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Double $D$-centers related donor-acceptor-pairs emission in fluorescent silicon carbide

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Abstract: A new boron-induced deeper acceptor level ($D^*$-center) different from the $D$-center in nitrogen-boron co-doped 6H fluorescent silicon carbide (f-SiC) is revealed by measuring the temperature-dependent photoluminescence (PL). The $D^*$-center is correlated to the dominate donor-acceptor-pair (DAP) recombination at low temperature ranges in f-SiC with a PL peak around 1.90 eV. A hole-trap with an energy level that lies between the $D^*$-center and the $D$-center is predicted to exist in the f-SiC samples. A two-step thermal ionization involving the hole-trap is proposed to explain the evolution of both $D^*$-center and $D$-center related temperature-dependent DAP recombination.

1. Introduction

White light-emitting diodes (LEDs) are very promising devices to be massively applied to lighting and display industries. Ideally, a white LED is expected to be robust and compact with high luminescence efficacy. At present, the most widespread commercial white LED device consists of a nitride-based blue-LED chip over-coated by a yellow phosphor layer such as cerium-doped yttrium aluminum garnet, i.e., (YAG):Ce [1]. However, the issue of yellow phosphor degradation can give rise to poor color rendering index (CRI) and low luminescence efficacy [2–5]. Besides, the assembly process for uniformly covering blue-LED chip with yellow phosphor layer is very complicated [2, 3]. In addition, the cost and supply issues coming along with the inclusion of rare earth (RE) elements (e.g., cerium) in phosphors also need to be concerned [4]. On the other hand, it has been demonstrated [2] that the donor and acceptor co-doped SiC, i.e., fluorescent silicon carbide (f-SiC), can be implemented as a new type phosphor in white LED which contains no RE elements [5]. To be specific, the nitrogen (N) and boron (B) co-doped f-SiC has been proposed as a passive medium of light-emission by optical pumping where it can emit broadband and strong orange-yellow light. Whereas, compared to the interband transition in direct band gap materials, SiC as an indirect band gap material has very low rate of donor-acceptor-pair (DAP) recombination. Hence for the light-emission medium based on SiC it is crucial to have a large volume medium with high density of DAP in order to enhance radiative emission via DAP recombination. Fortunately, by applying the Fast Sublimation Growth Process (FSGP) for f-SiC growth [6], the heavy N-B co-doping above $10^{18}$ cm$^{-3}$ and the growth rate up to 200 µm · h$^{-1}$ [7] have been achieved. Furthermore, f-SiC can be excited by nitride-based near-ultraviolet (NUV) LEDs where f-SiC is a well-established platform for the growth of nitride-based NUV LEDs. By further integrating the nitrogen-aluminum co-doped SiC which contributes to blue-greenish emission [3] with the N-B co-doped f-SiC, the white light emission with high CRI can be achieved via optically pumping the SiC bilayer by the nitride-based NUV LED [4, 5].

It has been widely accepted that the broadband emission with $\lambda_{\text{peak}} \approx 580$ nm ($\sim$2.14 eV) in B-N co-doped 6H-SiC at room temperature (RT) is from the phonon replicas of DAP recombination [8], where the full width at half maximum of the emission spectrum can range from 110 nm [2] to 120 nm [9]. The three shallow donor levels on different lattice sites (two quasi-cubic and one hexagonal) are introduced by N-dopant [10], whereas the deep acceptor level, i.e., $D$-center [8], is introduced by B-dopant. However, it has been observed that the broadband emission at RT
in 6H f-SiC contains another weaker emission peak around 640 nm where its origin is still unknown [7,11]. On the other hand, Greulich-Weber [12] observed an extrarecombination center (so called $D'$-center) along with $D$-center by measuring the Photoluminescence-detected Electron Paramagnetic Resonance (PL-EPR) spectrum on B-doped 6H-SiC. Therein, three $g$-factors were derived for $D'$-center against one for $D$-center, indicating $D'$-center as a new type of acceptor-like center which can stay on three different lattice sites in 6H-SiC. In addition, it was suggested that $D'$-center might enroll in the emission process related to the low-energy flank of the PL spectrum.

