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Photoluminescence Quantum Yield of Fluorescent Silicon Carbide Determined by an Integrating Sphere Setup

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ABSTRACT: The excitation-dependent photoluminescence quantum yield (PL-QY) of strong n-type nitrogen–boron codoped 6H fluorescent silicon carbide (f-SiC) at room temperature is experimentally determined for the first time. The PL-QY measurements are realized by an integrating sphere setup based on a classical two-measurement approach. In particular, in accordance to the difference between our in-lab setup and the standard setup of the two-measurement approach, we have technically modified the experimental design, the data processing algorithm, and the estimation of relative uncertainty. The measured highest PL-QY of f-SiC samples is found to reach above 30%. We compare the PL-QYs at a certain excitation power of all f-SiC samples by considering their intrinsic defect densities. Finally, the evolution of the excitation power-dependent PL-QY of f-SiC is attributed to both band-to-band and impurity-assisted Auger recombination.

1. INTRODUCTION

White light-emitting diode (LED) light sources have been massively implemented in almost every aspect of industries and daily lives. Compared to traditional white light solutions, e.g., incandescent light bulbs, white LED light sources have several advantages. For instance, white LED light sources are more energy efficient, contain no mercury or other hazardous elements, and require no warm-up period. There are three configurations of white LED light sources. The first is the so-called tricolor configuration that consists of a red, a green, and a blue LED; however, the color mixing corresponding to this design is not very smooth. The second is the most commercialized type that is made of a blue LED covered by yellow phosphors. As blue LEDs and yellow phosphors are very efficient, this type of white LED can induce high luminescence efficiency. However, as the typical yellow phosphor is made of cerium-doped yttrium aluminum garnet, i.e., (YAG):Ce, its degradation issue would cause the white LED light source to have a low color rendering index (CRI). Moreover, the cost and supply issues regarding the rare earth elements in yellow phosphors, e.g., Ce in (YAG):Ce, should be also concerned. The last configuration is composed of a near-ultraviolet (NUV) LED covered by red/green/blue phosphors. Note that this type of white LED light source can induce high CRI, but the efficiency of the red phosphor is quite low. Fortunately, a new type of inorganic phosphor grown by Kamiyama et al., i.e., the donor and acceptor codoped fluorescent silicon carbide (f-SiC), which contains no rare earth elements and has no degradation issues, is anticipated to realize NUV excitation-based white light emission that could reach an optimized tradeoff between the luminescent efficacy and CRI. By getting heavily nitrogen–boron (N–B) codoped, f-SiC can be applied as a passive wavelength conversion medium, where strong orange-yellowish light emission with large full width at half-maximum (FWHM) can be generated by optically pumping f-SiC via a NUV light source, e.g., a nitride-based NUV LED chip. It is also worth noting that SiC is regarded as a better platform for the integration of a nitride-based NUV LED chip compared to the prevalent sapphire substrate. In addition, another type of f-SiC that is nitrogen–aluminum (N–Al) codoped is anticipated to emit blue-green light by NUV light source pumping. It has been proposed that a new type of white LED light source with high CRI can be achieved by growing the stacking structure that contains a nitride-based NUV LED chip, a N–B as well as a N–Al codoped f-SiC layer as shown in Figure 1.

Figure 1. Schematic diagram of the stacking structure of a white LED based on N–B and N–Al codoped f-SiC thin films.

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Since N–Al codoped SiC does not show photoluminescence (PL) at room temperature (RT), in the scope of this research, f-SiC usually refers to N–B codoped SiC. Two methods have been proposed to enhance the intensities of the donor–acceptor pair (DAP) recombination events in f-SiC, i.e., increase the density of DAP and the sample thickness. Luckily, the above-mentioned two methods have been successfully implemented in the epilayer growth of f-SiC, thanks to the advent of fast sublimation growth process (FSGP) method developed by Syvajärvi et al.¹⁰ which makes the current f-SiC have N–B codoping beyond 10¹⁸ cm⁻³. In addition, with the FSGP method, it is also easy to achieve sufficient epilayer thickness since the growth rate of FSGP can be up to 200 µm·h⁻¹.¹⁷ Furthermore, the densities of the 1-D (i.e., micropipe), two-dimensional (i.e., stacking fault), and three-dimensional⁶ (i.e., polytype switch, carbon inclusion, and silicon droplet) defects in f-SiC have been drastically decreased to the negligible levels⁶,⁹ by applying the FSGP method for the growth of f-SiC epilayers. Meanwhile, the source SiC material for FSGP is prepared via the modified physical vapor transport technique developed by Wellmann et al.¹⁰,¹¹ where the stable nitrogen doping and low dislocation densities in the source SiC material have been realized.

