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# Photoluminescence and Raman spectroscopy characterization of boron- and nitrogen-doped 6H silicon carbide

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**Abstract.** Nitrogen-boron doped 6H-SiC epilayers grown on low off-axis 6H-SiC substrates have been characterized by photoluminescence and Raman spectroscopy. The photoluminescence results show that a doping larger than $10^{18}$ cm$^{-3}$ is favorable to observe the luminescence and addition of nitrogen leads to an increased luminescence. A dopant concentration difference larger than $4\text{x}10^{18}$ cm$^{-3}$ is proposed to achieve intense photoluminescence. Raman spectroscopy further confirmed the doping type and concentrations for the samples. The results indicate that N-B doped SiC can serve as a good wavelength converter in white LEDs applications.

## Introduction

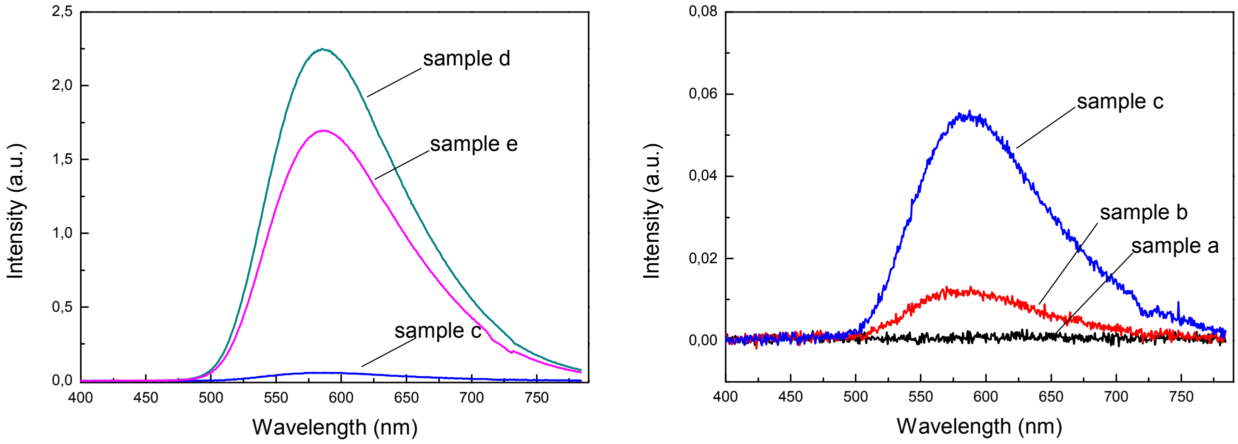
To date, white light-emitting diodes (LEDs) are the most promising candidates for the illumination market to replace conventional incandescent lamps as energy-saving and environmental friendly light sources. One common method to realize white LEDs is using a UV or blue LED whose light is partially or fully used to optically excite wavelength converters. Therefore, high-efficiency wavelength converters with a high color rendering index (CRI) value and long lifetime are indispensable. Nitrogen (N) and boron (B) doped 6H-silicon carbide (SiC) has been proven as a highly efficient wavelength converter [1]. Combined donor-acceptor-pair (DAP) band luminescence from N-B and nitrogen-aluminium (N-Al) doped 6H-SiC can cover most of the visible spectral range and thus white light with CRI larger than 90 could be produced based on the simulated results [2]. Furthermore, SiC is a well established substrate material for nitride growth and has excellent thermal conductivity.

