Systematic study of Shockley–Read–Hall and radiative recombination in GaN on Al₂O₃, freestanding GaN, and GaN on Si

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Abstract

Here we study and correlate structural, electrical, and optical properties of three GaN samples: GaN grown by metalorganic chemical vapor deposition on sapphire (GaN/Al₂O₃), freestanding GaN crystals grown by the high nitrogen pressure solution method (HNPS GaN), and GaN grown by hydride vapor phase epitaxy on silicon (GaN/Si). Defect and impurity densities and carrier concentrations are quantified by x-ray diffraction, secondary mass ion spectroscopy, and Hall effect studies, respectively. Power-dependent photoluminescence measurements reveal GaN near-band-edge emissions from all samples having mixtures of free exciton and band-to-band transitions. Only the defect luminescence in the GaN/Si sample remains unsaturated, in contrast to those from the HNPS GaN and GaN/Al₂O₃ samples. Carrier lifetimes, extracted from time-resolved photoluminescence measurements, and internal quantum efficiencies, extracted from temperature-dependent photoluminescence measurements, are used to extract radiative and nonradiative lifetimes. Shockley–Read–Hall (A) and radiative recombination coefficients (B) are then calculated accordingly. Overall, the A coefficient is observed to be highly sensitive to the point defect density rather than dislocation density, as evidenced by three orders of magnitude reduction in threading dislocation density reducing the A coefficient by one order of magnitude only. The B coefficient, while comparable in the higher quality and lowly doped GaN/Al₂O₃ and HNPS GaN samples, was severely degraded in the GaN/Si sample due to high threading dislocation density and doping concentration.

1. Introduction

Gallium nitride (GaN) based devices find use in a wide range of photonics applications: Ultraviolet (UV) photodetectors [1], light emitting and laser diodes [2], and p-i-n betavoltaic cells [3]. The limited availability and high cost of freestanding substrates necessitates that GaN be heteroepitaxially grown on lattice-mismatched non-native substrates (i.e. sapphire, silicon carbide, and silicon). Such lattice mismatch generates high threading dislocation density (TDD ~10⁸–10¹⁰ cm⁻²) [4], which creates current leakage paths and non-radiative recombination centers in devices [5, 6]. Point defects such as vacancies and impurities (whose concentrations are typically dominated by material growth chemistry and conditions), have also been shown to degrade device performance [7]. The quantification of the effect of threading dislocations and point defects in GaN on recombination characteristics is important for the design of efficient GaN-based photonic devices.

In this study, structural, electrical, and optical properties of GaN crystals grown by multiple techniques (i.e. metalorganic chemical vapor deposition (MOCVD), high nitrogen pressure solution (HNPS), and
hydride vapor phase epitaxy (HVPE)) and on several common substrates (freestanding GaN, Al2O3, Si) are experimentally studied. Shockley-Read-Hall and radiative recombination in GaN on Al2O3, freestanding GaN, and GaN on Si samples are systematically studied and compared. We found the A coefficient to be strongly correlated to point defect density rather than TDD, while the B coefficient was found to be constant except for TDD > 10^{10} cm^{-2} and doping concentration >5 × 10^{18} cm^{-3}.

2. Experiment

Three GaN samples were studied in this work: a 5 µm thick GaN layer grown by MOCVD on sapphire (GaN/Al2O3 sample), a 325 µm thick freestanding GaN crystal grown by the HNPS method (HNPS GaN sample), and 500 nm thick GaN grown by HVPE on silicon with a 200 nm thick AlN buffer layer (GaN/Si). Growth conditions have been reported in the literature previously [8–10]. Structural characterizations (i.e. x-ray diffraction and secondary mass ion spectroscopy measurements) were conducted to quantify the defect and impurity densities. Electrical characterizations (i.e. van der Pauw Hall measurements) were conducted to extract the free carrier type and concentrations. Finally, optical characterizations (i.e. temperature-, time-resolved-, and power-dependent-photoluminescence measurements) were conducted to extract internal quantum efficiencies, carrier lifetimes, and A and B recombination coefficients.

