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Abstract
As an alternative to the conventional phosphors in white LEDs, a donor and acceptor co-doped fluorescent 6H-SiC can be used as an ultraviolet-to-visible light converter without any need of rare-earth metals. From experimental data we provide an explanation to how light can be obtained at room temperature by a balance of the donors and acceptors. A steady-state recombination rate model is used to demonstrate that the luminescence in fluorescent SiC can be enhanced by controlling the donor and acceptor doping levels. A doping criterion for optimization of this luminescence is thus proposed.

(Some figures may appear in colour only in the online journal)

1. Introduction

White light-emitting diodes (LEDs) are anticipated to replace the traditional incandescent light bulbs and fluorescent lamps in the near future due to their high efficacy and large energy saving in illumination [1, 2]. High-efficiency III-nitride LEDs are now commercially available with efficacies surpassing those of the conventional light sources. They have rapidly evolved in white LED illumination. For generation of white light emission, three different approaches are developed. These are a blue LED with yellow phosphors, an ultraviolet (UV) LED with red, green and blue phosphors, and a device that combines red, green and blue LEDs [2]. The advantage of the blue LED with yellow phosphors is its higher efficacy compared with the other two approaches. Therefore, today's white LEDs are commonly made by a combination of III-nitride-based blue LEDs and a coating of yellow phosphors such as cerium-doped yttrium aluminium garnets [1], which are becoming less available since

they contain rare-earth metals. However, the main problem with such white LEDs is that the colour temperature is very high and the colour-rendering index is very low. A real white LED should cover the full spectral range from blue to red.

Recently, an alternative approach has been suggested to realize a true white LED by an all semiconductor integration of a near UV-LED stack on donor and acceptor co-doped SiC substrates [3, 4]. Such donor and acceptor doped substrates absorb the near UV light from the GaN-based stack and re-emit visible light via donor–acceptor pair (DAP) recombinations. Therefore, this wide bandgap semiconductor can be used as a fluorescent medium for white LEDs instead of conventional phosphors. Two successive fluorescent SiC (f-SiC) layers, in which one is doped by nitrogen (N) and aluminium (Al) and another one is doped by N and boron (B), are used as a substrate for the growth of the III-nitride-based near UV-LED stack. Boron is a deeper acceptor than aluminium. The N

1

J. Phys. D: Appl. Phys. **45** (2012) 235107

J W Sun *et al*

and B co-doped f-SiC emits yellow-orange light while the N and Al co-doped f-SiC emits blue-green light. It has been demonstrated that the CIE chromaticity coordinates of *x* and *y* in N- and B-doped SiC are 0.486 and 0.465 while those in the N- and Al-doped SiC are 0.137 and 0.085, respectively [3]. Therefore, by a combination of these two spectra, a full range of visible spectra similar to the sunlight spectrum can be realized [3]. Moreover, it has been demonstrated that a nitride-based NUV LED stack having a peak wavelength of 385 nm is grown directly on the f-SiC material to make the device [3]. This opens up the way to develop white LEDs with high colour-rendering index but without any need of rare-earth-doped phosphors.

Although SiC is an indirect bandgap semiconductor, it has been demonstrated that SiC can be used as a light-emitting material. Early blue LEDs were produced by 6H-SiC p–n homojunctions [5]. The blue light comes from the DAP recombination between N donors and Al acceptors in the p–n homojunctions. Although such devices exhibited only a power efficiency of ∼0.05–0.07% (25–35 μW for a forward current of 20 mA at 3.2 V) [5], they demonstrated that the suggested approach to get blue light from the recombination between N donors and Al acceptors should be realistic. In addition, compared with the electroluminescence from 6H-SiC p–n homojunctions, this approach by using the near UV light excitation from the nitride stack enables one to distribute the carriers of a large volume instead of a thin interface of p–n junction at which the injection carrier concentration is very high and non-radiative recombination probability may also be high due to the interface defects. More importantly, it has recently been found that N and B co-doped SiC exhibited a high-efficient orange-yellow light emission at room temperature [3, 4]. Furthermore, a prototype of such a warm-white LED made by the integration of a nitride-based near UV-LED stack on the N- and B-doped f-SiC substrate has been successfully demonstrated in [3]. We believe that if such DAP emissions in the f-SiC layers can be controlled by proper doping levels, the integration of the nitride UV-LED stack on the f-SiC substrates can be anticipated to achieve white light emission with a high colour-rendering index and stability/reproducibility of colour quality. This would provide an alternative way to achieve real white light without the use of rare-earth doped phosphors.