## Experiments and Results

To investigate the route to optimized dopant concentrations of N and B, five samples with various N and B concentrations were studied. The epilayers were grown on 6H-SiC (0001) substrates having 1.4 degree off-orientation in the $[11\bar{2}0]$ direction by the fast sublimation growth process [3] at a

**Table 1.** Dopant concentrations and normalized PL peak intensities of the samples

| Sample | B concentration [cm$^{-3}$] | N concentration [cm$^{-3}$] | Doping type | PL peak intensity [Normalized to sample d] |
|---|---|---|---|---|
| a | $8.0 \times 10^{18}$ | $4.0 \times 10^{16}$ | P | 0.0 % |
| b | $6.9 \times 10^{18}$ | $3.2 \times 10^{18}$ | P | 6.6 % |
| c | $6.9 \times 10^{18}$ | $6.0 \times 10^{18}$ | P | 8.3 % |
| d | $4.4 \times 10^{18}$ | $9.0 \times 10^{18}$ | N | 100 % |
| e | $5.2 \times 10^{18}$ | $9.2 \times 10^{18}$ | N | 77.1 % |



(a) (b)

**Fig. 1.** Measured PL spectra of B-N doped 6H-SiC samples: (a) Comparison of samples a, b, and c; (b) Comparison of samples c, d, and e.

temperature of 1725 °C. The growth process is driven by a temperature gradient created between the source, in the form of a polycrystalline SiC plate, and the substrate. The B was introduced into the epilayers by co-doping from the source and N incorporation was controlled by adjusting $N_2$ gas pressure during the growth. The atomic dopant concentrations measured by secondary ion mass spectrometry (SIMS) are listed in Table 1, where the N concentration of sample a was close to the background doping level and therefore might not be accurate.

Photoluminescence (PL) measurements were performed by using an Olympus reflected fluorescence system microscope, a 377 nm diode laser as excitation source (focused by a 20X objective), and an Instrument System CAS 140B spectrometer. The integration time was 10 seconds with excitation power density of 0.02 W/cm$^2$, and the measurements were performed at room temperature. The measured PL spectra are shown in Fig. 1, and the integrated PL peak intensities were normalized to the strongest sample (d) and are listed in Table 1. One can see that the high-level p-type sample (a) exhibits extremely low DAP emission intensity, while the low-level p-type samples (b, c) have relatively stronger DAP emissions but still at a low level. Intense DAP emission was observed in n-type samples (d, e), while the strongest DAP emission occurred in sample d, which has the largest concentration difference of $4.6 \times 10^{18}$ cm$^{-3}$. Despite the intensity differences, all the DAP emission spectra show the same peak wavelength at 587 nm and the same full width at half maximum (FWHM) of 120 nm. This result is expected because the spectrum shape of the DAP emission is usually determined by the Coulomb interaction and phonon coupling rather than by the carrier populations [4, 5]. Due to the same dopant materials and experimental conditions, the same value of FWHM was obtained. From the above results, it is clear that both the doping type and the concentration difference affect the DAP emission intensity but do not introduce a change in the peak wavelength and FWHM.