As knowing the photoluminescence quantum yield (PL-QY) of f-SiC, i.e., the ratio of the emitted photons to the absorbed photons of the f-SiC thin film, is of great importance for the evaluation of the upper limit of the external quantum efficiency of the entire white LED device shown in Figure 1. In this research, we demonstrate the experimental methodology regarding the determination of the PL-QY on n-type f-SiC samples. Note that only n-type f-SiC shows strong emission at RT where the reason regarding the distinctive luminescent behaviors of n- and p-type f-SiCs has been investigated before.¹² In addition, we also give the explanation for the physical mechanism corresponding to the incident power-dependent PL-QY of f-SiC.

There are two categories for the PL-QY measurement on a fluorescent material, i.e., the relative and absolute techniques.¹³ For the relative technique, a standard f-SiC sample is needed whose PL-QY is already known. It is required that the standard f-SiC should have similar excitation, absorption, and emission properties to those of the sample to be measured. Since it is difficult to fully duplicate the experimental conditions in which the reference spectra of the standard f-SiC are measured in our lab, in this research, we adopt the absolute techniques for the PL-QY measurements. As f-SiC is a solid thin-film sample with high refractive index, the issues of anisotropic light emission and wave-guiding effects¹⁴ could greatly affect the accuracy of the results of PL-QY measurement. A direct solution might be mapping the light emission to the solid angle distribution where the ratio of the detected PL emission to the whole PL emission can be determined by referring the experimental conditions related to PL excitation/detection. However, this solution is quite cumbersome and not so viable where heavy workload is required and the interval of the solid angle needs to be carefully chosen. On the other hand, integrating sphere has been recognized as the standard equipment for measuring the PL-QY of solid thin films.¹⁵,¹⁶ By implementing integrating sphere into PL-QY measurements, all of the reflected and emitted light can be collected where the concern regarding the angular dependence of the PL emission is no longer needed. Therefore, the integrating sphere-based measurement system has been widely applied in the determination of PL-QY of solid thin films.¹⁴,¹⁶–¹⁹ There are two types of methodologies based on the integrating sphere system for absolute determination of PL-QY, i.e., three-measurement¹⁴,¹⁷,¹⁹ and two-measurement approaches. In fact, the two-measurement approach proposed by Johnson et al.¹⁸ was derived from the three-measurement one developed by de Mello et al.¹⁴ Afterward, Leyre et al.¹⁰ have theoretically proved that the values of the PL-QY determined by these two approaches are identical. In this research, by applying an integrating sphere system, we developed the experimental procedure regarding the determination of f-SiC’s PL-QY derived from the classical two-measurement approach. The reason behind the differences in the PL-QY of all f-SiC samples under the same excitation power was investigated. Additionally, we also tried to elaborate the trend of PL-QY against the changed excitation power regarding the certain f-SiC sample as well.

2. RESULTS AND DISCUSSION

2.1. PL-QY of Strong n-Type f-SiC. In this research, three N–B codoped strong n-type f-SiC samples, i.e., F-1/2/3, were employed in PL-QY measurements, where the basic parameters for these three f-SiC samples are summarized in Table 1.