In this study, we identify a new boron-induced acceptor level here called $D^*$-center, which is deeper than the well-known $D$-center by measuring the temperature-dependent PL intensity spectra on 6H f-SiC. This new acceptor level corresponds to the dominating DAP recombination at low temperatures with peak photon energy around 1.90 eV. By referring previous research outputs of first-principles calculations on SiC material, the lattice structures of both $D^*$-center and $D$-center (together we call them the double $D$-centers) are derived. Moreover, we compare the density of either the boron-induced acceptor in f-SiC samples with different doping conditions. In addition, we suggest the existence of a hole-trap, i.e., HS2 center, with an energy level that lies between that of the double $D$-centers. In the end, we propose a two-stage hole thermal ionization model related to the HS2 center which could explain the thermal quenching of PL intensity on $p$-type f-SiC and the PL intensity increase on $n$-type f-SiC as the temperature increases.

### Table 1. Parameters of three 6H f-SiC samples A, B and C. The dopant concentrations ($N_d$ for nitrogen | $N_a$ for boron) were measured by time-of-flight secondary-ion mass spectroscopy (TOF-SIMS). The maximum PL intensities of all samples and the corresponding temperatures were also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$ pressure (mbar)</td>
<td>0.1</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Growth rate ($\mu$m · h$^{-1}$)</td>
<td>92</td>
<td>96</td>
<td>90</td>
</tr>
<tr>
<td>$d_{sub}$ ($\mu$m)</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{epi}$ ($\mu$m)</td>
<td>46</td>
<td>48</td>
<td>45</td>
</tr>
<tr>
<td>Dim. (cm$^2$)</td>
<td>0.8×0.4</td>
<td>0.8×0.8</td>
<td>0.5×0.5</td>
</tr>
<tr>
<td>$N_d$ ($\times10^{18}$ cm$^{-3}$)</td>
<td>3.2</td>
<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td>$N_a$ ($\times10^{18}$ cm$^{-3}$)</td>
<td>6.9</td>
<td>6.9</td>
<td>4.4</td>
</tr>
<tr>
<td>Max. PL intensity ($\times10^6$ arb. unit)</td>
<td>0.78 (at 75 K)</td>
<td>0.99 (at 290 K)</td>
<td>1.34 (at 75 K)</td>
</tr>
</tbody>
</table>

### 2. Experimental details

The specifications of the three 6H f-SiC samples are summarized in Table 1. The three samples, labelled as A to C, are strong| intermediate $p$-type and $n$-type 6H f-SiC, respectively. The epilayer of each sample was grown with low off-axis (orientation: (1120) ± 1.4°) on the (0001) plane of the 250 $\mu$m thick 6H-SiC substrates (SiCrystal GmbH) using FSGP at 1725°C, where all the epilayers were with Si-face on the top. Apart from introducing N and B in the source material for FSGP, extra nitrogen gas ($N_2$) was supplied during the growth. The temperature-dependent PL intensities of the samples are measured by a micro-PL system. The micro-PL system consisted of a continuous diode laser ($\lambda=375$ nm) and an optical spectrometer (SHAMROCK SR-303I-A Spectrograph, Andor Technology). Both the input laser source and the emission signal to be detected were fiber-coupled to a 50× microscope lens in a front excitation | front detection configuration, where the laser power density on the sample surface was $\sim78.6$ mW · cm$^{-2}$. The frequency for PL signal acquisition was set to 40 Hz with 300 times of accumulation. The temperature of the samples is controlled by a cryostat system from Oxford Instruments where liquid nitrogen is used to vary the temperatures from 65 K to RT.
Fig. 1. Normalized PL intensity spectra at different temperatures [(a) sample A: 75-195 K; (b) sample B: 75-255 K; (c) sample C: 75-290 K], where the PL intensities above 195 K for sample A and above 255 K for sample B were comparable to ambient noise level. Insets: the temperature-dependent peak intensities of the PL spectra of each sample.
3. Results and discussion

Fig. 1 shows the normalized temperature-dependent PL intensity spectra of the three samples. It is obvious to see that in all the samples there are two competing radiative recombination processes, where one of them dominates at relative lower temperatures while the other process becomes dominating at high temperatures. PL spectra with comparable contributions from the two processes were also observed at intermediate temperatures. The main recombination scheme at low temperatures with PL peak around 1.89-1.91 eV indicates a second D-center with deeper acceptor level (D*-center). In addition, the less smooth line shapes at the low-energy flanks of all the PL spectra indicate the site-dependent behavior of the D*-center since there might be the superposition of several luminescence spectra corresponding to the D*-centers on different lattice sites. Moreover, the recombination which dominates at elevated temperatures with PL peak around 2.10-2.14 eV is related to the well-known D-center.