To realize such semiconductor white LEDs, the key issue is to resolve how the emission efficiency in f-SiC layers can be improved by controlling the doping content. In previous works [4, 6], we reported the observation of room temperature luminescence in N and B co-doped f-SiC. However, it is still unknown as to how the doping levels affect the emission efficiency and what is the doping criterion for optimization of luminescence.

In this work, we focus on the impact of doping levels on the luminescence intensity and quantum efficiency in f-SiC grown by the fast sublimation growth process (FSGP) [7]. N and B are used as donor and acceptor species, as an example, to demonstrate how luminescence can be controlled by a balance of donor and acceptor doping levels. As a consequence, a doping criterion for optimization of this luminescence is proposed.

2. Experimental

Thick 6H-SiC layers (50–80 μm) were grown on 1.4° off-axis 6H-SiC (0 0 0 1) substrates by the FSGP. The growth was performed in a high-purity graphite crucible at 1750 °C for one hour. N doping was controlled by adjusting the N_2 gas growth pressure. B doping was achieved using a polycrystalline SiC source containing different boron concentrations. To determine N and B doping concentrations in the epilayers, secondary ion mass spectroscopy (SIMS) measurements were performed by a modified Cameca IMS 4f equipment with an O^{2+} ion source. Photoluminescence (PL) spectra were collected at room temperature using a frequency-doubled Ar^+-ion laser for excitation operated at $\lambda = 244$ nm with a high excitation power density of ∼60 W cm^{-2}. A Jobin Yvon-Horiba Triax 550 spectrometer, fitted with a 600 grooves mm^{-1} grating and a cooled charge coupled device camera, completed the setup. In a previous work [4], an internal quantum efficiency (IQE) value of 95% was estimated by a comparison of integrated photon counts in GaN at 10 K with photon counts in f-SiC at 250 K, in which the IQE of GaN at 10 K was assumed to be 100%. In this work, all IQE values are obtained from the measurements of directly measured external quantum efficiencies (EQEs) by a system with an integrated sphere, an excitation source and a calibrated monochromatic meter combined with a photomultiplier. And we obtained IQE values at a high excitation density of 27 W cm^{-2}. The excitation source, which is a 355 nm-frequency-tripled YAG CW laser with a beam diameter of 1 mm, was introduced into the integrated sphere and was led to the f-SiC samples. A ratio of PL photon number to absorbed excitation photon number provided the EQEs, and they were divided by a theoretical light extraction efficiency to give IQEs. A light extraction value of 6% from the layers was used for determining the IQE.

3. Results and discussion

Table 1 shows the growth condition and SIMS results for three series of samples (labelled A, B, C series) grown by using the source with B concentrations of 5×10^{17}, 1×10^{18} and 4×10^{18} cm^{-3}, respectively. At room temperature, these N and B co-doped samples exhibit very efficient visible luminescence. Figure 1 shows, for instance, the picture of yellowish emission from an N and B co-doped 6H-SiC epilayer under the excitation of 375 nm from two commercial UV nitride LEDs. This simple excitation configuration is essentially identical to the designed white LED structure. The only difference is that these two UV LEDs are separated for excitation purpose and far away from the f-SiC layers rather than being as a direct integration of a nitride UV-LED stack on f-SiC. Clearly, the fluorescent SiC has efficient emissions at room temperature even under such weak excitation of UV LEDs.