Table 1. Parameters for the Three f-SiC Samples at RT, where \(d_{epi}/d_{sub}\) Refers to the Substrate/Epilayer Thickness

<table>
<thead>
<tr>
<th>sample</th>
<th>F-1</th>
<th>F-2</th>
<th>F-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{sub} (\mu m))</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>(d_{epi} (\mu m))</td>
<td>45</td>
<td>150</td>
<td>250</td>
</tr>
<tr>
<td>(N_d (x10^{18} \text{cm}^{-3}))</td>
<td>9.2</td>
<td>2.85</td>
<td>2.55</td>
</tr>
<tr>
<td>(N_a (x10^{18} \text{cm}^{-3}))</td>
<td>5.2</td>
<td>1.10</td>
<td>1.50</td>
</tr>
<tr>
<td>(N_a/N_d)</td>
<td>1.77</td>
<td>2.60</td>
<td>1.70</td>
</tr>
</tbody>
</table>

\(N_a\) and \(N_d\) are measured by time-of-flight secondary-ion mass spectroscopy.

By applying the FSGP method,⁶ the epilayers of the f-SiC samples were grown on the (0001) plane of the commercial 6H-SiC substrates (SiCrystal GmbH) with low off-axis (orientation \(\langle 11 \bar{2} 0 \rangle \pm 1.4^\circ\)) at 1725 °C. Note that sample F-1 and samples F-2/3 were grown in two separate batches. For the experimental design, data processing algorithm, and the estimation of uncertainty regarding the PL-QY determination of f-SiC samples, refer to Section 4.1. The PL-QYs of each sample were excited under seven different incident beam powers, i.e., 0.25, 0.5, 1, 2, 5, 8, and 14 mW, to study the power dependency of f-SiC’s PL-QY. Note that the PL-QYs for all three samples were measured twice with the incident beam power from 0.25 to 8 mW, where the measurements corresponding to the beam incidence of 14 mW were only launched for once due to the unstable fiber-coupled maximum output power of the laser source. The uncertainties of the measured PL-QYs for each sample with specific incident power have been estimated using eq 11, where all of the \(\eta_{PL}\) values together with the respective mean values of \(\eta_{PL}\) are presented in Figure 2.

From Figure 2, it is clearly seen that the PL-QYs of F-1 under all incident powers are lower than those of F-2/3. On the other hand, we also measured the time-resolved photoluminescence (TRPL) of these three samples, where different numbers of spots were characterized on different samples (F-1, nine; F-2/3, three). The TRPL measurement results are summarized in Figure 3, and the related experimental details are given in Section 4.2. Compared to F-1, F-2/3 have slower...
get absorbed within the depth of 0 to $Z_{eff}$. Meanwhile, it is considered that almost all of the other half of photons are absorbed within the depth of $Z_{eff}$ of 45 $\mu$m, which means the proportions of the photons being absorbed by the substrates for all three samples can be negligible. Hence, it is believed that with the identical effective penetration depth, $Z_{eff}$ as well as sufficient epilayer thickness, $d_{epi}$ for all three samples, the differences regarding their PL-QYs are not correlated to their different sample thicknesses. In addition, the reason why sample F-2 has slightly higher PL-QY compared to that of F-3 is still not clear. By considering the emission of each f-SiC sample, which is mainly contributed by the upper part of the respective epilayer, i.e., from the epilayer surface to $Z_{eff}$ as a point source, the proportion of the emission from the edges of each f-SiC sample is proportional to its sample thickness, $d$. Therefore, the PL-QY of F-3 might be more underestimated due to its lesser sample thickness compared to that of F-2, which causes the measured PL-QY of F-3 to be lower than that of F-2. Another reason can be derived from the doping conditions of F-2/3. Regarding the summarized $N_0/N_d$ in Table 1, we can see that only the $N_0/N_d$ for F-2 is higher than that of F-1/3, where the higher proportion of n-type dopant in F-2 might further compensate the non-radiative behavior regarding the shallow N-induced donors.

2.2. Auger Recombination in f-SiC. In addition, an obvious tendency can be observed from Figure 2 that the PL-QY of the n-type 6H f-SiC sample increases with the decrease in incident power. We believe that this phenomenon is caused by the enhanced Auger recombination in the f-SiC sample when the incident power density on the sample is increased.