The determination of the energy level of D-center is still in controversial [8, 13, 14], and there is still lack of direct experimental approach to determine the lattice structure of either the D-center or the D*-center. The possible molecular configurations of the D-center have been predicted by first-principles calculations [15–17]. Since the boron-induced acceptors have the same electronic structures in 3C, 4H and 6H-SiC [18], the theoretically predicted properties of D-center for one of these polytypes of SiC can also be applied to the other two polytypes. At first, a prevailing hypothesis [8, 15] claimed that D-center is correlated to a B-atom on Si-sublattice (B_{Si}) together with a carbon vacancy (V_{C}), i.e., a B_{Si}+V_{C} complex. Latter, it was revealed by ab initio calculation from Aradi et al. [16] that B_{Si}+V_{C} complex is more like donor rather than acceptor where its energy level is 1.9 eV above the valence band maximum (E_{v}), i.e., E_{v}+1.9 eV. Instead, they pointed out that the D-center in 4H-SiC could originate from a Si-sublattice occupied by a B-atom together with the neighboring Si-antisite, i.e., the B_{Si} + Si_{C} complex. This configuration has to be on the cubic site oriented along c-axis giving rise to an acceptor level of E_{v}+0.53 eV, which matches quite well to the most accepted experimental value, i.e., E_{v}+0.58 eV [8]. On the other hand, the calculations on 3C-SiC by Bockstedte et al. [17] indicated that the complex composed of a B-atom occupying a C-sublattice associated with the neighboring C-antisite, i.e., the B_{C}+C_{Si} complex, has an energy level of E_{v}+0.70 eV. Therefore, we believe that the B_{Si} + Si_{C} complex is associated with the D-center, whereas the B_{C}+C_{Si} complex could be correlated to the D*-center. Here, we believed that the D*-center corresponds to the D*-center reported by Greulich [12]. Two reasons are given here: D*-center is related to the PL spectrum at the low-energy flank; the less smooth line shape corresponding to the D*-center dominated luminescence indicates the site-dependent behavior of D*-center, where both behaviors of the D*-center is quite identical to those of the D*-center reported in Ref. [12]. Besides, the D*-center should also have axial symmetry along c-axis [12]. The possible geometries of the D*-center have been shown in Fig. 2(a), where the related complex could stay on either hexagonal (h) or cubic sites (k_{1} or k_{2}) in 6H-SiC. Accordingly, the proposed geometries of the D-center in 6H-SiC are presented in Fig. 2(b), where the related complex might stay on either of the cubic sites (k_{1}, k_{2}) in 6H-SiC. Moreover, the suggested energy levels of the D*-center and the D-center also agree with the conclusions from the previous research [17, 19, 20] where the B_{C} related acceptor levels should be deeper than the B_{Si} related acceptor levels in SiC.

