

A Degradation Phenomenon of SiC Blue LEDs

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The emission color shift phenomenon of 6H-SiC blue LEDs from blue to greenish-blue is observed. This degradation phenomenon is concerned with the damages generated by sawing the diode edge. In addition, it was revealed that blue LEDs having the p-type layer of higher carrier concentration in the order of 10^{18} cm^{-3} were considerably degraded. As a result, it is considered that the crystallinity of the p-type layer plays an important role in the degradation phenomenon.

1. Introduction

SiC (6H-polytype) is a suitable material for blue light-emitting diodes (LEDs) because it has a large band-gap (3.0eV) and the p-n junction can be made easily. By the LPE method, SiC blue LEDs have been already fabricated. However, it was reported that some LEDs change their emission color from blue to greenish-blue by operation at ordinary forward currents, and this degradation occurs at the sawed edges and develops in the entire layer.¹⁾ The degradation phenomenon also took place in some of our SiC blue LEDs fabricated by the LPE method. Furthermore, it occurred in spite of preparing the LEDs by careful cleaving, not by sawing.

To solve this problem, the relation between the amount of Al dopant in the p-type layer and the degradation phenomenon of the SiC blue LEDs was investigated.

2. Fabrication and evaluation of p-type layers

The SiC epitaxial layer was fabricated by the dipping technique²⁾ which is one of the LPE methods. The crucibles and substrate-holders were made of high density ($d=1.84$) graphite. Spectroscopic analysis of the graphite showed that traces of any elements were scarcely found except Vanadium. Before crystal growth, the crucibles and substrate-holders were baked for two hours at about 1800°C under vacuum at 2×10^{-6} Torr. Polycrystalline Si (10-N grade) and Al (6-N grade)

for p-type dopant were used. The epitaxial growth of the p-type layer on the n-type 6H-SiC substrate was carried out under the following conditions. The crucible filled with Si and a small amount of Al dopant (0~2.21 at.%) was evacuated under vacuum at 2×10^{-6} Torr and prebaked at 700°C to reduce the adsorbed gases. After the baking process, the vacuum was broken by introducing purified Ar gas, and the crucible was heated up to 1700°C and maintained at the same temperature under purified Ar gas flow of 2 l/min . The substrate fixed to the holder was dipped in the Si melt for 150 minutes. Before the growth, the meltback of the substrate was carried out for a brief time. Then the substrate was pulled up from the Si melt, and immersed into a mixed solution of HF and HNO_3 to remove the residual Si. The thickness of the growth layer was about $5 \mu\text{m}$.

Evaluation of the p-type epitaxial layers doped with various amounts of Al added in the Si melt was carried out by the Van der Pauw method, photoluminescence (PL) measurement and X-ray diffraction analysis.

Figure 1 shows the electrical properties of the p-type epitaxial layers. The carrier concentration decreases, and the mobility increases by decreasing the amount of Al content. At 0.11 at.% amounts of Al content, the carrier concentration and mobility are $7.4 \times 10^{16} \text{ cm}^{-3}$ and $45 \text{ cm}^2/\text{v}\cdot\text{sec}$, respectively.

Figure 2 shows the PL spectra of the p-type

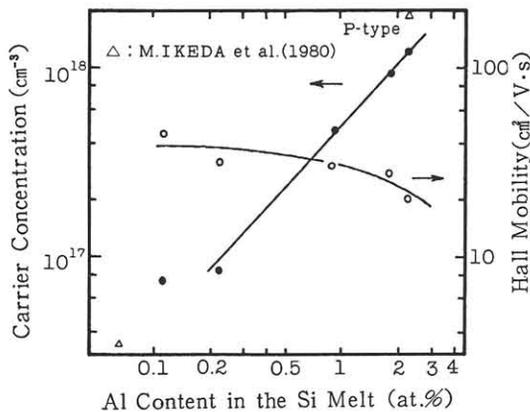


Figure 1 Carrier concentration and Hall mobility of Al-doped SiC epitaxial layers (300K).

layers at 77K. Above 0.90 at.% amounts of Al content, peak I and peak II are noticeable. These peaks are considered to be due to D-A pair transitions between N donors and Al acceptors, which are composed of C series.³⁾ Below 0.45 at.% amounts of Al, the shape of spectrum tends to be a single broad peak. The PL spectrum of undoped layer shifts to the region of longer wavelength and its intensity is very weak. And the conduction type of this layer was n-type. It is assumed that residual nitrogen is doped in the epitaxial layer unintentionally.

The dependence of the PL intensity ($\lambda_p \approx 470\text{nm}$) of each p-type layer on the amount of Al in the Si melt at 77K is shown in Figure 3. The PL intensity increases considerably by decreasing the amount of Al. It is considered that at small amounts of Al content, the crystallinity of the p-type layer is relatively good and the non-radiative transitions are reduced.