In particular, it has been observed that a fast decay component emerges during free carrier absorption (FCA) measurement on SiC at elevated injection levels, where this fast decay channel is attributed to band-to-band Auger recombination. Moreover, it is well known that the rate of Auger recombination is proportional to the cube of the total carrier densities, i.e., $n_0 + \Delta n$, where $\Delta n$ refers to the density of nonequilibrium carriers. As the focused incident beam spot on the sample port of the integrating sphere has the diameter of 3 mm, the calculated injection level on f-SiC samples corresponding to the range of the incident beam power, i.e., 250 $\mu$W to 14 mW, is from $1.33 \times 10^{18}$ to $7.47 \times 10^{19}$ cm$^{-3}$s$^{-1}$. Therefore, the change of the Auger recombination rate is expected to be more than 1 order of magnitude in the PL-QY measurements. On the other hand, it is worth mentioning that the phononless $e^-e^-h^+$ related Auger recombination becomes prominent for strong n-type SiC, where the shallow donors could be involved in an impurity-assisted Auger process. This could also be one of the major causes regarding why the PL-QY of F-1 is far lower as its $N_d$ is much higher compared to that of F-2/3. Future work about the characterization of the carrier lifetimes in f-SiC at high injection levels by the experimental technique like time-resolved FCA is needed to study how the PL-QY is degraded by Auger recombination and its carrier dynamics.

3. CONCLUSIONS

In this research, we have designed the experimental scheme related to the absolute PL-QY determination on f-SiC samples, where the measurement methodology was based on a modified two-measurement approach using an integrating sphere. The algorithm corresponding to the data processing and the uncertainty estimation of PL-QY experimental results were also
developed. This newly developed PL-QY determination procedure is suitable for measuring the PL-QY of the thin-film sample with very weak emission (compared to the intensity of the excitation beam), e.g., indirect band gap thin films. The excitation power-dependent PL-QY of the three n-type 6H f-SiC samples, i.e., F-1/2/3, have been measured. By combining the PL-QY and TRPL measurement results for these three f-SiC samples, it was revealed that the PL-QY of f-SiC can be influenced by its densities of $E_1/E_2$ centers, which are the major nonradiative centers in f-SiC. A clear tendency where the PL-QY of f-SiC sample increases with the decreasing incident power indicates strong Auger recombination in f-SiC at high injection levels. It is believed that the Auger recombination in strong n-type f-SiC can be enhanced by the increased density of either injected carriers or the n-type dopant, where the latter could induce impurity-assisted phononless $e^-e^-h^+$ type of Auger recombination related to shallow donors.

4. EXPERIMENTAL SECTION

4.1. PL-QY Determination. For the determination of PL-QY of f-SiC samples, an integrating sphere (OL 700-71, Gooch & Housego) with a diameter of 6 in., a continuous diode NUV laser with $\lambda = 375$ nm (LBX-375 HPE), and an optical spectrometer (CAS 140B, Instrument Systems GmbH) were employed. Note that the integrating sphere applied in this measurement has only one sample port on the edge of the integrating sphere. This makes the measurement condition different from that of the classical two-measurement approach where the sample is placed at the center of the integrating sphere. Therefore, the classical two-measurement approach has to be modified to match our measurement condition. In addition, the related algorithm of experimental data processing and the evaluation of relative uncertainty regarding the estimation of PL-QY have to be redeveloped as well. The important symbols and corresponding descriptions applied in this experiment are summarized in Table 2.

<table>
<thead>
<tr>
<th>symbol</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_a$</td>
<td>original, without sample excitation</td>
</tr>
<tr>
<td>$L_o$</td>
<td>attenuated, with sample excitation</td>
</tr>
<tr>
<td>$P_i$</td>
<td>overall</td>
</tr>
<tr>
<td>$P_{PLFEFD}$</td>
<td>front excited–front detected</td>
</tr>
<tr>
<td>$P_{PLFRFD}$</td>
<td>front excited–back detected</td>
</tr>
<tr>
<td>$P_{PLBEBD}$</td>
<td>back excited–front detected</td>
</tr>
<tr>
<td>$P_{PLBEFD}$</td>
<td>back excited–back detected</td>
</tr>
<tr>
<td>$I_{E synopsis}(\lambda)$</td>
<td>source beam</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>front excited–front detected PL of f-SiC</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>front excited–back detected PL of f-SiC</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>(1 Measured spectrum, range: 350–784 nm, with OD filter)</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>source beam</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>tail part of the source beam existing in $I_{E synopsis,W,dir}(\lambda)$</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>front excited–front detected PL of f-SiC</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>scaling factor</td>
</tr>
<tr>
<td>$I_{E synopsis,W,dir}(\lambda)$</td>
<td>Savitzky–Golay filter</td>
</tr>
<tr>
<td>$T_{SUB}$</td>
<td>transmittance of the f-SiC substrate</td>
</tr>
</tbody>
</table>

