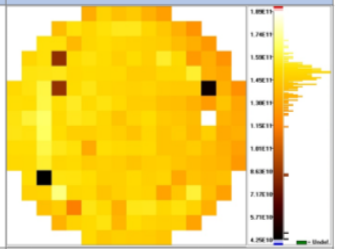
	Conventional	Method A	Method B
Image	Not measurable	Not measurable	
Resistivity[Ω·cm]	-	-	1.6 E11 ~ 1.7E11

Fig. 4. High resistivity measurement results for three different SiC crystal substrates measured by COREMA (Contactless Resistivity Mapper) system.

Summary

In order to obtain the high-resistivity HPSI-SiC ingot, the SiC crystals were grown using by PVT method at growth temperature of 2000 ~ 2400 °C with adoption three different growth atmosphere of N_2+Ar, H/Ar ratio:10% and 30% under growth pressure of 1 ~ 40 torr for 100h. The SiC ingot grown by conventional growth with adoption N_2+Ar atmosphere, it shows convex shape, the polytype incorporation of was suppressed, and resistivity was lower. In contrast, Method A (Method B) adoption of H/Ar ratio:10% (30%) shows polytype inclusion (no inclusion) relatively higher resistivity of 10E2 mΩ·cm (highest of 1.7E11 mΩ·cm). The crystal growth with adoption proper H/Ar gas ratio can pave the way to manufacture high quality and suppression of polytype inclusion as well as high-resistivity HPSI-SiC crystal.

Acknowledgements

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