Fluorescent SiC and its application to white light-emitting diodes*

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Abstract: Fluorescent-SiC (f-SiC), which contains donor and acceptor impurities with optimum concentrations, has high conversion efficiency from NUV to visible light caused by donor-acceptor-pair (DAP) recombination. This material can be used as a substrate for a near UV light-emitting diode (LED) stack, and leads to monolithic white LED device with suitable spectral property for general lighting applications. In this paper, we describe basic technologies of the white LED, such as optical properties of f-SiC substrate, and epitaxial growth of NUV stack on the f-SiC substrate.

Key words: white LED; phosphor; SiC; donor-acceptor-pair; GaN; general lighting
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1. Introduction

White light-emitting diodes (LEDs) consisting of nitride-based blue LED chip and over-coated phosphor are very promising devices for general lighting applications. A combination of a blue-LED chip and yellow phosphor such as YAG:Ce[1] has been greatly advanced, and their luminous efficacy has already taken over that of fluorescence tubes. However, there are still some problems with conventional white LEDs; a low yield of the color quality, a low total flux, a low color rendering index (CRI), high-cost and a short lifetime. These problems are still serious obstacles for the expansion of white LED to enter into the general lighting applications.

Because the conventional white LED mentioned above emits blue light and yellow light, the CRI is very low mainly due to the lack of green and red color[1]. By adding the red phosphor to the white LED, the luminous efficacy steeply drops even though the CRI improves. Another white LED comprising a UV-LED and three-color phosphors have also been developed to improve the color rendering property[2]. However, this type of device has a low emission efficiency, because of the low efficiency of red phosphors. Thus, the color rendering index and emission efficiency are in a trade-off relationship. Figure 1 shows a relationship between the luminous efficacy and CRI of current white LEDs. The very high luminous efficacies have been realized only in the low CRI range, and there has been no demonstrations in required range (CRI $>$ 84, luminous efficacy $>$ 120 lm/W) for the general lighting applications. In addition, the combination of a single-spectrum LED and phosphors has an intrinsic instability of color against temperature change and divergence angle variation. Moreover, complicated assembly processes are required to set the phosphors uniformly on the LED chip.

Donor-and-acceptor (DA)-doped SiC is a promising candidate for phosphor material in white LEDs[3]. It has many advantages such as a uniform concentration of impurities, excellent thermal conductivity for high-power-operated LEDs and is a well-established substrate material for nitride epitaxial layers. This can be excited by nitride-based near ultraviolet (NUV) LEDs, which can be monolithically stacked on the SiC substrate. Moreover, two types of donor and acceptor pairs (DAPs), N–B and N–Al DAPs, in the 6H-SiC layers can cover almost all the visible spectral range. Therefore, white LEDs with DA-doped SiC are also expected to provide an excellent CRI. The key is how high the quantum efficiency of DAP recombination in the SiC epilayer is.

In this paper, we propose a new fluorescent material, a donor-and acceptor-doped 6H-SiC, and describe basic investigations into monolithic white LED.

2. Optical properties of donor-and-acceptor doped SiC

Figure 2 shows the photoluminescence spectra of nitrogen

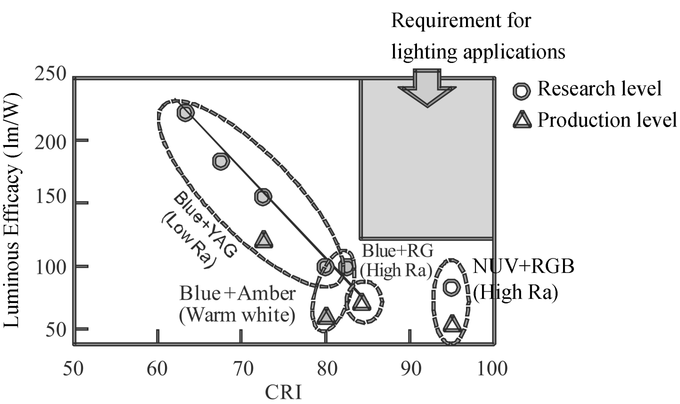

Fig. 1. Relationship between luminous efficacy and color rendering index (CRI) for current white LEDs.