3. Results

3.1. Structural characterization

Symmetric (002) and asymmetric (102) ω scans of GaN were conducted using a PANalytical Philips X’pert MRD System with 0.154056 nm Cu K-alpha 1 source to quantify the threading dislocation density (TDD) of each sample. Densities of screw (TDD_{screw}) and edge type (TDD_{edge}) dislocations were calculated by inputting experimentally measured (002) and (102) full-width-at-half-maximum (FWHM), β_{002} and β_{102}, into the following equations [11, 12]:

\[ \text{TDD}_{\text{screw}} = \frac{\beta^2_{002}}{4.35 b_{\text{screw}}^2} \]

\[ \text{TDD}_{\text{edge}} = \frac{\beta^2_{102} - \beta^2_{002}}{4.35 b_{\text{edge}}^2} \]  

where b_{edge} and b_{screw} are the Burgers vector lengths of 0.3189 and 0.5185 nm for edge- and screw-type dislocations, respectively, and β_{002} and β_{102} are in radians. Total TDD is found by summing TDD_{edge} and TDD_{screw}, which totals to (2.93 ± 0.02) × 10^9, (2.8 ± 0.1) × 10^9, and (5.59 ± 0.1) × 10^{10} cm^{-2} for the GaN/Al2O3, HNPS GaN, and GaN/Si samples studied in this work (table 1).

Secondary Ion Mass Spectroscopy (SIMS) measurements were used to determine the concentrations of Si, H, C, and O impurities in each GaN sample. A Physical Electronics TRIFT III Time of Flight SIMS with a 3 kV Ca^+ ion beam was utilized. The detector was set up to detect the negative secondary atomic ions, Si, H, C, and O, and the detection limits were 1 × 10^15, 7 × 10^16, 5 × 10^15, and 5 × 10^15 cm^{-3} for Si, H, C, and O, respectively. For the GaN/Al2O3 sample, H and C were found to be the dominant impurities with concentrations of 2.4 and 1.3 × 10^{15} cm^{-3}, respectively. For the HNPS GaN sample, Si was identified as the dominant impurity with a concentration of 3.0 × 10^{17} cm^{-3}. For the GaN/Si sample, Si, H, and C were found to be in the 10^{17} cm^{-3} range (table 1).

3.2. Electrical characterization

Room temperature free electron concentration (n_0) and Hall mobility (\mu_h) of each sample were determined by Hall effect measurements in Van der Pauw configuration using an Accent HL5500 PC Hall effect...
were found to be 1.3 cm defects, though earlier literature reports indicate that the HNPS growth method leads to a high for the highest cm is 4.66 eV for 266 nm excitation. This yields a maximum G of 4.9 decreased significantly with increasing cm is attributed to a combination of intrinsic V

Optical characterization

Power-dependent photoluminescence (PDPL) measurements were performed to investigate the nature of the GaN near-band-edge (NBE) emissions at room-temperature. A frequency-quadrupled continuous-wave Nd:YAG (266 nm) laser with a spot size of \( \sim 1800 \mu m^2 \) was implemented, and laser power (\( P_{\text{Laser}} \)) was varied from 0.1 to 3.5 mW via a crossed polarizer setup. This yielded an incident excitation intensity range of \( \sim 5-195 \) W cm\(^{-2} \). Sample luminescence was then collected via an Acton SP-300i spectrometer with 300 grooves mm\(^{-1} \) grating blazed at 500 nm and a CCD camera. The spectrometer resolution was 0.2 nm and, after calibrating the PL spectra to the UV peaks of a HgNe lamp, peak positions were accurate to within ±0.01 eV. The steady-state carrier concentration from the PL excitation was determined by first calculating the generation rate G, which can be found via [14]:

\[
G = \frac{P_{\text{Laser}}\alpha(1 - R)}{A_{\text{spot}}E_{\text{photon}}},
\]

where \( P_{\text{Laser}} \) is from 0.1–3.5 mW, \( \alpha \) is the absorption coefficient of GaN at 266 nm and is equal to 2.24 \( \times 10^{3} \) cm\(^{-1} \) [15], \( R \) is the reflectivity and was 0.11 for all 3 samples, \( A_{\text{spot}} \) is the laser spot size, and \( E_{\text{photon}} \) is 4.66 eV for 266 nm excitation. This yields a maximum G of 4.9 \( \times 10^{3} \) cm\(^{-3} \) s\(^{-1} \) for the highest excitation condition and, when multiplied by the effective carrier lifetimes determined later in the time-resolved experiment, yields a maximum steady-state carrier concentration of \( <1.7 \times 10^{16} \) cm\(^{-3} \) for all samples. Figure 1 plots the room-temperature PDPL spectra for GaN/Al\(_2\)O\(_3\), HNPS GaN, and GaN/Si samples, respectively, as \( P_{\text{Laser}} \) was increased from 0.1 to 3.5 mW.