PL spectra were collected under a saturated excitation power density (∼60 W cm^{-2}) to make most of the donors and acceptors essentially non-ionized. Figure 2(*a*) shows the room temperature PL spectra for the three series of samples grown with sources containing B concentrations of 5×10^{17}, 1×10^{18} and 4×10^{18} cm^{-3}, respectively. As seen in table 1, for each

Table 1. Growth conditions and SIMS results of nitrogen and boron concentrations in three series of 6H-SiC epilayers (A, B and C series).

Sample	A_1	A_2	A_3	B_1	B_2	C_1	C_2	C_3
N_2 pressure (mbar)	1×10^{-5}	1×10^{-2}	1×10^{-1}	1×10^{-2}	5×10^{-1}	1×10^{-2}	1×10^{-1}	5×10^{-1}
[B] in the source (cm^{-3})		5×10^{17}		1×10^{18}			4×10^{18}	
[B] in the epilayer (cm^{-3})	3×10^{17}	3×10^{17}	3×10^{17}	6×10^{17}	6×10^{17}	2×10^{18}	2×10^{18}	2.7×10^{18}
[N] in the epilayer (cm^{-3})	4×10^{17}	8×10^{17}	3×10^{18}	3×10^{18}	6×10^{18}	1×10^{18}	2.5×10^{18}	4×10^{18}
Conductive type	n	n	n	n	n	p	n	n
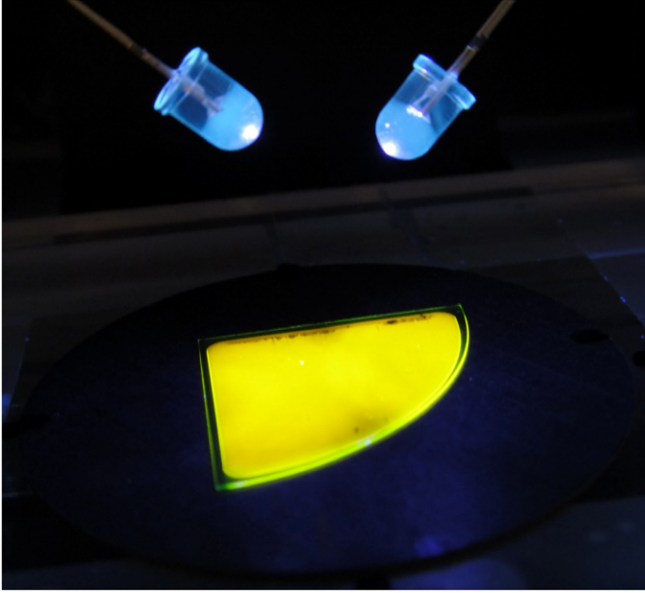
Figure 1. A picture of efficient yellowish emission from nitrogen and boron co-doped 6H-SiC under the excitation of 375 nm from two commercial UV LEDs. The sample was grown on one quarter of a two inch 6H-SiC wafer.

of the series, the source used for growth contains an almost constant B concentration but the N_2 growth pressure is changed to adjust the N doping. All samples give a broad emission band centred at ~584 nm (2.12 eV), which has already been attributed to the N–B DAP emission in 6H-SiC [8, 9]. The photon energy from the DAP transition is given by

$$E_{\text{DAP}} = E_{\text{G}} - E_{\text{D}} - E_{\text{A}} + E_{\text{C}}, \tag{1}$$