Figure 4. Four configurations related to the PL emission from a f-SiC sample (i.e., f-SiC epilayer + 6H-SiC substrate). As for the subscripts of the names of PL signals, “F”, “B”, “E”, and “D” represent front, back, excitation, and detection, respectively, where the front side of the f-SiC sample refers to the side of epilayer.

and $P_{PLFEFD}/P_{PLFRFD}$ (the total integrated PL intensity from the sample is denoted $P_i$), to extract sample’s PL-QY. Note that the aforementioned notations, i.e., $L_a, L_o, P_i$ are adopted from de Mello et al.14 Figure 5 shows the experimental design based on the 6 in. diameter integrating sphere OL 700-71 for the PL-QY determination on f-SiC samples in this research. It is worth mentioning that the incident beam power was calibrated by measuring it at the sample port with a power meter (energy meter PM100D with a silicon detector S130VC, Thorlabs, Inc.) before steps 1 and 4 to ensure the same incident power for the reflectance/transmittance fiber optic probe (FOP). The spectra recorded through the four steps of the PL-QY measurement are summarized in Table 3 with specifications. Taking the measurement results of sample F-1 with the incident power of 5 mW based on the experimental setup shown in Figure 5 as an example, the measured spectra defined in Table 3 are shown in Figure 6.

4.1.2. Data Processing Algorithm. In step 1, a certified Reflectance Standard (Ref-Std), which is made of pressed poly(tetrafluoroethylene) powder packed in a 2 in. diameter holder, was installed on the sample port for measuring the original spectra of the excitation beam, where the Ref-Std was
The optical density (OD) is used for preventing light leakage through the sample port. \( I_{\text{SRC,W}} \) and \( I_{\text{SRC,N}} \) are the two spectra related to the original emission spectrum measured in different wavelength ranges, i.e., the wide mode (350–784 nm) and the narrow mode (390–784 nm), respectively. Normally, an optical density filter (OD filter) was used when measuring \( I_{\text{SRC,W}} \) to prevent the absolute intensity of its main peak centered at 375 nm from exceeding the upper detection limit of the optical spectrometer. Here, we obtain the expression of the integrated intensity of the original emission spectrum \( L_a \) shown in eq 2, where Refl-Std(\( \lambda \)) refers to the reflectance spectrum of the Refl-Std.

\[
L_a = \int_{369 \text{nm}}^{382 \text{nm}} \frac{I_{\text{SRC,W}}(\lambda)}{\text{Refl-Std}(\lambda)} d\lambda
\]  

Figure 5. Diagram of the modified experimental procedure for PL-QY measurements on f-SiC samples. (a) Step 1, measurement of \( L_a \). (b) Top view of the integrating sphere during step 1. (c) Steps 2 and 3, measurement of \( L_a \) and PL-\( \text{FEFD,W} \), where the beam was directed toward the vicinity of the sample port (i.e., comparison mode) for step 2. (d) Step 4, measurement of PL-\( \text{FEFD,N} \).