The lattice spacing of the (006) planes was measured by X-ray diffraction. The dependence of the (006) lattice spacing of the p-type layers on the amount of Al added in the Si melt is shown in Figure 4. The calculated lattice spacing value of these planes is 2.5153 \AA ($a_0 = 3.081 \text{ \AA}$, $C_0 = 15.092 \text{ \AA}$; ASTM). Although the measured value

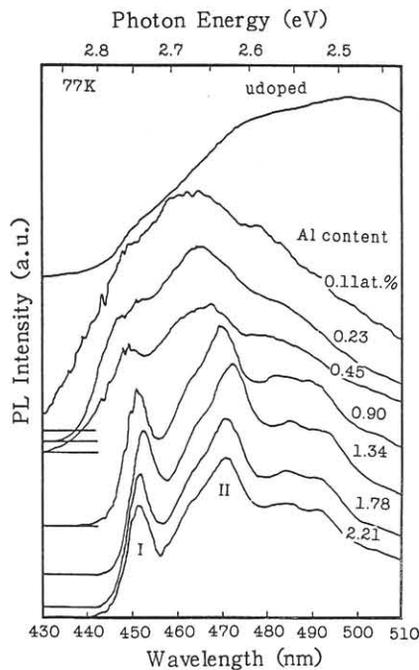


Figure 2 Photoluminescence spectra of Al-doped SiC epitaxial layers (77K).

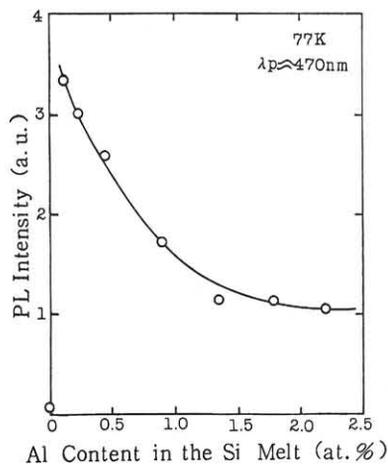


Figure 3 Photoluminescence intensity of the main peak at the wavelength near 470nm of Al-doped SiC epitaxial layers (77K).

of each p-type layer is almost in agreement with the calculated one up to 0.45 at.% amounts of Al, it tends to increase by adding further Al to the Si melt. The carrier concentration was $1.3 \times 10^{18} \text{ cm}^{-3}$ at 2.21 at.% amounts of Al content (as shown in Figure 1), but Al contained in the p-type layer

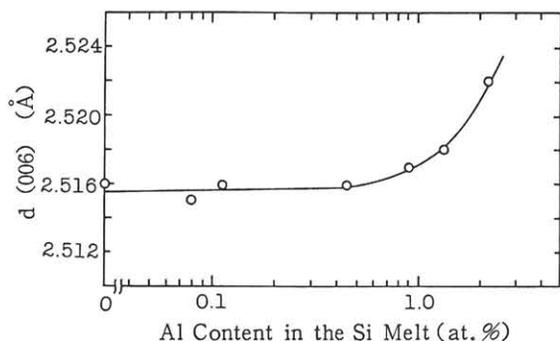


Figure 4 Lattice spacing (006) of Al-doped SiC epitaxial layers (300K).

is estimated at about $5 \times 10^{19} \text{cm}^{-3}$.⁴⁾ Therefore, it is considered that the increase of lattice spacing of the (006) planes is related to the excess number of Al-C bonds. (Al atoms substitute for Si in SiC and its ionic radius is larger than Si.)

3. Degradation of SiC blue LEDs

The fabrication process of our SiC blue LEDs is as follows. The n and p-type SiC epitaxial layers were grown on the n-type 6H-SiC substrate. The growth temperature of both layers was about 1700°C. As the doping materials for the n-type phosphor layer, Si_3N_4 and Al were added in the Si melt at the amounts of $\approx 4.3 \times 10^{-4}$ wt.% and 0.077 at.%, respectively. The carrier concentration and mobility of the n-type layer were $\approx 4 \times 10^{17} \text{cm}^{-3}$, $\approx 100 \text{cm}^2/\text{V}\cdot\text{sec}$, respectively. For the growth of the p-type layers, various amounts of Al (0~2.21 at.%) were added in the Si melt. The electrodes of the p-type layer and substrate were Al-Si alloy and Au-Ni, respectively. Chips (0.25 x 0.25 mm² in size) were prepared from epitaxial wafers by careful cleaving, because in our blue LEDs the sample fabricated by sawing shows the same rapid degradation phenomenon reported elsewhere.¹⁾ The SiC blue LED lamps (resin mold) were fabricated using these diode chips. The hue of these LED lamps before aging was pure blue ($\lambda_p \approx 453 \text{nm}$).

