特集 Mechanism of Nitrogen Incorporation in Sublimation Growth of SiC*

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SiC is expected as a semiconductor material for high power , high frequency and high temperature devices. Devices produced from SiC critically depend on the production of SiC single-crystals of high crystalline quality and controlled impurity content. It is important to control the resistivity of substrate by impurity doping concentration to fabricate low resistivity or high resistivity SiC substrate. It becomes possible to control wide range doping concentration in SiC crystal by clarifying the mechanism of impurity incorporation. We proposed the mechanism of nitrogen incorporation in the sublimation growth of SiC. We speculated that the difference in the doping concentration of nitrogen in the C-face and the Si-face grown SiC crystal is related to the presence of the C-vacancy during the crystal growth.

Key words : Silicon carbide, Doping, Single crystal growth, Sublimation growth

1. INTRODUCTION

Silicon carbide (SiC) is the key material for high power, high frequency and high temperature devices.[1] Generally, vertical power devices are fabricated on the low resistivity substrate. On the other hand, high frequency devices are fabricated on the high resistivity substrate.[2] It is important to control the resistivity of substrate by impurity doping concentration to fabricate low resistivity or high resistivity SiC substrate. For SiC, nitrogen is the n-type dopant. In n-type SiC, doping concentration of nitrogen in SiC crystal grown on the C-face in sublimation growth is higher than that on the Si-face.[2) 3)] It is difficult to control to low doping concentration of nitrogen in SiC crystal grown on the C-face and high doping concentration of nitrogen in SiC crystal grown on the Si-face. It becomes possible to control wide range doping concentration in SiC crystal by clarifying the mechanism of nitrogen incorporation. In SiC, nitrogen dopant substitutes on the C site and forms a shallow donor level as speculated on the basis of first-principles calculations.[4] Therefore, the SiC crystal grown on the C-face leads to the higher nitrogen incorporation during the growth, thereby, high doping concentration. In this paper we report the deep photoluminescence (PL) investigations carried out on the SiC crystals grown on the Si-face and the C-face. The mechanism of nitrogen incorporation in the sublimation growth of SiC is proposed.

2. EXPERIMENTAL PROCEDURE

6H- and 4H-SiC crystals were grown by the sublimation growth. 6H-SiC crystals were grown on the Si-face and the C-face of 6H-SiC seed crystals, respectively. And 4H-SiC crystals were grown on the C-face of 4H-SiC seed crystals. Nitrogen doping was performed by adding the nitrogen gas to the source ambient during growth. The SiC single crystals were grown at the seed temperature between 2200℃ and 2300℃ and the growth rate of about 0.3mm/h. The SiC crystals were evaluated by PL spectroscopy at room temperature. The crystals were excited by the 325nm line of a He-Cd laser with an incident power of about 2mW. The photomultiplier was used as the detector of illumination. The nitrogen concentration of the grown crystals were measured by SIMS. The nitrogen doping concentration in SiC crystals were more than $1\times10^{18}cm^{-3}$.

3. RESULTS AND DISCUSSION

The room temperature PL spectra of undoped 6H-SiC crystal are shown in **Fig. 1**. The deep PL spectrum of undoped 6H-SiC crystal grown on the C-face consisted of the broad emissions of 2.21, 1.88, 1.03, and 0.75eV. These emissions were not reported and unknown. On the other hand, undoped 6H-SiC crystal grown on the Si-face showed a single weak emission peak at 1.34eV. This emission originated from an internal transition of the neutral Si-vacancy.[5] The nitrogen concentration was

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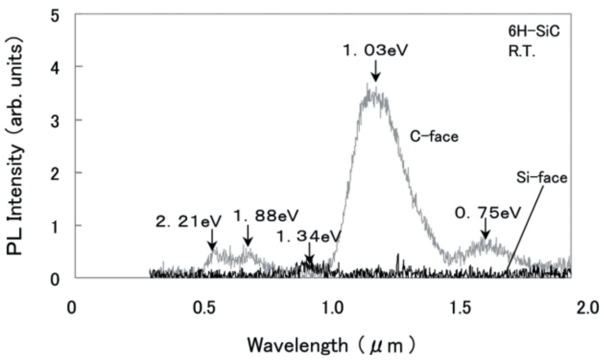

Fig. 1 PL spectra of undoped 6H-SiC crystals grown on the C-face and the Si-face.