The insets of Fig. 1 show the temperature-dependent peak PL intensity of each sample, and it can be seen that the absolute PL intensities of both p-type samples (A|B) decrease with increasing temperature. While the trend of the peak PL intensity of the strong n-type sample (C) against the rising temperature exhibits a continuous decline up til 190 K, afterwards it keeps increasing at temperatures higher than 190 K. The same tendencies regarding the overall PL intensity drop on all samples within the temperature range of 75 K up to 190 K indicates the existence of an extra hole-trap which hinders the DAP recombination related to the D*-center. A possible candidate of this hole-trap could be HS2 with the energy level of E_{v}+0.63 eV [21].
Fig. 2. Geometry of: (a) the $D^*$-center ($E_v + 0.70$ eV), which is associated with a C-sublattice occupied by boron ($B_C$) next to a carbon antisite ($C_{Si}$) on either cubic or hexagonal site; (b) the $D$-center ($E_v + 0.53$ eV), which is associated with a Si-sublattice occupied by boron ($B_{Si}$) next to a silicon antisite ($Si_{C}$) on either $k_1$ or $k_2$ (cubic) site; (c) the hole-trap HS2 ($E_v + 0.63$ eV), which consists of a carbon split interstitial $C_{sp^{<100>}}$ with neighboring carbon vacancy ($V_{C}$). Note that 2x3 and 2x2 unit cells of 6H-SiC are presented in (a)|(b) and (c), respectively. N-atoms which replace the C-atoms on all cubic and hexagonal sites are also marked in (a)|(b). A unit cell of 6H-SiC crystal is highlighted in (c) marked with the corresponding stacking sequence. All the structures are presented in the (1120) plane.
HS2 is the dominant hole-trap in SiC [22] where only the carbon displacement is required, indicating its low formation energy. With high energy electron irradiation (>170 keV), it was observed that the HS2 center concentration starts to decrease in 4H-SiC, indicating HS2 is a vacancy-interstitial pair (Frenkel pair) [23]. According to the carbon interstitial structure related to HS2, the most probable candidate could be the Si-C or C-C dumbbell-like atoms pair (also called split interstitial) oriented along ⟨100⟩ direction on the carbon site, i.e., $C_{sp}(100)$ or $C_{spSi}(100)$ (‘SP’ refers to split), respectively. Note that they are the dominant carbon interstitials in SiC with the lowest formation energies regardless of the doping type [24]. Hence it is reasonable to assume that HS2 center consists of either $C_{sp}(100)$ or $C_{spSi}(100)$ with a neighboring $V_C$. Fig. 2(c) shows one of the proposed configurations of HS2 center with $C_{sp}(100)+V_C$ complex, in which another potential geometry related to HS2 ($C_{spSi}(100)+V_C$) can be obtained by replacing the interstitial carbon $C_I$ with the interstitial silicon $Si_I$. In addition, the signal overlapping of the $D^*$-center and the HS2 center was observed from the deep level transient spectroscopy (DLTS) at around 256 K [22]. This evidence strengthens our hypothesis that HS2 center participates in the double $D^*$-centers related DAP recombination.

From the crystalline growth point of view, it is also reasonable that the lattice structures of both $D^*$-center and $D^*$-center can be formed during the sublimation growth of 6H f-SiC. As the N-dopant on the Si-face of the epilayer prefers occupying C-site, and the B-dopant could occupy either Si- or C-site [25], there might be a competition between N-atoms and B-atoms for the occupation of the C-site. Therefore, it can be derived that with higher concentration of N-dopant there will be higher probability for the formation of $B_{Si}$ which is one of the components of the $D^*$-center complex. It has to be noted that the Si/C ratio is around 2 to 3 within the typical growth temperature range (1600°C to 2000°C) of FSGP [6] which is apparently the Si-rich condition. The results of ab initio calculations [26] have revealed that the formation of Si-antisite (Si$_C$), which is one of the components of $D^*$-center complex, is more favored in n-type sample under Si-rich condition. To sum up, based on the crystal growth condition of our 6H f-SiC samples shown in Table 1, the contrast on the density of the $D^*$-center of the three samples can be derived where C > B > A. According to the insets of Fig. 1, the PL intensity of sample C keeps increasing after 190 K where the $D^*$-center related DAP recombination is the dominating radiative recombination process. Besides, the overall PL intensities of sample A decrease to ambient noise level at the temperature (195 K) lower than that of sample B (255 K) due to the weaker $D^*$-center related luminescence in sample A compared to sample B. Hence we can see that keeping the high contrast between the concentrations of the N-dopant and the B-dopant is essential for the sufficient formation of the $D^*$-center.