where E_{G}, E_{D} and E_{A} are the band gap (3.0 eV for 6H-SiC), donor, and acceptor binding energies, respectively. The average Coulomb energy $E_{\text{C}} = e^2/4\pi\varepsilon_0\varepsilon R$ can be roughly estimated by letting the pair separation $R = (3/4\pi N_{\text{D}})^{1/3}$, with donor concentration $N_{\text{D}} \sim 10^{18}$ cm^{-3}, giving $E_{\text{C}} \sim 0.024$ eV. The N binding energies were determined to be 0.081 eV for hexagonal sites, and 0.138 and 0.142 eV for cubic sites in 6H-SiC from the infrared absorption measurements [10]. Since the DAP emission in SiC is usually dominated by its phonon replicas (mainly longitudinal optical (LO) phonon line at the maximum of the DAP emission band) [8], we also take into account the energy of the LO phonon $E_{\text{LO}} = 104$ meV. Assuming that N binding energy is ~0.1 eV, we find the maximum of the DAP emission band at $E_{\text{DAP}} - E_{\text{LO}} = 3.0 - 0.1 - 0.7 + 0.024 - 0.104 = 2.12$ eV, which gives the boron binding energy ~ 0.7 eV. Although both the shallow B
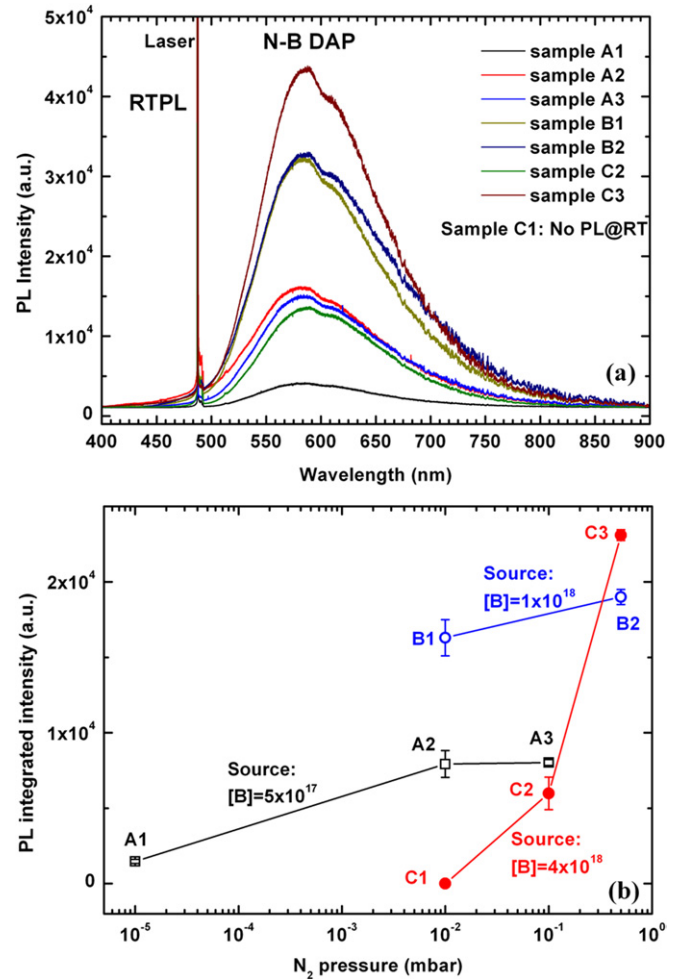
Figure 2. (*a*) Room temperature PL spectra of three series of samples listed in table 1. (*b*) PL integrated intensity as a function of N_2 gas growth pressure for three series of samples grown with a source containing boron concentrations of 5×10^{17}, 1×10^{18}, 4×10^{18} cm^{-3}, respectively.

level (0.3, 0.35 eV) [9, 10] and deep B level (0.58, 0.7, 0.698–0.723 eV) [8–10] have been largely reported by either electrical or optical measurements, there is no observation of DAP luminescence coming from the shallow B level and all the DAP emissions demonstrate that the B acceptor has a similar binding energy of ~0.7 eV regardless of the polytypes [8, 9, 11].