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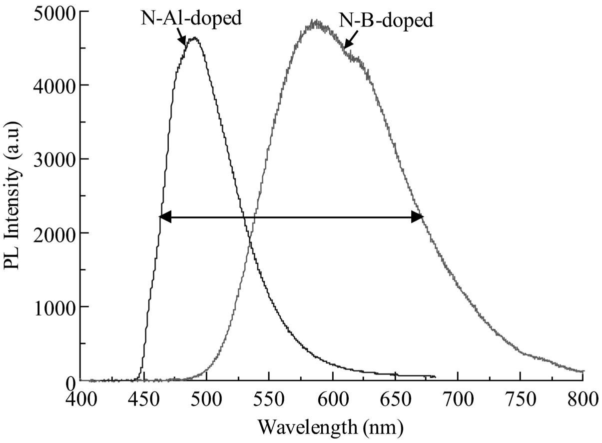

Fig. 2. Photoluminescence spectra of f-SiC epilayers.

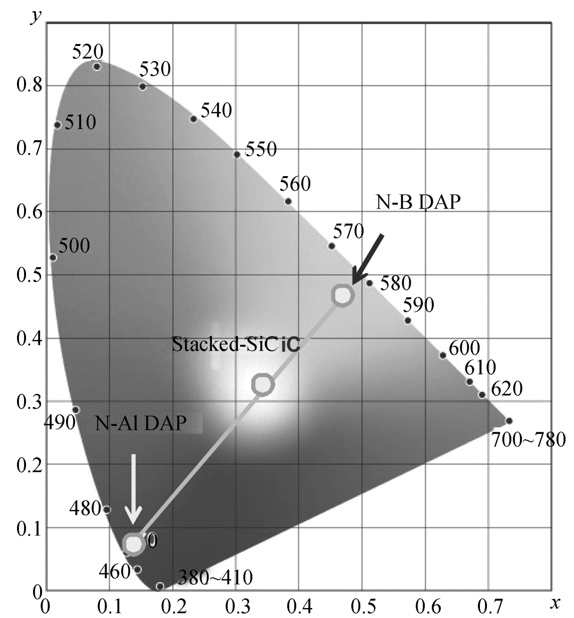

Fig. 3. CIE chromaticity coordinate plot of f-SiCs.

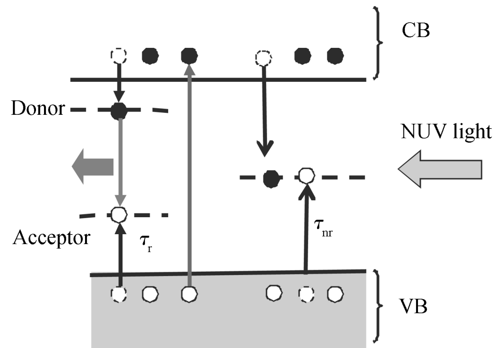

Fig. 4. Band diagram of f-SiC.

(N)-and-boron (B)-doped and nitrogen (N)-and-aluminum (Al)-doped 6H-SiC epilayers produced by a closed sublimation technique[4]. The pairs of the doped impurities correspond to donor and acceptor, respectively, and these broad light emissions are caused by donor–acceptor pair (DAP) recombinations. The N-and-B-doped SiC emits a yellow–orange light, while the N-and-Al-doped SiC emits blue–green light as in the figure. Therefore, to combine these two spectra, a full-range of visible spectrum similar to the sun-light spectrum can be produced. This means that the f-SiC epilayers doped with donor and acceptor impurities are promising phosphor materials for high color rendering index. The CIE Chromaticity coordinates of these two f-SiCs are also measured as shown in Fig. 3. The chromaticity coordinates of x and y in N-and-B-doped SiC are 0.486 and 0.465, respectively, and those in N-and-Al-doped SiC are 0.137 and 0.085, respectively. To mix these two epilayers, pure white color can be generated.

For high emission efficiency in f-SiC epilayers, high quality and appropriate doping concentration are indispensable. Figure 4 shows the energy band diagram of f-SiC. The NUV light excitation generates electrons in the conduction band and holes in the valence band. These carriers are partly trapped in the donor and acceptor states, and partly trapped in the defect states. The former carriers recombine with emission of photons, and the later carriers recombine without emission of photons. The internal quantum efficiency (IQE) should be determined by,