Table 3. Procedure of Recording One Set of Spectra for the PL-QY Determination for the f-SiC Sample Using the Experimental Configuration Shown in Figure 5a

<table>
<thead>
<tr>
<th>step no.</th>
<th>spectrum name</th>
<th>toward sample port</th>
<th>range of ( \lambda )</th>
<th>connected FOP</th>
<th>beam switch</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( I_{\text{SRC,W}}(\lambda) )</td>
<td>Reff-Std</td>
<td>wide</td>
<td>Refl.</td>
<td>Samp.</td>
</tr>
<tr>
<td>2</td>
<td>( I_{\text{SRC,N}}(\lambda) )</td>
<td>Reff-Std</td>
<td>narrow</td>
<td>Refl.</td>
<td>Samp.</td>
</tr>
<tr>
<td>3</td>
<td>( I_{\text{FEFD,W,dir}}(\lambda) )</td>
<td>sample holder</td>
<td>narrow</td>
<td>Refl.</td>
<td>Comp.</td>
</tr>
<tr>
<td>4</td>
<td>( I_{\text{FEFD,N,dir}}(\lambda) )</td>
<td>f-SiC front</td>
<td>narrow</td>
<td>Refl.</td>
<td>Samp.</td>
</tr>
<tr>
<td>5</td>
<td>( I_{\text{FEFD,N,ind}}(\lambda) )</td>
<td>f-SiC front</td>
<td>wide</td>
<td>Tran.</td>
<td>Samp.</td>
</tr>
</tbody>
</table>

Note that the “wide” and “narrow” modes under “range of \( \lambda \)” refer to 350–784 and 390–784 nm, respectively. “W” and “N” in subscripts of spectrum name are also related to the wide and narrow modes, respectively. “ind” and “dir” refer to the indirect and direct incidence of the excitation beam on the sample port with the sample holder mounted, which correspond to the comparison mode (comp.) and sample mode (samp.), respectively. In addition, \( I_{\text{SRC,W}}(\lambda) \) \( / \) \( I_{\text{FEFD,W}}(\lambda) \) were recorded using the same parameter setting, i.e., integration time, time of collection, and choosing OD filter or not, and so were \( I_{\text{SRC,N}}(\lambda) \) \( / \) \( I_{\text{FEFD,N,dir}}(\lambda) \) \( / \) \( I_{\text{FEFD,N,ind}}(\lambda) \).

Figure 6. One set of spectra for the extraction of the PL-QY at certain incident power (here taking the measurement results corresponding to sample F-1 at an incident power of 5 mW as an example). According to the procedure of PL-QY measurement summarized in Table 3, the spectra recorded in steps 1–5 are presented in (a), whereas the spectrum recorded in step 4 is presented in (b). Note that the zoomed spectra in (a) at the predefined narrow wavelength range, i.e., 390–784 nm, are presented in inset (a-i), whereas the respective normalized spectra are shown in inset (a-ii). Inset (b-i) shows the zoomed spectrum of \( I_{\text{FEFD,N}} \) at the 350–500 nm range.

In panel (a) of Figure 6, the spectrum of \( I_{\text{FEFD,N,dir}} \) which includes the spectrum of \( I_{\text{FEFD,W}} \) was also measured with the OD filter. From the normalized spectrum of \( I_{\text{FEFD,W,dir}} \) shown in inset (a-ii) of Figure 6, we can see that by adding the OD filter the line shape of \( I_{\text{FEFD,W,dir}} \) is affected by ambient noise due to its weak intensity. In addition, the spectrum presented in panel (b) of Figure 6, i.e., \( I_{\text{FEFD,N}} \), which reflects the information of the line shapes related to \( I_{\text{FEFD,N,dir}} \) measured without the OD filter. It can be expected that if the OD filter was added during the measurements of \( I_{\text{FEFD,N}} \), the related spectrum would be also affected by the ambient noise. As a consequence, we decided to measure the spectra that were used for extracting the PL emission spectra without adding the OD filter. To establish the correlation between the spectra measured with/without the OD filter, a scaling ratio (SCR)
expressed by eq 3 is needed. Note that the values of both components in eq 3 should be similar since the degree of attenuation resulted by the OD filter is a constant. Accordingly, the extracted PL spectra related to the FEFD/FEBD configuration have to be scaled down by a factor of SCR to calculate PL-QY. The modified expression for PL-QY is shown in eq 4 where the value of PL-QY is denoted by \( \eta_{PL} \) and \( P_{PL,FEFD}/P_{PL,FEBD} \) refers to the integrated PL intensity of \( P_{PL,FEFD}(\lambda)/P_{PL,FEBD}(\lambda) \), respectively.