From figure 2(*b*), it is seen that the PL intensity depends not only on the B concentration in the source but also the N_2 gas growth pressure. This indicates that the PL intensity is related to both N and B doping concentrations in the epilayers. Table 1 shows the SIMS results of N and B concentrations in three series of 6H-SiC. Evidently, the increase in N_2
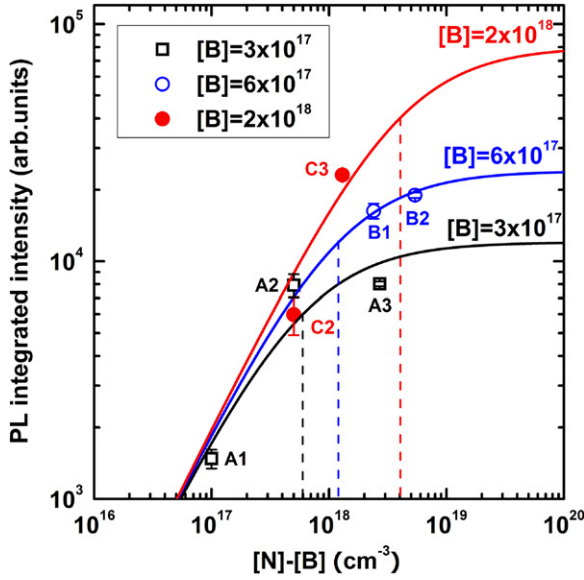
Figure 3. Room temperature PL integrated intensity as a function of the difference of nitrogen and boron concentrations ([N] − [B]) in the epilayers for three series of samples listed in table 1. Solid lines are the fitting curves according to equation (4) with boron concentrations of 3×10^{17}, 6×10^{17}, 2×10^{18} cm^{-3}, respectively. Dashed lines represent the case of [N] − [B] = 2[B] in which the equilibrium Fermi level falls at the donor level.

gas pressure results in the increase in nitrogen concentration (denoted by [N]) in the epilayers. For each of the series, the boron concentration (denoted by [B]) in the epilayers is almost constant, which is around 50–60% of the boron concentration in the source. From the combination of PL and SIMS results, it is evident that the PL intensity is largely dependent on the nitrogen and boron doping concentrations. It should be noted that no visible PL can be observed at room temperature in the samples which have a higher boron concentration than nitrogen, namely, p-type, see sample C_1 for instance. This can be explained as follows. Since the nitrogen donor is much shallower than the boron acceptor; the Bohr radius of nitrogen is much larger than that of boron. Thus, for a given DAP, the radiative recombination rate is determined by the Bohr radius of nitrogen [12]. Assuming that all donors and acceptors become neutral at high excitation, the PL intensity can then be explained in terms of the number of contributing sites and overlap of the electron and hole wave functions [12]. Therefore, there are more radiative recombination centres in the case when the N concentration is higher than the B concentration. There could still be some radiative recombination centres in sample C_1, while the non-radiative recombinations dominate.

To understand the influence of nitrogen and boron doping on the luminescence of f-SiC, we plot the PL intensities of the three series of samples as a function of the difference of nitrogen and boron concentrations (hereafter denoted as [N] − [B]), see figure 3. For samples A_1 to A_3 with a constant boron concentration [B] = 3×10^{17} cm^{-3}, the PL intensity first increases when [N] − [B] increases to 5×10^{17} cm^{-3}. However, a further increase in [N] − [B] to 2.7×10^{18} cm^{-3}, which is almost one order of magnitude higher than the boron

concentration [B], does not increase the luminescence intensity (sample A_3). In samples B_1 and B_2 with boron doping of 6×10^{17} cm^{-3}, the value of [N] − [B] increases from 2.4×10^{18} to 5.4×10^{18} cm^{-3} while PL intensities from these samples have no significant difference. However, the intensities are twice as high as those collected on the A-series of samples having a lower boron concentration. Note that in samples B_1 and B_2, the value of [N] − [B] is always higher than [B]. Finally, in samples C_2 and C_3 (with [B] = 2×10^{18} cm^{-3}), it is clear that the increase in [N] − [B] from 5×10^{17} to 1.3×10^{18} cm^{-3} results in a significant increase in PL intensity. From these three series of samples, we can tentatively conclude that the increase in [N] − [B] can enhance the PL intensity in the case of [N] − [B] < [B] while the PL intensity becomes saturated when [N] − [B] > [B].