$$\text{IQE} = \frac{1}{1 + \tau_r/\tau_{nr}}, \quad (1)$$

where τ_r is radiative lifetime corresponding to trapping time of holes to acceptor states, and τ_{nr} is non-radiative lifetime corresponding to trapping time of holes to defect states. The radiative lifetime is dominated by the doping concentrations of donor and acceptor impurities, and the non-radiative lifetime is determined by the quality of the crystal. For a high-rate of radiative recombination, a higher donor concentration than acceptor concentration is preferred, because of the great difference between ionization energies. In addition, the crystalline quality of SiC is greatly varied among several crystal growth techniques. We examined the carrier lifetimes of several kinds of n-type 6H-SiC crystal. These carrier lifetimes correspond to non-radiative recombination times in the above definition, because of the lack of acceptor impurities. In addition, the carrier lifetimes greatly correlate with full-width at half maximums (FWHMs) of X-ray rocking curve (0006). The best quality SiC can be obtained by chemical vapor deposition (CVD) and fast sublimation growth process (FSGP)[5], where the carrier lifetime is about 2 μs. However, the SiC crystal grown by the popular growth method, physical vapor transport (PVT) method, has quite a short carrier lifetime of 20–100 ns. From the above equation, we can estimate IQEs for different kinds of f-SiC, which contains impurities N and B as a function of B concentration. Figure 5 shows the estimated IQEs with an assumption that N concentration is fixed at B concentration + 10^{18} cm^{-3}. While the low-quality f-SiC has low IQE even under the high doping concentration, the high quality f-SiC produced by FSGP exhibits very high IQE with relatively low doping concentration. To produce high performance f-SiC, appropriate growth technique such as the FSGP method must be necessary. The FSGP growth also satisfies the requirement of thickness of more than 200 μm which is necessary for absorption of NUV excitation, because it has very high growth rate of up to 1 mm/h.

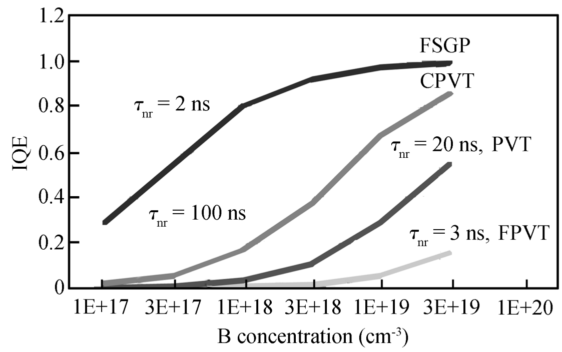

Fig. 5. IQEs as a function of B concentration for f-SiCs with a variation of non-radiative lifetime.

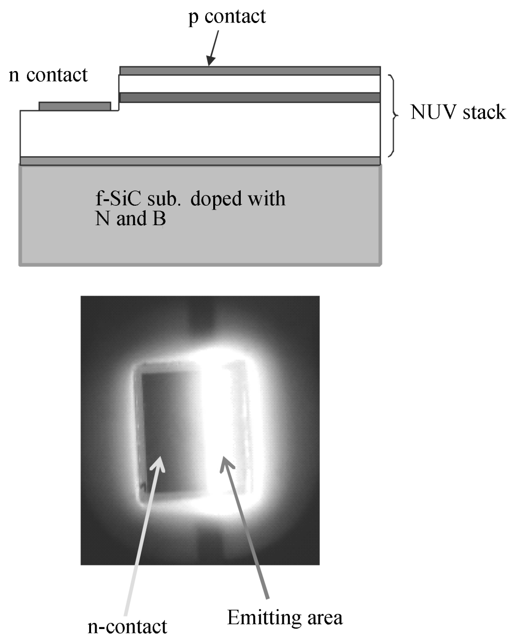

Fig. 6. Schematic diagram of warm-white LED and photograph sowing the operation.

3. Fabrication of warm-white LED

Although the development of the high-quality f-SiC has not been completed, a warm-white LED was fabricated for the first demonstration by using a single N-and-B doped PVT-grown f-SiC substrate. Figure 6 shows a schematic diagram and a photograph showing the operation of the warm-white LED. The size of the chip is 500×500 μm^2, and the emitting area is almost the half of the chip, because the anode and cathode electrodes are both formed on the surface of nitride stack. The nitride-based NUV stack having the peak wavelength of 385 nm was grown directly of the f-SiC substrate. The LED chip was mounted on ceramic base plate with flip-chip geometry. Warm-white emission with a peak wavelength of 590 nm was confirmed. This device is certainly proved to work with a combination of f-SiC substrate and nitride-based NUV stack, while the luminous efficacy is not sufficient at this stage. If the crystalline quality of both f-SiC and NUV stack would be advanced, the performance will surely be improved for practical use in general light applications.

4. Conclusion

In summary, we propose a new monolithic white LED using a combination of the f-SiC substrate and nitride-based near UV stack. Based on the recombination of donor acceptor pairs, the f-SiC works as a phosphor for the emission of visible light. Two types of f-SiC, where one is doped with N and B and another is doped with N and Al, can cover the whole visible spectral range. However, an optimization of the doping concentration and improvement of the crystalline quality are critical issues for high luminous efficacy in the white LEDs. The fast sublimation growth process is a promising growth method of f-SiC, because it enables us to grow high crystalline quality with density of non- radiative centers.

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