\[
SCR = \frac{1}{2} \times \frac{\int_{390nm}^{784nm} P_{SRC,W}(\lambda) d\lambda}{\int_{390nm}^{784nm} I_{SRC,N}(\lambda) d\lambda} + \frac{1}{2} \times \frac{\int_{390nm}^{784nm} P_{FEFD,W,dir}(\lambda) d\lambda}{\int_{390nm}^{784nm} I_{FEFD,N,dir}(\lambda) d\lambda}
\]

\[
\eta_{PL} = \frac{1}{SCR} \times \frac{P_{PL,FEFD} + P_{PL,FEBD}}{I_{SRC,W} L_a - I_c}
\]

\[
= \frac{1}{SCR} \times \frac{\int_{450nm}^{784nm} PL_{FEFD}(\lambda) + PL_{FEFD}(\lambda) d\lambda}{I_{SRC,W} - I_c}
\]

From the inset (a-i) of Figure 6, we can see that the line shapes of the spectra of the excitation beam measured with/without the OD filter (i.e., \( I_{SRC,W}/I_{SRC,N} \)) are identical and so are the two spectra of the PL emission with FEFD configuration (\( I_{FEFD,W,dir} \) and \( I_{FEFD,N,dir} \)). It is confirmed that spectra are scaled down by the OD filter regardless of the wavelength; hence, it is reasonable to apply SCR for PL-QY calculation. The upper limit of the detectable wavelength (i.e., 784 nm), which is also shown in eqs 3 and 4, is actually caused by the limitation of the optical spectrometer. It is believed that the PL intensity of the f-SiC samples with wavelength shorter than the lower limits of the integrals in eq 4 (i.e., 450 nm) can be negligible. In the inset (a-i) of Figure 6, it is clearly seen that the spectrum of the excitation beam has a tail part that consists of two sharp peaks at \( \sim 406.4 \) and \( \sim 757.4 \) nm and two broad peaks at \( \sim 440 \) and \( \sim 470 \) nm. This tail part is still distinguishable in the spectrum of \( I_{FEFD,N,dir} \) corresponding to the PL emission excited by the FEFD configuration. Hence, it is essential to split \( PL_{FEFD}(\lambda) \) from \( I_{FEFD,N,dir} \). Later, we will show that \( PL_{FEFD}(\lambda) \) can be recovered by \( I_{FEFD,B} \). Since \( PL_{FEFD}(\lambda) \) and \( PL_{FEFD}(\lambda) \) are induced under the same excitation condition with the source beam incidence at the air/f-SiC epilayer interface, the line shapes of these two spectra should be identical. In step 2, the sample holder, which is used for fixing the f-SiC sample, was installed on the sample port, where the line shape of the measured spectrum in this step (\( I_{FEFD,N,dir} \)) is considered to represent the line shape of the tail part of the excitation beam. Moreover, although \( I_{SRC,N} \) also represents the tail part of the excitation beam, the line shapes of \( I_{SRC,N} \) and \( I_{FEFD,N,dir} \) are slightly different, as shown in the inset (a-i) of Figure 6. Here, we believe that the line shape of \( I_{FEFD,N,dir} \) is more representative of the tail part of the excitation beam enclosed in \( I_{FEFD,N,dir} \). In step 3, an f-SiC sample was mounted on the sample holder with the epilayer side facing toward the sample port. For \( I_{FEFD,N,dir} \), we have introduced that this spectrum contains \( PL_{FEFD}(\lambda) \), which was measured without adding the OD filter. Meanwhile, by recording \( I_{FEFD,W,dir} \) which was measured in wide mode with the OD filter, one can obtain the integrated intensity of the attenuated source beam after PL excitation (\( I_a \)), as shown in eq 5.

