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Polytype Stabilization of High-purity Semi-insulating 4H-SiC Crystal via the PVT Method

Kai-li MAO [1, 2] *, Ying-min WANG [2], Ru-sheng WEI [2], Bin LI [2], Wei XU [2], Li-zhong WANG [2]

[1] *Department of Materials Science & Engineering, Xi'an University of Technology, Xi'an 710048, China*
[2] *The 2nd Research Institute of China Electronics Technology Group Corporation, Taiyuan 030024, China*

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Because the conditions under which semi-insulating 4H-SiC crystals can grow are so specific, other polytypes such as 15R and 6H can easily emerge during the growth process. In this work, a polytype stabilization technology was developed by altering the following parameters: growth temperature, temperature field distribution, and C/Si ratio. In the growth process of high-purity semi-insulating 4H-SiC crystals, the generation of undesirable polytypes was prevented, and a crystal 100 % 4H-SiC polytype was obtained. A high C/Si ratio in powder source was shown to be advantageous for the stabilization of the 4H polytype. Several methods were applied to evaluate the quality of crystals precisely; these methods include Raman mapping, X-ray diffraction, and resistivity mapping. Results showed that the 3inch-wafer was entirely made of 4H polytype, the mean value of FWHM was approximately 40 arcsec, and the distribution of the resistivity value was between $10^6\,\Omega\cdot$cm and $10^7\,\Omega\cdot$cm.

Keywords: high-purity semi-insulating, 4H-SiC, polytype stabilization, sublimation method.

1. INTRODUCTION

The SiC crystal has been considered as an ideal wide bandgap semiconductor material owing to its advantages in high frequency, high power, and high-temperature electronic field [1, 2, 3]. In terms of polytype structure, the 3C, 6H, 4H, and 15R structures are the most common ones from among over 250 polytypes. 4H semi-insulating SiC substrates are regarded as ideal substrates for high-frequency devices because the devices made on the SiC substrates have been shown to exhibit lower dielectric loss and parasitic capacitance. Semi-insulating SiC bulk crystals can be grown via vanadium doping or by using high-purity materials. Commercial semi-insulating SiC substrates are available but can only be bought from limited suppliers.

In terms of the relationship between structure and temperature, the growth window of 4H polytype is narrow. Given that the stacking energies of several polytypes are extremely close to one another, the 4H polytype can easily transform to 6H, 15R, or other polytypes when the conditions are slightly changed. The polytype will change in terms of structure of the crystal, micropipes, dislocations and other defects are generated in the vicinity of the polytype area. These defects negatively affect the usable area and device yield. As H. J. Rost and E. Tymicki [4, 5] have reported, suitable nitrogen doping can prevent the polytype formation during n-type 4H-SiC growth. However, the growth of high-purity semi-insulating SiC crystals requires a comparatively low nitrogen background concentration, which is normally less than 10^{17}cm^3. At present, the 4H polytype stabilization method in the high purity semi insulating SiC single crystal growth process has not been reported, even though this stabilization is a key point for high purity semi-insulting 4H-SiC crystal growth. It is therefore crucial that a procedure to control 4H polytype stabilization be developed. In this paper, a polytype stabilization technology was successfully applied in high purity semi-insulating 4H-SiC crystal growth by adjusting the growth temperature, temperature field distribution, and C/Si ratio.

2. EXPERIMENTAL DETAILS

High-purity semi-insulating 4H-SiC crystals were grown via the PVT method. The growth process was carried out in an argon environment and the growth pressure was kept within the 5 – 20 mbar range. The growth temperature was maintained at 2150 °C to 2300 °C. The crystal growth rate was controlled at 100 μm/h to 300 μm/h. 3-inch 4°-off 4H-SiC substrates were used as seed. The purity of the SiC powder was above 99.995 %. The seed mounting procedure was done according to the process outlined by K.L. Mao, W. Xu, Y.M. Wang et al. [6]. Zhe Chuan Feng reported that the narrow available conditions present great chanllengens to the growth of the 4H polytype [7]. According to the relationship between the temperature of the environment and main SiC polytypes produced, the growth temperature of 4H polytype is lower than that of 6H polytype [8]. In stabilization of the 4H polytype, factors like nucleation, grown pressure, interface, temperature gradient, and C/Si ratio are crucial.