For the GaN/Al\(_2\)O\(_3\) sample in figure 1(a), a yellow luminescence (YL) band was observed with a peak at \( \sim 2.25 \) eV, a slight blue luminescence (BL) band was observed around 2.8 eV, an ultraviolet luminescence (UVL) shoulder was observed at \( \sim 3.25 \) eV, and the NBE emission was observed at 3.42 eV. The YL band in the GaN/Al\(_2\)O\(_3\) sample was attributed to a combination of intrinsic \( V_{\text{Ga}} \) and extrinsic \( C_{\text{Ga}} \)-related defects, as both have been shown to contribute to YL luminescence in GaN [16]. The BL band in the GaN/Al\(_2\)O\(_3\) sample is attributed to carbon-related defects [17]. The UVL band was attributed to a free electron—shallow acceptor transition [18]. A peak at 3.35 eV, also observed as a weak, low-energy shoulder of the NBE for the HNPS GaN and GaN/Si samples, was attributed to a band-to-impurity transition [19]. For the HNPS GaN sample in figure 1(b), a strong YL band was observed with a peak at \( \sim 2.25 \) eV, and in addition to the NBE emission with a peak energy of 3.40 eV, a UVL peak was observed at \( \sim 3.25 \) eV. The intensity of the YL band in the HNPS GaN sample is strong, despite a lower C concentration in the HNPS GaN sample than that in the GaN/Al\(_2\)O\(_3\) sample (see table 1: 8 \( \times 10^{15} \) vs 1.3 \( \times 10^{17} \) cm\(^{-3} \)). It is difficult to separate YL emission from \( C_{\text{N}} \) and \( V_{\text{Ga}} \) defects, though earlier literature reports indicate that the HNPS growth method leads to a high density of \( V_{\text{Ga}} \) defects [20]. Given the stronger YL and lower C concentration, however, we believe the YL in
Figure 2. (color online) Room-temperature (300 K), power-dependent, spectrally integrated intensities of the (a) NBE luminescence, and (b) Defect Luminescence (YL + BL) for GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples. For the NBE luminescence and defect luminescence, the integrated intensities were over the energy intervals 3.2–3.55 and 1.75–3.1 eV, respectively. Power law fitting was conducted to determine the excitation dependencies for each sample, respectively. The shading represents the 90% confidence interval for each fit.

the HNPS GaN sample is attributed primarily to V$_{Ga}$ and its complexes. For the GaN/Si sample, (figure 1(c)), YL (at 2.25 eV), BL (at 2.8 eV), and NBE luminescence (at 3.38 eV) were observed. Similar to the GaN/Al$_2$O$_3$ sample, the YL in the GaN/Si sample was attributed to V$_{Ga}$ and C$_N$ complexes, and the BL to carbon-impurities. The silicon concentrations in the HNPS GaN and GaN/Si samples were determined to be nearly two orders of magnitude higher than in the GaN/Al$_2$O$_3$ sample. Moderate silicon concentrations have been shown to enhance YL emission [21], and high silicon concentrations have been shown to enhance the NBE/radiative recombination by contributing additional free carriers [22]. The silicon impurity concentrations of 3–4 × 10$^{17}$ cm$^{-3}$ in the HNPS GaN and GaN/Si samples are too low to significantly enhance the NBE/radiative recombination over the GaN/Al$_2$O$_3$ sample, however. At 10$^{17}$ cm$^{-3}$ levels, though, silicon may act to slightly enhance the YL intensity in the HNPS GaN and GaN/Si samples.

Next, the GaN NBE emissions were studied. The emission energy of the GaN NBE is slightly different for each sample: 3.42, 3.40, and 3.38 eV for the GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples, respectively. The difference in the NBE emission energy is due to the different strain state, with the GaN/Al$_2$O$_3$ and GaN/Si samples being under compressive and tensile residual strain from the heteroepitaxy, respectively. The compressive strain acts to increase the NBE emission energy while tensile strain decreases it, in agreement with our observations [23]. The exciton binding energy in GaN is on the order of ~25 meV [24], meaning that the GaN NBE at room temperature (kT ~26 meV) may be a superposition of band-to-band and excitonic transitions. The power-law dependences of defect-related luminescence (DL) and GaN NBE emission, obtained by varying the excitation intensity, are critical in understanding the SRH and NBE recombination characteristics of the GaN samples in this work. Figure 2(a) plots the integrated intensity of the room-temperature GaN NBE emission (I$_{NBE}^{GaN}$) vs P$_{Laser}$ for the three GaN samples. The integration was performed over the energy interval 3.2–3.55 eV, and I$_{NBE}^{GaN}$ was fit to the following equation to determine its excitation dependence:

$$I_{NBE}^{GaN} = A_1(P_{Laser})^\gamma,$$

where $\gamma$ is the power law coefficient for I$_{NBE}^{GaN}$ and $A_1$ is a fitting parameter. In the literature, $\gamma$ values of 1 and 2 for the GaN NBE emission have been associated with free exciton recombination and band-to-band recombination, respectively, while a $\gamma$ value in the range 1 to 2 is indicative of an intermediate system involving both recombination mechanisms [25]. For the GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples in this work, intermediate $\gamma$ values of ~1.63, 1.45, and 1.18 were derived, respectively.

The NBE peaks from exciton and band-to-band recombination should be separated by the exciton binding energy, but thermal and impurity broadening at room-temperature prevent the two peaks from being resolvable. The varying n$_0$ between samples obscures a direct comparison of the relative amount of free exciton/band-to-band recombination in each sample. Under the same n$_0$, a lower $\gamma$ implies a greater contribution from free exciton recombination in the room-temperature NBE makeup [25]. It has been reported in the literature, however, that a high n$_0$ can lead to a linear dependence of I$_{NBE}^{GaN}$ on P$_{Laser}$ [26], which masks the true amount of free exciton and band-to-band recombination in the GaN/Si sample (which
and (5) cm$^{-0.11}$ for the GaN samples.

Using the TRPL setup, and using $R$ and HNPS GaN samples have $\tau_{eff}$ and C sample, shows normalized TRPL decay curves for each sample. was fit to the following equation to determine its excitation dependence:

$$I(t) = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2),$$

where $\chi$ is the power law coefficient for $I_{DL}$. $I_{DL}$ values of 41 ($266$ nm, spot size $10\times10^3$ mm$^2$, pulse width $150$ fs, $1$ nJ per pulse) and a Hamamatsu streak camera with a temporal resolution of $\Delta t = 5\times10^{-14}$ cm$^{-3}$. The integration was performed over the energy interval $1.75$–$3.1$ eV to sum contributions from both the YL and BL bands, and $I_{DL}$ was fit to the following equation to determine its excitation dependence:

$$I_{DL}^GaN = A_2 (P_{Laser})^{\chi},$$

where $\chi$ is the power law coefficient for $I_{DL}^GaN$, and $A_2$ is a fitting parameter. For the GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples in this work, $\chi$ values of $\sim0.70$, $0.68$, and $0.96$ were derived, respectively. In the case of the GaN/Si sample, the $\chi$ value is very close to 1, indicating unsaturated trap center behavior. However, the GaN/Al$_2$O$_3$ and HNPS GaN samples have $\chi$ values closer to 0.5, indicating that the defect luminescence centers are getting saturated. This behavior is attributed to a lower concentration of traps in the higher-quality GaN/Al$_2$O$_3$ and HNPS GaN samples, which leads to saturation of the $I_{DL}$. In contrast, as the lower-quality GaN/Si sample has a higher trap concentration, defect PL in this sample is unsaturated.

Time-resolved photoluminescence (TRPL) measurements were conducted to determine effective carrier lifetimes $\tau_{eff}$. A spectral interval from $3.3$–$3.6$ eV was chosen to measure the luminescence decay of the NBE emission in each sample. The TRPL setup consisted of a $2$-kHz repetition rate, frequency-tripled Ti:Al$_2$O$_3$ laser ($\lambda = 266$ nm, spot size $0.17$ mm$^2$, pulse width $150$ fs, $1$ nJ per pulse) and a Hamamatsu streak camera with a temporal resolution of $\sim1$ ps. The excited carrier concentration $n$ was therefore found to be $\sim1.6 \times 10^{17}$ cm$^{-3}$. Figure 3 shows normalized TRPL decay curves for each sample.