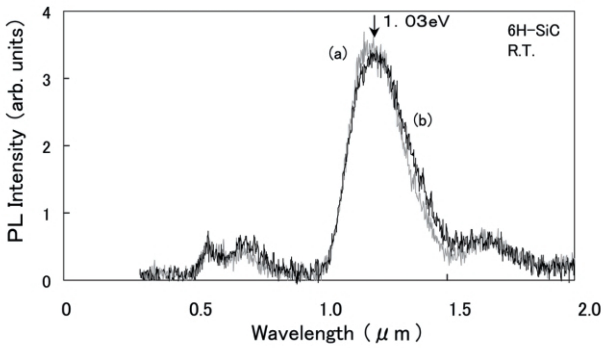

Fig. 2 PL spectra of 6H-SiC crystals grown on the C-face. The nitrogen concentrations are (a) 2X $10^{18}cm^{-3}$ and (b) 6X$10^{18}cm^{-3}$.

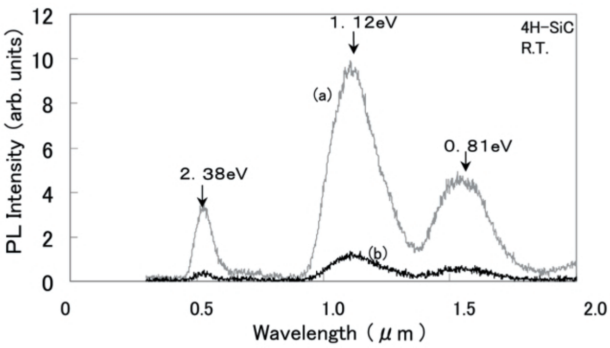

Fig. 3 PL spectra of 4H-SiC crystals grown on the C-face. The nitrogen concentrations are (a) 1X $10^{18}cm^{-3}$ and (b) 3X$10^{18}cm^{-3}$.

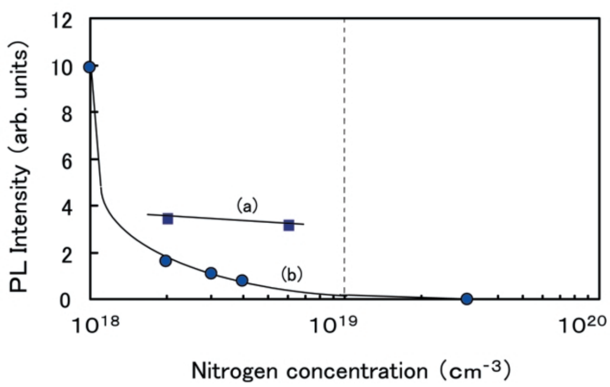

Fig. 4 PL intensity of (a) 1.03eV emission in 6H-SiC crystal and (b) 1.12eV peak in 4H-SiC crystal as a function of nitrogen concentration in the crystal.

$2\times10^{18}cm^{-3}$ in undoped 6H-SiC crystal grown on the C-face and $4\times10^{17}cm^{-3}$ undoped 6H-SiC crystal grown on the Si-face. Nitrogen concentration in undoped SiC crystal grown on the C-face is higher than that on the Si-face, which is similar to the result reported by Takahashi et al.[3] **Figure 2** shows the PL spectra of 6H-SiC crystals grown on the C-face with different nitrogen concentration. The emission intensity of 1.03eV in 6H-SiC crystal with more nitrogen concentration is lower than that with less nitrogen concentration. On the other hand, **Fig. 3** shows the PL spectra of 4H-SiC crystals grown on the C-face with different nitrogen concentration. The deep PL spectrum of 4H-SiC crystals grown on the C-face consisted of the broad emissions of 2.38, 1.12, and 0.81eV. These emission intensity in 4H-SiC crystal with more nitrogen concentration are lower than that with less nitrogen concentration. **Figure 4** shows nitrogen concentration dependence of PL emission intensity in 6H- and 4H-SiC crystals grown on the C-face. The emission intensity at 1.03eV in 6H-SiC and at 1.12eV in 4H-SiC decreased as nitrogen concentration increased. We found that the emission from the deep levels showed decreasing with the increasing nitrogen doping concentration.

In SiC, nitrogen atom on the C-site is more stable than that on the Si site, and forms a shallow donor level as speculated on the basis of first-principles calculations.[4] For SiC CVD epitaxial growth, nitrogen concentration in the grown epilayer is proportional to the Si/C ratio during epitaxial growth.[6) 7)] The decreased concentration of carbon relative to silicon allows the nitrogen to outcompete the carbon for the C-site of the growing SiC lattice. This also was applied to nitrogen ion implantation in SiC crystal.[8] Therefore it is possible to applied this to the sublimation growth. Nitrogen dopant substitutes on the C-site during the sublimation growth. If there are C-vacancies in SiC crystal, nitrogen atom substitutes on the C-vacancy and eliminates C-vacancy.