In this paper, the influence of the growth temperature on the polytype was initially studied. The polytypes were conveniently observed by introducing a small amount of nitrogen as the dopant during the initial experiments at a flow of 0.5 mL/min. To optimize the polytype stabilization method, we studied the temperature field and the C/Si ratios. The mapping function of the Horiba HR800 Raman

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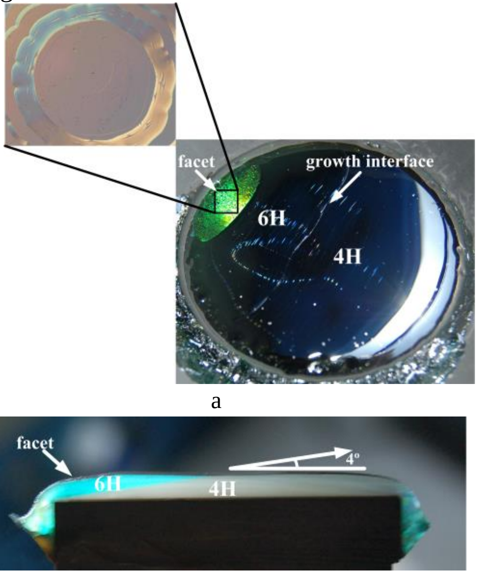
* Corresponding author. Tel.: +86-351-6523717; fax.: +86-351-6523726.
E-mail address: *maokaili001@aliyun.com* (K. Mao)

spectrograph was used to analyze the polytype distribution in the wafers. The resistivity of the entire wafers was measured using the COREMA system. The full width at half maxima (FWHM) was measured by the D8 discover system manufactured by Bruker Corporation.

3. RESULTS AND DISCUSSION

Fig. 1 displays the optical photographs of a SiC crystal grown at 2300 °C for 10 h. Along the (11-20) orientation, a cross-section of the crystal was obtained by using a diamond single cutting system. In Fig. 1 a, there was an evidently growth interface between 4H polytype and 6H polytype. The 6H polytype only appeared at the left side of the growth interface. In Fig. 1 b, the green 6H polytype originated from the opposite orientation of the secondary flat and extended to the surface of the crystal with an angle of 4°, which was the same as the off-angle of the seed. The area of the near-facet growth was evidently characteristic of the 6H polytype, but the area of the terrace growth was still characteristic of the 4H polytype. An observable growth interface was formed between these two polytype areas. Several hypothesizes have been conjectured to explain why the 4H polytype change to a 6H polytype. One of the possible conclusions is that the 6H polytype is always present around the growing 4H-SiC crystal. If the growth conditions (temperature, pressure, C/Si ratio, and so on) near the surface are unfavorable, the 6H polytype will emerge on the 0° interfaces.



a

b

Fig. 1. Optical photographs of SiC crystal growth at 2300 °C for 10 h: a – front image; b – cross section image

A growth temperature of 2300 °C is too high to confer enough energy to the 6H polytype to be present at the neighboring area of the 4H polytype. To reduce the 6H polytype, we decreased the growth temperature to 2150 °C. Fig. 2 shows the image of a SiC crystal grown at 2150 °C for 10 h. Under these new conditions, the green 6H polytype was no longer formed at an angle; rather, it formed in random areas. This result shows that reduction of the 6H polytype can be achieved by lowering growth temperature. It has been reported that a nearly flat and slightly convex growth front, and the C/Si ratio are also crucial aspects of polytype stabilization [7, 9, 10]. In the present paper, the convex of the temperature field was reduced by depressing the radial temperature grads, which was achieved by changing the structure of the graphite crucible. A crystal grown at 2150 °C for 10 h is showed in Fig. 3. The 6H polytype only appeared at the crystal edge. Though the area of 6H polytype was clearly reduced, many small slits emerged in the crystal and extended to the surface. These slits tended to be several millimeters deep, but they did not extend down to the bottom of the crystal. The 6H polytype emerges at the position between the slits, and this finding is in agreement with the reports of D. Siche, H. J. Rost, J. Doerschel, et al. [11]. These researchers found that these slit defects seemed to be a high local concentration of dislocations with basal components, which prevent crystal growth in a way similar to the Frank mechanism of micropipe generation. However, in nitrogen-doped 4H-SiC crystals, the slit length decreased, which confirms the correlation between slit generation and polytype stability, because nitrogen doping has been proved to stabilize the 4H polytype. It also indicates that lowering the nitrogen concentration decreases the quality of the crystal and leads to the generation of slit defects.