Aging of blue LED lamps was performed up to

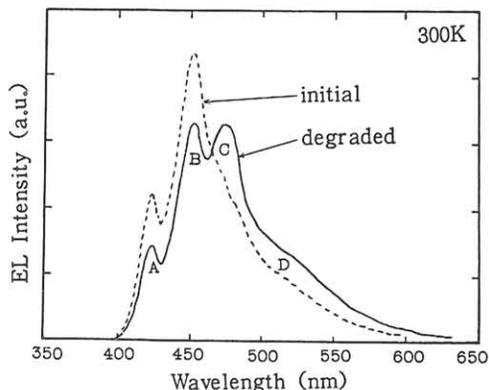


Figure 5 Electroluminescence spectra of a typical degraded SiC blue LED lamp (300K).

1000 hours at forward currents of 64 A/cm² (at R.T.). The hue of the emission light of some of these lamps changed from blue to greenish-blue by aging. The electroluminescence (EL) spectrum of a typical degraded LED lamp is shown in Figure 5 together with its initial spectrum. The chip having the p-type layer of higher concentration in the order of 10^{18}cm^{-3} was used for this lamp. As shown in Figure 5, the peak A ($\approx 423 \text{nm}$) and B ($\approx 453 \text{nm}$) due to free-exciton and localized centers, respectively, decrease, while the peak C ($\approx 474 \text{nm}$) due to the D-A pair²⁾ and hump D increase after the degradation. Thus, the EL spectrum of the degraded diode shifts to the region of longer wavelength.

As for the cause of degradation of pure blue LEDs, we have assumed several mechanisms. First, as a result of the diffusion of Al from the p-type layer into the main phosphor n-type layer, which may gradually occur over a long time, transitions between the N donor and Al acceptor (peak C shown in Figure 5) increase. Secondly, the reason for hump D to increase is assumed as follows. The intermediate states (3C-like?) of band-gaps lower than the 6H modification are generated by the development of stacking faults from the p-type layer having the extended lattice spacing of (006) planes. As another mechanism of the degradation, it is thought that defects may be generated near the p-n junction or may diffuse from the p-type layer into the main

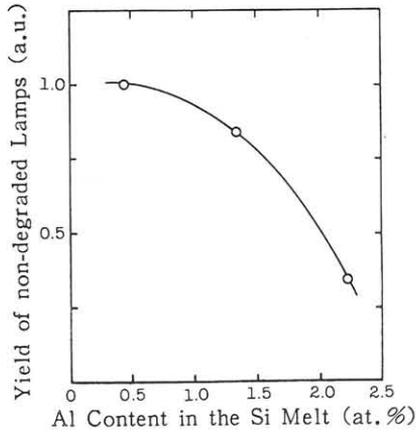


Figure 6 Yield of non-degraded SiC blue LED lamps after 230 hours of operation at 64 A/cm^2 (300K).

phosphor n-type layer. However, before and after the degradation of the LED lamps, the n-value (1.8~3.5) obtained by the forward I-V characteristics measurements scarcely changed.

The relation between the yield of non-degraded LED lamps and the amount of Al dopant added in the Si melt for the growth of the p-type layer was studied (Figure 6). The n-type layers of each LED were grown under the same growth conditions mentioned above. The yield of non-degraded LED lamps increases by decreasing the amount of Al dopant for the p-type layers.

The dependence of the EL intensity of the LEDs on the amount of Al is also shown in Figure 7. The EL intensity tends to increase by decreasing the amount of Al dopant for the p-type layer. We attribute this to the improvement of the crystallinity of the p-type layer by decreasing the amount of Al, and the increase of the injection efficiency of the carriers. And the light generated in the p-type layer may increase by decreasing the carrier concentration of the p-type layer. Furthermore, it is thought that light absorption by the p-type layer decreases due to decrease of Al content.

Therefore, it is certain that the acceptor concentration of the p-type layer relates to the degradation of the SiC blue LEDs.

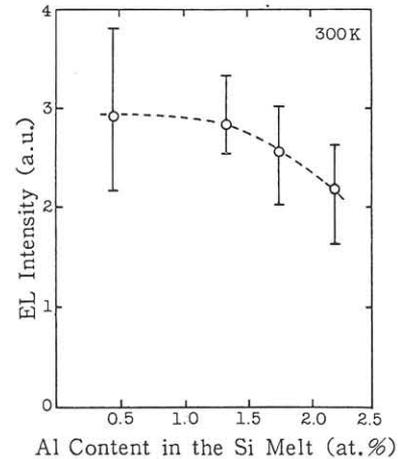


Figure 7 Electroluminescence intensity of the SiC blue LEDs (300K).

4. Conclusion

By evaluating of the p-type layer, we found that the excess acceptor (Al) concentration influenced the crystallinity of the p-type layer. Using a p-type layer of the carrier concentration under 10^{18} cm^{-3} , the degradation of SiC blue LED lamps was greatly reduced.

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