Figure 5 shows schematic illustrations of the growing surfaces on the C-face and Si-face. The surface of the C-face is terminated with C atoms. For SiC sublimation growth on the C-face, as the growth temperature is higher than 2200°C, C atoms terminated can be desorbed. When C atoms is desorbed, C-vacancies are formed. Under less nitrogen atoms, the C-vacancy is left during the growth and then SiC crystal with the C-vacancy is grown. Under more nitrogen atoms, nitrogen atoms substitute on the C-sites and C-vacancies are decreased. On the other hand, the surface of Si-face is terminated with Si atoms. For SiC sublimation growth on the Si-face, Si atoms terminated can be desorbed. When Si atoms are desorbed, the Si-vacancies are formed. The C-vacancies are not formed. As the C-vacancy is easy to be formed during the sublimation growth on the C-face, we think that the nitrogen atom occupy the C-vacancy during the doping growth and leads to the decrease in the C-vacancy concentration as reflected by the PL analysis. Thereby, the nitrogen concentration in SiC crystal grown on the C-face is higher than that on the Si-face. The observed deep levels may be related to the C-vacancy. From these results, we propose that the difference in the doping concentration of nitrogen in the C-face and the Si-face grown SiC crystal is related to the presence of the C-vacancy during the crystal growth.

In **Fig. 4**, the behavior of the emission intensity from the deep levels is different between 6H-SiC and 4H-SiC. In order to clear this difference, nitrogen doped 6H-SiC and 4H-SiC crystals were grown on the C-face at a time and were evaluated about the nitrogen incorporation. The results are shown in **Table 1**. The nitrogen concentration in 6H-SiC crystal is more than that in 4H-SiC crystal, is similar to the result reported by Ohtani et al.[9] They reported that the macrosteps and the small steps exist on the C-face of 6H-SiC crystals and the macrosteps exist on the C-face of 4H-SiC crystals and the macrosteps incorporate less nitrogen than the small steps. On the other hand, the carrier concentration is not different between 6H-SiC and 4H-SiC. Therefore 6H-SiC crystals incorporate more nitrogen than 4H-SiC crystals but the carrier concentration of 6H-SiC crystals is less than that of 4H-SiC crystals. This shows 6H-SiC crystals incorporate less nitrogen in C-site than 4H-SiC crystals. This is the reason nitrogen is not incorporated in C-vacancy but in the small steps for 6H-SiC crystals. For 4H-SiC crystals, nitrogen is incorporated in C-vacancy due to no small steps. Therefore there are more C-vacancy in 6H-SiC crystals. We think that this shows the emission from the deep levels in 6H-SiC crystals is higher intensity than that in 4H-SiC crystals in the case of nitrogen doped C-face growth.

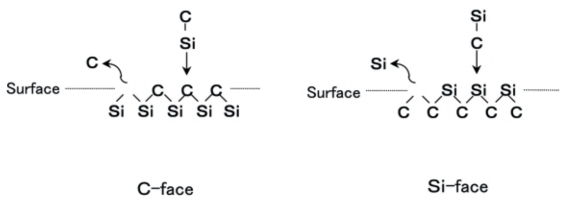

Fig. 5 Schematic illustrations of the growing surfaces on the C-face and the Si-face in the sublimation growth.

Table 1 Nitrogen concentration and carrier concentration for 6H-SiC and 4H-SiC crystals grown on the C-face.

	Nitogen concentration (cm^{-3})	Carrier concentration (cm^{-3})
6H	6×10^{18}	2×10^{18}
4H	3×10^{18}	3×10^{18}

4. CONCLUSION

The deep PL spectrum of 6H-SiC and 4H-SiC crystals grown on the C-face consisted of the multiple broad emissions, respectively. These emissions from the deep levels showed decreasing with the increasing nitrogen doping concentration. As the C-vacancy is easy to be formed during the sublimation growth on the C-face, we think that the nitrogen atom occupy the C-vacancy during the doping growth and leads to the decrease in the C-vacancy concentration. The observed deep levels may be related to the C-vacancy. We speculated that the difference in the doping concentration of nitrogen in the C-face and the Si-face grown SiC crystal is related to the presence of the C-vacancy during the crystal growth.

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