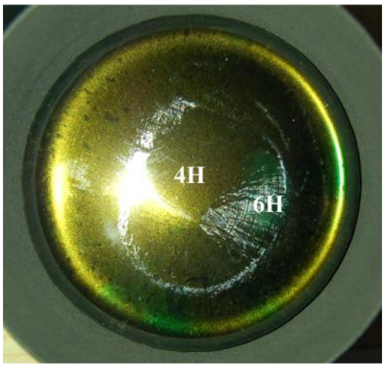


Fig. 2. Optical images of SiC crystal growth at 2150 °C for 10 h

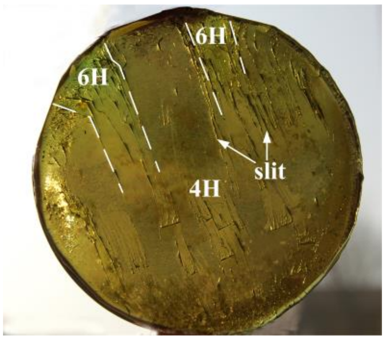


Fig. 3. Optical photographs of the SiC crystal after adjusting the temperature field

Because there is evidence that overuse of nitrogen doping depresses the resistivity of high purity semi-insulating SiC crystal, to achieve a successful result, the nitrogen concentration needs to be kept lower than 1E17 cm^{-3}. However, slit defects emerge in the crystal if the nitrogen concentration is too low. The gas phase C/Si ratio is less than 0.6 when 4H-SiC crystals are grown at 2150 °C [12]. To solve this problem, the authors attempted to change the C/Si ratios of the source by adding high-purity carbon powder. When the C/Si ratio in the powder source was increased to 1.6, a 4H-SiC crystal without any other polytype was achieved. Fig. 4 shows an image of an unintentionally doping SiC crystal grown at 2150 °C for 100 h. The crystal growth rate reached as high as 210 μm/h. The image shows that the crystal surface was slick, and no slits were found in the crystal.

In Table 1, parameters affecting the polytype occurrence are presented for the most common SiC polytypes. g is defined as the ratio of Nh (hexagonal position atom number) and $Nh+Nc$ (total atom number in unit cell). $g=Nh/(Nh+Nc)$. Vc means the density of C-vacancies. R. Yakimova et al. considered that introduction of carbon vacancies caused by an excess of silicon, leads to compression of the crystal lattice thus supporting the cubic structure of the layer, which is more favorable from energy standpoint than the hexagonal one [14].

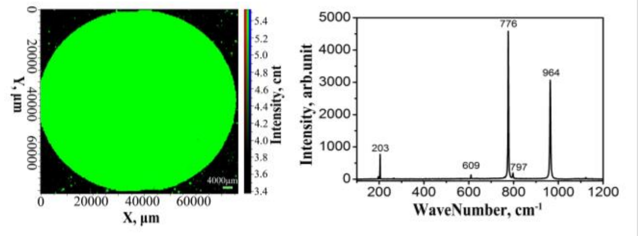
In this paper, for 4H-SiC crystal, the hexagonality is 50 %, the C/Si ratio is close to unity, and the density of C-vacancies is lowest. Author suggests that additional carbon powder can effectively reduce the silicon concentration in the gas phase through reacted with gas-phased silicon, when gas-phased silicon transport from bottom to top of crucibles. It means that the C/Si ratio in the gas phase is relatively higher than in the gas phase without carbon powder. A C-rich environment is advantageous for stabilizing the 4H polytype. As shown in Fig. 4, the use of a suitable C/Si ratio in the powder source also prevents slit defects. This article postulates that the slits are caused by a higher Si/C ratio during the initial growth process. By this method, over ten high-purity semi-insulating 4H-SiC crystals had been grown.

Fig. 4. Optical image of the SiC crystal after changing C/Si ratio

Table 1. Degree of hexagonality, C/Si ratio in the solid phase and concentration of carbon vacancies [13]

Polytype	3C	6H	15R	4H
g	0	0.33	0.4	0.5
[C]/[Si] ratio	0.9560	0.9785	0.9881	0.9990
$Vc \cdot 10^{20} cm^{-3}$	33.6	16.3	15.1	7.3