Regarding the formation of $D^*$-center during the growth of f-SiC epilayer, it has been pointed out that the formation energy of $C_{Si}$ is ~6.2 eV lower than that of SiC in p-type 3C-SiC [26], where the difference on the formation energy is found to be smaller in n-type 3C-SiC [27]. On the other hand, in p-type 4H-SiC [28], it is observed that the formation of $B_C$ is favored over $B_{Si}$ in a Si-rich condition within a wide temperature range from 1400°C to 1800°C. Hence we believe there exists high probabilities of the formations of the $D^*$-center related complex ($B_C+C_{Si}$) in all three samples. As shown in the insets of Fig. 1, the PL intensities of all three samples at 75 K where the $D^*$-center related DAP recombination dominates the luminescence process are quite strong.

We further analyzed the temperature-dependent luminescence properties of all the three samples, which are influenced by the double $D^*$-centers related DAP recombination and the hole-trapping by HS2 center. Note that the different density distributions of these three centers were taken into consideration. We extracted the temperature-dependent mean PL intensities within two ranges of the photon energy, i.e., 1.55-1.65 eV and 2.25-2.35 eV, respectively for all samples as shown in the Arrhenius plots in Fig. 3. The $D^*$-center related PL mainly contributes to the 1.55-1.65 eV range whereas the $D^*$-center related PL mainly has influence on the 2.25-2.35 eV
Fig. 3. The Arrhenius plots representing the temperature-dependent mean PL intensities of all three samples within the photon energy range of: (a) 1.55-1.65 eV and (b) 2.25-2.35 eV.

range. In Fig. 3(a), it can be seen that the PL intensities of the low-energy flanks of both p-type samples decrease with the rise of the temperature. Here we believed that the non-equilibrium holes captured by the $D^*$-center might get sufficient thermal energies at high temperatures and get thermally activated to the HS2 center, which could cause more trapped holes at the HS2 center and less $D^*$-center related luminescence. This thermal process is indicated by the red dashed arrow pointing to the energy level of HS2 center as shown in Fig. 4. In addition, the PL intensity of the low energy flank of sample C tends to stop decreasing at high temperatures, indicating the strong influence from the increasing trend of the $D$-center related luminescence at high energy flank. Here, it is considered that the trapped non-equilibrium holes on HS2 might have a chance to be thermally activated to the $D$-center at high temperatures, where the related thermal process is also indicated in Fig. 4 by the dashed arrow pointing to the energy level of

Fig. 4. A schematic band diagram of the double $D$-centers related DAP recombination together with the HS2 center related hole-trapping in f-SiC. Two normalized PL spectra in the inset represent the typical PL line shape (here taking sample C as an example) at either low temperature (75 K) or high temperature (290 K) corresponding to either the $D^*$-center or $D$-center dominated DAP recombination, respectively. The photos showing the luminescence from sample C at both 75 K and 285 K are presented in two round frames separately. The energy level of different nitrogen-induced donor levels ($h, k_1, k_2$), double $D$-centers and the HS2 center are indicated. The two red dashed arrows designate the possible thermal ionization processes of the non-equilibrium holes at elevated temperatures.
As we have speculated that higher abundance D-center might be formed in sample C during the growth compared to those two p-type samples, the trapped holes get higher chance to be thermally activated to the D-center at elevated temperatures causing greater D-center related DAP recombination.

4. Conclusion

In summary, we have characterized three 6H f-SiC samples, which are strong n-type and intermediate|strong p-type, respectively, by applying temperature-dependent PL spectroscopy. We found a new boron-induced acceptor level \((D'\text{-center})\) which is deeper than the well-known D-center. The existence of double D-centers confirms the previously reported D- and D′-center detected by the PL-EPR spectroscopy. In addition, the decreasing trends of the \(D^*\)-center related luminescence with increasing temperature at the low energy flanks in the PL spectra of all three samples are attributed to the existence of a hole trap, i.e., the HS2 center. By combining the previous research results based on the first-principles calculations on SiC material, we propose the lattice structures and the related energy levels of the double D-centers as well as the HS2 center where the energy level of the HS2 center is found to stay in between those of the double D-centers. By considering the doping conditions of the three samples, it is suggested that N-doping could facilitate the formation of D-center. A two-step thermal ionization model of the non-equilibrium holes driven by the HS2 center is proposed to explain the trend of the \(D^*\) | D-center related DAP recombination with increasing temperature.

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References