\[
L_a = \int_{360nm}^{382nm} I_{FEFD,W}(\lambda) d\lambda
\]
representing the line shape of the tail part of the excitation spectrum at FEFD mode has been measured in step 2. Therefore, we got the analytical expression of $I_{\text{FEFD,N,dir}}$ at the PL-active spectral region, which corresponds to the linear recombination of PL$_{\text{FEFD}}(\lambda)$ and $I_{\text{FEFD,N,ind}}$ as shown in eq 9. By solving eq 9 using least-squares regression, one can get $PL_{\text{FEFD}}(\lambda)$ via eq 10. An example of the extraction of the relative uncertainty of PL-QY corresponds to the PL excitation under FEFD and FEBD respectively. In addition, $\sigma_{\text{PL}}$ is composed of two components that have to be considered by following the law of propagation uncertainty, where the expression of $\eta_{\text{PL}}$ refers to eq 11. In eq 11, $U_{\text{FEFD}}$, $U_{\text{FEBD}}$, $U_{\text{SCR}}$ and $U_{\text{L}}$ refer to the relative uncertainties of $P_{\text{L,FEFD}}$, $P_{\text{L,FEBD}}$, $L_{\text{L}}$, $L_{\text{L}}$ and SCR, respectively. In addition, $\sigma_{\text{L,FEFD,FEBD, LL, SCR}}$ corresponds to the standard deviations of each variable shown in eq 11, and the expressions included in the angle brackets are related to the respective mean values.

$$\begin{align*}
U_{\text{PL}} &= \left( \frac{P_{\text{FEBD}}}{P_{\text{FEFD}} + P_{\text{FEBD}} + P_{\text{FEBD}}} \right)^2 \sigma_{\text{FEFD}}^2 \\
&+ \left( \frac{P_{\text{FEBD}}}{P_{\text{FEBD}} + P_{\text{FEBD}} + P_{\text{FEBD}}} \right)^2 \sigma_{\text{FEBD}}^2 \\
&+ \left( \frac{L_{\text{L}}}{L_{\text{L}} + L_{\text{L}}} \right)^2 \sigma_{\text{L,FEFD}}^2 \\
&+ \left( \frac{L_{\text{L}}}{L_{\text{L}} + L_{\text{L}}} \right)^2 \sigma_{\text{L,FEBD}}^2 \\
&+ \sigma_{\text{L, SCR}}^2 \\
\end{align*}$$

(11)

4.1.3. Relative Uncertainty. Accordingly, in this research, we can see that $P_{\text{L}}$ is composed of two components that correspond to the PL excitation under FEFD and FEBD modes. The expression of the relative uncertainty of PL-QY has to be considered by following the law of propagation uncertainty, where the expression of $\eta_{\text{PL}}$ refers to eq 11. In eq 11, $U_{\text{FEFD}}$, $U_{\text{FEBD}}$, $U_{\text{L}}$, $U_{\text{L}}$, and $U_{\text{SCR}}$ refer to the relative uncertainties of $P_{\text{L,FEFD}}$, $P_{\text{L,FEBD}}$, $L_{\text{L}}$, $L_{\text{L}}$ and SCR, respectively. In addition, $\sigma_{\text{L,FEFD,FEBD, LL, SCR}}$ corresponds to the standard deviations of each variable shown in eq 11, and the expressions included in the angle brackets are related to the respective mean values.

$$\begin{align*}
PL_{\text{FEFD}}(\lambda) &= a_{\text{FEFD}}(\lambda) \\
\end{align*}$$

(10)

4.2. TRPL Measurement. In this research, the TRPL measurements on f-SiC samples are realized by the time-correlated single-photon counting (TCSPC) system from PicoQuant GmbH. The key components of the TCSPC system are (a) a picosecond laser diode head (LDH-D-C-375) with $\lambda$ of 375 nm and FWHM of $\sim$44 ps; (b) a computer-controlled diode laser driver (PDL 828 "Sepia II", two channel version); (c) a hybrid photomultiplier detector assembly (PMA Hybrid 40); and (d) a TCSPC board (TimeHarp 260 PICO) with a digital resolution of around 25 ps. Both the injected laser pulse and the emitted photon signal are fiber-coupled to a 50x microscope lens with the configuration of front excitation—front detection. After excitation, the emitted photons are filtered by a 405 nm long-pass filter and then transferred to a photomultiplier tube. A 2 ms time span for photon decay sampling, a 500 Hz repetition rate of laser pulse (i.e., 80 ns resolution), a 1 h integration time were chosen for the TRPL measurement.

**REFERENCES**