To explain the relationship between the PL intensity and the difference of the nitrogen and boron doping concentrations, we consider the steady-state recombination rate via the DAP transition using the model of Aukerman and Millea [13]. In this model, only one donor and one acceptor level are considered. It is assumed that only one transition occurs between electrons captured on donors and holes captured on acceptors and there are no other non-radiative levels in the band gap. Assuming that donors and acceptors become essentially non-ionized under the large steady-state excitation, the net recombination rate U via the DAP transition is given by [13]

$$U = N_m t \left(1 + \frac{t + n_1 C_n + p_1 C_p}{n C_n + p C_p} \right)^{-1}, \quad (2)$$

where N_m is the concentration of the minority impurity, t is the transition probability of the DAP recombination, n and p are non-equilibrium carriers, $n_1 = N_C e^{(-E_D)/kT}$ ($p_1 = N_V e^{(-E_A)/kT}$) is the electron (hole) concentration when the Fermi level falls at the donor (acceptor) energy level E_D (E_A), C_n (C_p) is the capture probability of electrons (holes) by ionized D$^+$A$^-$ pairs. By applying this model for n-type SiC, we can get $n_1 \gg p_1$ due to $E_D \ll E_A$. The electron capture probability is given by $C_n = \sigma_n v_n$ with definitions of electron capture cross section σ_n and thermal velocity v_n. The capture cross section can be estimated by the Bohr radius α, giving $\sigma \sim \pi \alpha^2$ [14]. For a rough estimation, one can expect $(\alpha_D^2/\alpha_A^2) \approx (E_A^2/E_D^2) \gg 1$ [14], where α_D (α_A) is the donor (acceptor) Bohr radius. This leads to a reasonable conclusion that $C_n \gg C_p$ in our case of n-type SiC ($n > p$), hence, $n_1 C_n \gg p_1 C_p$ and $n C_n \gg p C_p$. If $t < n_1 C_n$ is assumed, equation (2) reduces to
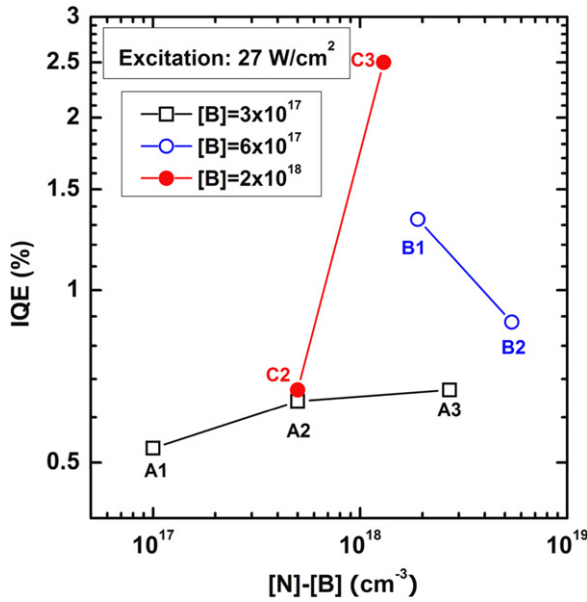
$$U = N_m t \left(1 + \frac{n_1}{n} \right)^{-1}. \quad (3)$$

If the non-equilibrium electron concentration n can be roughly estimated by the equilibrium electron concentration

$$n_0 = \frac{(N_D - N_A) N_C}{N_A g_D} e^{\frac{-E_D}{kT}},$$

equation (3) becomes

$$U = N_A t \left(1 + \frac{N_A g_D}{N_D - N_A} \right)^{-1}, \quad (4)$$

Figure 4. IQE as a function of the difference of nitrogen and boron doping concentrations ([N] − [B]) for three series of samples with boron doping concentrations of 3×10^{17}, 6×10^{17}, 2×10^{18} cm^{-3}, respectively.

where N_D and N_A are the donor and acceptor concentrations, N_C is the effective conduction-band state density, g_D is the donor degeneracy factor and we use $g_D = 2$ in SiC.