For the GaN/Al$_2$O$_3$ and HNPS GaN samples, a biexponential decay was observed. Biexponential decay behavior has been reported in literature for GaN before, and has been attributed to capture at multiple deep levels [29]. For $266$ nm excitation, carriers are mostly generated within $100$ nm of the surface since the absorption coefficient of GaN is roughly $2.24 \times 10^5$ cm$^{-1}$. Therefore, the biexponential decay was attributed to a fast component representing nonradiative decay at the surface states, and a slower nonradiative decay representative of the bulk nonradiative recombination [30]. The TRPL decay for the GaN/Al$_2$O$_3$ and HNPS GaN samples were thus fit to the following function:

$$I(t) = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2),$$

where $\tau_1$ and $\tau_2$ represent the fast and slow decay lifetimes, and $C_1$ and $C_2$ are the fast and slow decay amplitudes. For the GaN/Al$_2$O$_3$ sample, $\tau_1$ and $\tau_2$ values of $56$ ($\pm4$) and $380$ ($\pm14$) ps were calculated. For the HNPS GaN sample, $\tau_1$ and $\tau_2$ values of $41$ ($\pm1$) and $302$ ($\pm14$) ps were calculated (table 2). For the GaN/Si sample, a monoexponential decay was observed, and $\tau_1$, (equal to $\tau_{eff}$), was calculated to be $20$ ($\pm1$)
ps (table 2). The monoexponential decay for the highly defective GaN/Si sample is due to the overall recombination rate being dominated by nonradiative recombination at the surface. For the GaN/Al$_2$O$_3$ sample, both $\tau_1$ and $\tau_2$ were longer than for the HNPS GaN sample, indicative of a higher quality surface and bulk.

Due to the biexponential decay of the GaN/Al$_2$O$_3$ and HNPS GaN samples, it was necessary to derive a single $\tau_{eff}$ for later calculations of the radiative and nonradiative lifetimes. Here, $\tau_{eff}$ is calculated via the averaging of the time over the intensity decay curve [31]:

$$\tau_{eff} = \frac{\int t \times I(t) \, dt}{\int I(t) \, dt}. \quad (7)$$

For a biexponential decay model, equation (6) can be substituted for $I(t)$ in equation (7), allowing $\tau_{eff}$ to be calculated as [31]:

$$\tau_{eff} = \frac{C_1 \tau_1^2 + C_2 \tau_2^2}{C_1 \tau_1 + C_2 \tau_2}, \quad (8)$$

which yields $\tau_{eff}$ of (342 ± 12) and (221 ± 11) ps for the GaN/Al$_2$O$_3$ and HNPS GaN samples, respectively. $C_1$ and $C_2$, $\tau_1$ and $\tau_2$, and $\tau_{eff}$ for all samples are listed in table 2.

Temperature-dependent photoluminescence (TDPL) was conducted with the addition of a liquid He bath cryostat and a PID temperature controller to allow the temperature to be varied from 1.4 to 300 K to determine the internal quantum efficiencies ($\eta_{IQE}$), and finally extract the A and B coefficients for each sample. The traditional ABC model used to study steady-state carrier recombination in semiconductors is expressed via [32]:

$$G = A n + B n^2 + C n^3, \quad (9)$$

where $G$ is the generation rate and is equal to the recombination rate in the steady-state, $n$ is the carrier concentration, $A$ is the SRH recombination coefficient, $B$ is the radiative coefficient, and $C$ is the Auger recombination coefficient. In quantum well structures the carrier leakage may contribute to second, third, and higher-order terms as well [33], though these can be ignored for the study of bulk materials. The ratio of radiative recombination to the overall rate of recombination is then used to calculate $\eta_{IQE}$ via [32]:

$$\eta_{IQE} = \frac{B n^2}{G}. \quad (10)$$

At sufficiently low temperatures (i.e. 1.4 K), $\eta_{IQE}$ is assumed to be unity due to the thermal deactivation of SRH recombination centers [34], and $\eta_{IQE}$ was thus calculated via the low-temperature high temperature (LT-HT) method [35]:

$$\eta_{IQE} = \frac{I(300 K)}{I(1.4 K)} \times 100\%, \quad (11)$$

where $I$ (300 K) and $I$ (1.4 K) are the spectrally integrated PL intensities of the GaN NBE emission at 300 K and 1.4 K, respectively. The integration was performed over the energy interval of 3.3–3.55 eV for the 1.4 K emissions, and 3.2–3.55 eV for the 300 K emissions. The lower integration limit for the 300 K NBE emissions was shifted downward to account for the decrease in bandgap with increasing temperature. There have been reports that $\eta_{IQE}$ at low temperatures (∼5 K) is not precisely unity, but rather close to unity (∼0.9) when samples have sufficiently high concentrations of SRH centers, and the average distance between them is on the order of the exciton Bohr diameter [36]. Here our measurements are conducted at even lower temperatures (1.4 K) and the GaN/Al$_2$O$_3$ and HNPS GaN samples exhibited saturated SRH behavior in figure 2(b), which indicates a lower defect concentration, and thus indicates that the assumption of unity