Fig. 5 shows the Raman mapping image of the wafer tested using the Horiba HR800 Raman test system. In the mapping image Fig. 5 a, the scanning step size is set to 2 mm. The characteristic peak 203 cm^{-1} and 150 cm^{-1} of raman spectrum were used to distinguished the 4H and 6H polytype, respectively. If there is a peak of 203 ± 1 cm^{-1}, the measurement points are labeled as green color. Whereas, the peak of 150 ± 1 cm^{-1} appears, the measurement points are labeled as red color. From the mapping image of whole 3 inch wafer, the results show that the wafer is made up of 100 % 4H polytype. Fig. 5 b shows the characteristic spectrum of 4H-SiC. This success in achieving a purely 4H polytype wafer supports the authors' conclusion that variation in polytypes can be prevented by manipulation of growth conditions. The parameter C/Si ratio has been shown to be most important [15]. A higher C/Si ratio in powder source is advantageous to the stabilization of 4H polytype.



a b

Fig. 5. Raman mapping image of the 3-inch high purity semi-insulating 4H-SiC wafe: a – mapping image; b – Raman spectrum

For high purity semi insulating SiC, the elimination of residual impurities at least to the level of 5E16 cm^{-3} is necessary; especially, nitrogen in the ambient and boron in graphite parts have to be taken into account [16]. Table 2 lists the impurities in high-purity semi-insulating 4H-SiC wafer that was analyzed via the SIMS technique. The concentrations of nitrogen and boron are 2.6E16 cm^{-3} and 2.4E16 cm^{-3}, respectively. The surface resistivity of the entire wafer surface was measured using a COREMA test system. Fig. 6 shows the mapping image of resistivity. The scanning step size is set to 4.45 mm. Resistivity limits apply to entire wafer surface except for edge exclusion area, which is 2.5 mm for 76.2 mm substrates. As shown by the picture, the resistivity values range from 10^{6} Ω·cm to 10^{7} Ω·cm. According to the SIMS data, the concentration of aluminum is under the limit of detection, the resistivity is affected mainly by the concentrations of nitrogen and boron. The resistivity values should be improved by reducing the concentrations of nitrogen and boron further.

Table 2. SMIS analysis of high-purity semi-insulating 4H-SiC

Element	Concentration, cm^{-3}
N	2.6E16
B	2.4E16
Al	3E14
V	<5E13

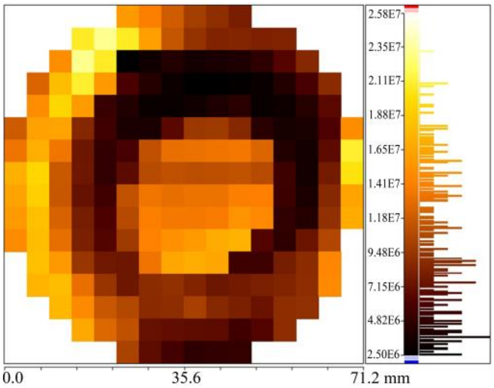


Fig. 6. Resistivity mapping image of the 3-inch high-purity semi-insulating 4H-SiC wafer

In Fig. 7, the mean FWHM of the XRD rocking curve for five points was used to evaluate the quality of the high-purity semi-insulating 4H-SiC wafer. The data were measured from the silicon face of the 4H-SiC wafer. The first point is set at the center of the wafer. The remaining four points are evenly distributed on the wafer, which are set beginning from the direction perpendicular to the Primary flat. The distance of the four points from the center position is 25 mm. The mean FWHM of the wafer is approximately 40 arcsec. This result shows that the crystal is of finest quality.

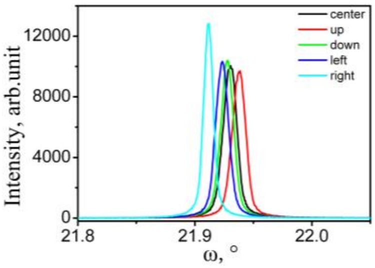


Fig. 7. Five points XRD rocking curve of the 3-inch high-purity semi-insulating 4H-SiC wafer

4. CONCLUSIONS

Polytype stabilization is a key technology in the growth of high-purity semi-insulating 4H-SiC crystal. When growing the 4H-SiC crystals, the growth temperature, temperature field distribution and C/Si ratio affect the stability of the crystal structure. If the C/Si ratio is too low, slit defects occur in addition to the emergence of the 6H polytype. Under the non-doping condition, we can also obtain a crystal made up of 100 % 4H polytype by simultaneously adjusting several parameters, such as the growth temperature, temperature field distribution, and C/Si ratio. As the C/Si ratio was increased to 1.6, the quality of 4H-SiC crystal was improved.