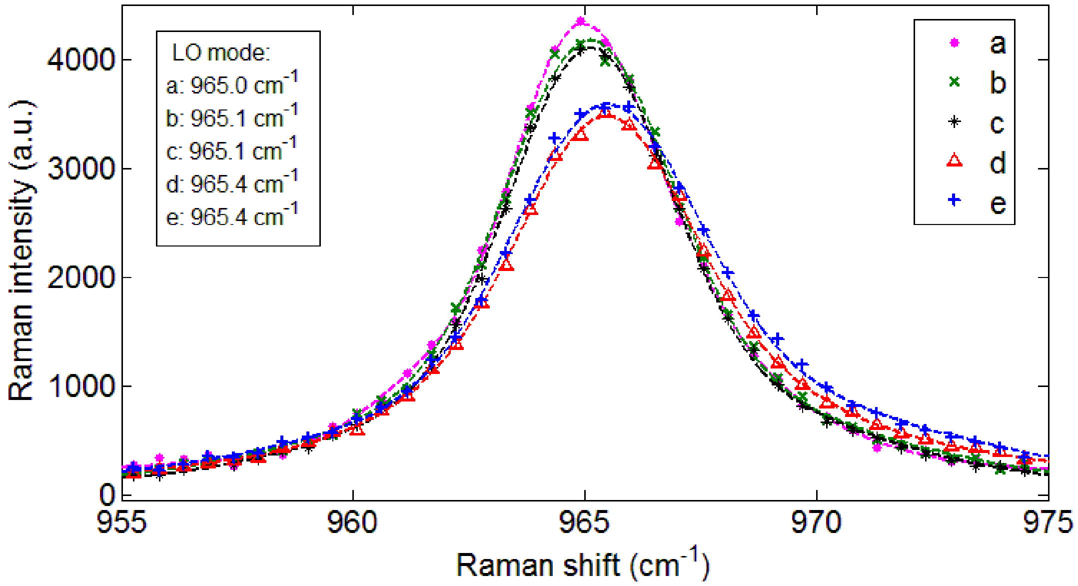


**Fig. 2.** LO mode in Raman spectra (inset: positions of LO modes of the SiC samples with different dopant concentrations; the peak height decreases in the order of a, b, c, e, d).

Raman scattering spectra of the 6H-SiC samples were acquired in a backscattering configuration using the 514.5 nm line from an Ar ion laser (5 mW). Longitudinal optical (LO) modes of the Raman spectra are shown in Fig. 2, and the mechanisms of the observed Raman shifts in p- and n-type samples are different. The LO mode is much more sensitive to the free electrons than to the free holes due to the large effective mass differences [6].

In p-type samples, very few acceptor states are ionized due to the large ionization energy, and the Raman shift is mainly attributed to the atomic size effect [7]. The B atom is considered to occupy a Si lattice position in SiC. The inter-atomic distance of a Si-C bond is longer than that of a B-C bond due to the smaller atomic radius of B. The biaxial tensile stress will be released which results in a decrease of the phonon oscillation frequency. So the LO mode shifts toward smaller wavenumbers with higher B concentrations.

In n-type samples, the predominant mechanism causing the Raman shift of the LO mode is the coupling interaction between LO phonons and overdamped plasmons, and the LO mode is then redefined as a longitudinal optical phonon-plasmon coupled (LOPC) mode. Although no obvious peak shift has been observed between sample d and e due to the relatively small concentration difference, the peak intensity of the LOPC mode decreases as expected when the N and B concentration difference increases from sample e to d. Furthermore, one can see from Fig. 2 that the LOPC modes of n-type samples occur at significantly higher wavenumbers than the p-type ones.

## Discussion and Conclusion

In N-B doped SiC, the acceptor states are almost fully occupied by photo-excited holes due to the large ionization energy, so the hole density at the acceptor states under the excitation condition could be assumed to be the same as the B doping concentration in the sample. On the other hand, the electron density at the donor states under the excitation condition is given by the product of N doping concentration and the electron occupancy probability at the donor states due to the small ionization energy of the donor states. Meanwhile, the electron occupancy probability is proportional to the electron quasi-Fermi level under the excitation condition. So the DAP recombination rate is proportional to the product of the B concentration, N concentration and electron occupancy probability under the excitation condition. Under the same excitation condition, the electron quasi-Fermi level is at a higher energy level in the n-type samples than in the p-type ones, and a larger N and B concentration difference leads to a higher electron quasi-Fermi level. As a result, the electron occupancy probability on donor states increases and so does the DAP recombination rate. This was confirmed by the SIMS and PL measurements results in this work. The detailed interpretation was illustrated in [8].

In conclusion, five samples with various B and N doping concentrations were investigated by photoluminescence and Raman spectroscopy. It is found that n-type doping with both B and N concentrations larger than $10^{18}$ cm$^{-3}$ is required to achieve intense DAP luminescence, and the concentration difference of the n-type sample needs to be larger than 4 x $10^{18}$ cm$^{-3}$ as concluded from this study. Doping type and concentrations of the samples were confirmed by the peak shift and intensity change of the LOPC mode in Raman spectra. With adjustment of doping concentrations, intense DAP luminescence peaked at 587 nm with a broad FWHM of 120 nm was obtained. Both peak wavelength and FWHM did not change with varying doping concentration at this doping level, which makes SiC a good candidate for a wavelength converter in white LEDs.

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