From equation (4), it is seen that the DAP radiative recombination rate in n-type f-SiC will saturate at a constant of $N_A t$ when $(N_D - N_A) \gg 2N_A$ while it significantly increases with the increase in $(N_D - N_A)$ in the case of $(N_D - N_A) < 2N_A$. Using equation (4) and letting $N_A = 3 \times 10^{17}$, 6×10^{17} and 2×10^{18} cm^{-3}, respectively, we can fit all three series of samples using a constant value of the parameter t and this explains very well why the PL intensity increases with the increase in [N]−[B] when [N]−[B] < 2[B] and the saturation occurs gradually in the case of [N] − [B] > 2[B]. Note that the equation $N_D - N_A = 2N_A$, namely $n_0 = n_1$, means the equilibrium Fermi level falls at the donor energy level E_D. This suggests that the PL intensity in f-SiC significantly increases with an increase in the equilibrium Fermi level E_F^0 until $E_F^0 = E_D$ which is due to the increase in $(N_D - N_A)$ while the PL intensity gradually saturates when $E_F^0 > E_D$. It should be noted that this model does not consider any non-radiative recombination centres. Actually, the higher doping may create some other defects at which carriers may recombine non-radiatively. We have observed that the PL intensity significantly drops in some samples in which the N concentration is much higher than the B concentration. This is because in the case of $(N_D - N_A) \gg 2N_A$, the radiative recombination rate is saturated while the crystal quality is degenerated due to the higher doping, and more non-radiative defects are thus created so that the luminescence is quenched.

To consider the contribution of the non-radiative defects, we plot the IQE as a function of the value of [N]−[B] in figure 4. In order to compare with PL data, we also use high excitation (27 W cm^{-2}) for the measurements. As seen in figure 4, the IQE shows almost the same trend with increasing [N] − [B] as

that of the PL intensity except for sample B_2. It is known that

$$\text{IQE} = \frac{1}{1 + (\tau_R / \tau_{NR})}, \qquad (5)$$

in which τ_R and τ_{NR} are the radiative and non-radiative lifetimes, respectively. From a comparison of figures 3 and 4, it is clear that the increase in the IQE (or PL intensity) is due to the increase in the DAP radiative recombination rate (thus a decrease in τ_R) when the value of [N] − [B] is increased. However, in the case of $(N_D - N_A) \gg 2N_A$, the radiative recombination rate gradually saturates, and a further increase in the doping results in more non-radiative recombination channels and thus τ_{NR} plays a more important role in the recombination, as indicated by the drop in IQE in sample B_2 having a higher doping. Although the performance of this proof-of-concept material is modest, with IQE efficiencies of 2.5% at a high excitation density of 27 W cm^{-2}, this work shows the potential path for higher efficiency white LEDs by a proper route of doping. To further increase the efficiencies, both the balance between donor and acceptor doping concentrations and control of crystal quality require further investigations.

4. Conclusion

In conclusion, we demonstrate that an efficient luminescence can be obtained at room temperature in nitrogen and boron co-doped 6H-SiC. It is found that the PL intensity increases with the increase in [N] − [B] and gradually saturates when [N] − [B] > 2[B] while the PL intensity will drop due to the non-radiative defects in the case of [N] − [B] $\gg$ 2[B]. Thus, the route to optimize the luminescence is that the B concentration should be higher than 2×10^{18} cm^{-3} and we suggest that the criterion of N and B doping is [N] − [B] $\sim$ 2[B]. The IQE observations indicate that the efficiency may be influenced by non-radiative recombination at an increased doping concentration.

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