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REFERENCES

1. **Palmour, J.W.** Energy Efficiency: The Commercial Pull for SiC Devices *Materials Science Forum* 527 – 529 2006: pp. 1129 – 1134.
2. **Ramezani, Z., Orouji, A., Keshavarzi, P.** A Novel Double-Recessed 4H-Sic MESFET Using Scattering the Electric Field for High Power and RF Applications *The Journal of Crystal Growth* 59 2014: pp. 202 – 209. http://dx.doi.org/10.1016/j.physe.2014.01.002
3. **Kondo, H., Takaba, H., Yamada, M., Urakami, Y., Okamoto, T., Kobayashi, M., Masuda, T., Gunjishima, I., Shigeto, K., Ooya, N., Sugiyama, N., Matsuse, A., Kozawa, T., Sato, T., Hirose, F., Yamauchi, S., Onda, S.** Development of RAF Quality 150 mm 4H-SiC Wafer *Materials Science Forum* 778 – 780 2014: pp. 17 – 21.
4. **Rost, H.J., Doerschel, J., Irmscher, K., Robberg, M., Schulz, D., Siche, D.** Polytype Stability in Nitrogen-Doped PVT Grown 2” 4H-Sic Crystal *The Journal of Crystal Growth* 275 2005: pp. e451 – e454. http://dx.doi.org/10.1016/j.jcrysgro.2004.11.018
5. **Tymicki, E., Grasza, K., Racka, K., Lukasiewicz, T., Piersa, K., Kosciewicz, K., Teklinska, D., Diduszko, R., Skupinski, P., Jakiela, R., Krupka, J.** Effect of Nitrogen Doping on the Growth of 4H Polytype on the 6H-SiC Seed by PVT Method *Materials Science Forum* 717 – 720 2012: pp. 29 – 32.
6. **Mao, K.L., Xu, W., Wang, Y.M., Tian, M., Wang, L.Z.** Effect of seed Mounting on Sic Crystal Quality By PVT Method *Electronics Process technology* 32 (6) 2011: 367 – 369.
7. **Feng, Z.C.** SiC Power Materials Devices and Applications. Springer, Berlin, 2004: pp. 91 – 94. http://dx.doi.org/10.1007/978-3-662-09877-6
8. **Feng, Z.C.** SiC Power Materials Devices and Applications. Springer, Berlin, 2004: pp. 14 – 16. http://dx.doi.org/10.1007/978-3-662-09877-6
9. **Chourou, K., Anikin, M., Bluet, J.M., Lauer, V., Guillot, G., Camassel, J., Juillaguet, S., Chaix, O., Pons, M., Madar, R.** Experimental Investigation of 4H-SiC Bulk Crystal Growth *Materials Science Forum* 264 – 268 1998: pp. 17 – 20.
10. **Schmitt, E., Straubinger, T., Rasp, M., Vogel, M., Wohlfart, A.** Polytype Stability and Defects in Differently Doped Bulk SiC *The Journal of Crystal Growth* 310 2008: pp. 966 – 970. http://dx.doi.org/10.1016/j.jcrysgro.2007.11.185
11. **Siche, D., Rost, H.J., Doerschel, J., Schulz, D., Wollweber, J.** Evolution of Domain Walls in 6H- And 4H-Sic Single Crystal *The Journal of Crystal Growth* 237 – 239 2002: pp. 1187 – 1191.
12. **Feng, Z.C.** SiC Power Materials Devices and Applications. Springer, Berlin, 2004: pp. 9 – 10. http://dx.doi.org/10.1007/978-3-662-09877-6
13. **Lebedev, A.A., Davydov, S.Yu.** A Vacancy Model of the Heteropolytype Epitaxy of SiC *Atomic Structure and Nonelectronic Properties of Semiconductors* 39 (3) 2005: pp. 277 – 280.
14. **Yakimova, R., Vasiliauskas, R., Eriksson, J., Syvajarvi, M.** Progress in 3C-SiC Growth and Novel Applications *Materials Science Forum* 711 2012: pp. 3 – 10.
15. **Ciechonski, R.R., Syvajarvi, M., Hassan, J.U., Yakimova, R.** Structural Instabilities in Growth of SiC Crystals *The Journal of Crystal Growth* 275 2005: pp. e461 – e466. http://dx.doi.org/10.1016/j.jcrysgro.2004.11.020
16. **Bickermann, M., Hofmann, D., Straubinger, T.L., Weingartner, R., Wellmann, P.J., Winnacker, A.** On the Preparation of Semi-Insualting Sic Bulk Crystals by the PVT Technique *Applied Surface Science* 184 2001: pp. 84 – 89. http://dx.doi.org/10.1016/S0169-4332(01)00481-0