### Table 2. Decay fitting constants derived from time resolved photoluminescence measurements: Fast and slow decay amplitudes ($C_1$ and $C_2$), fast and slow decay lifetimes ($\tau_1$ and $\tau_2$), and overall effective lifetime ($\tau_{eff}$) for GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples.

| Sample          | $C_1$   | $C_2$   | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_{eff}$ (ps) |
|-----------------|---------|---------|---------------|---------------|-------------------|
| GaN/Al$_2$O$_3$ | 0.47    | 0.52    | 56 ± 4        | 380 ± 14      | 342 ± 12          |
| HNPS GaN        | 0.79    | 0.24    | 41 ± 1        | 302 ± 14      | 221 ± 11          |
| GaN/Si          | 1       | n/a$^{-1}$ | 20 ± 1   | n/a$^{-1}$   | 20 ± 1            |
Figure 4. (color online) Normalized low- (1.4 K) and room- (300 K) temperature PL spectra of GaN/Al₂O₃, HNPS GaN, and GaN/Si samples. Dashed lines represent the room-temperature PL (scaled up by 20 times for viewing), while solid lines represent the low-temperature PL. For each sample, η_{IQE} was calculated by taking the ratio of the integrated GaN NBE intensities at low- and room-temperature. The increase in room-temperature PL intensity on the low-energy side of the HNPS GaN spectrum is due to the UVL peak (see figure 1(b)).

Table 3. Internal quantum efficiency (η_{IQE}), effective carrier lifetime (τ_{eff}), nonradiative lifetime (τ_{nonrad}), radiative lifetime (τ_{rad}), Shockley-Read-Hall recombination coefficient (A) and radiative recombination coefficient (B) of GaN/Al₂O₃, HNPS GaN, and GaN/Si samples.

| Sample      | η_{IQE} (%) | τ_{eff} (ps) | τ_{nonrad} (ps) | τ_{rad} (ns) | A (10⁹ s⁻¹) | B (10⁻¹⁰ cm³ s⁻¹) |
|-------------|-------------|--------------|-----------------|-------------|-------------|------------------|
| GaN/Al₂O₃  | 9.6         | 342 ± 12     | 378 ± 13        | 3.56 ± 0.12 | 2.6 ± 0.1    | 9.7 ± 0.3        |
| HNPS GaN   | 7.9         | 221 ± 11     | 240 ± 12        | 2.80 ± 0.14 | 4.2 ± 0.2    | 9.2 ± 0.5        |
| GaN/Si     | 1.9         | 20 ± 1       | 20 ± 1          | 1.05 ± 0.05 | 49.0 ± 0.5    | 1.4 ± 0.1        |

η_{IQE} at 1.4 K for these two samples is acceptable. For the GaN/Si sample with high defectivity, however, SRH saturation behavior was not observed, and η_{IQE} calculated by the LT-HT method may be overestimated. The implications of this η_{IQE} overestimation for the GaN/Si sample will be discussed later.

Figure 4 shows the normalized PL spectra of all samples at 1.4 and 300 K. For each sample, the 1.4 and 300 K emissions were normalized to the highest intensity PL peak in the 1.4 K PL spectra. For better visualization, the 300 K PL spectra for all samples were scaled up by 20 × . The η_{IQE} values of the GaN/Al₂O₃, HNPS GaN, and GaN/Si samples were determined as 9.6, 7.9, and 1.9%, respectively. Given the use of the unity η_{IQE} assumption at low temperature, these are upper bound values.

Using extracted η_{IQE} and τ_{eff}, the radiative lifetime τ_{rad} can be found via [35]:

\[ \tau_{rad} = \frac{\tau_{eff}}{\eta_{IQE}} \]

which yields τ_{rad} of 3.56 (±0.12), 2.80 (±0.14), and 1.05 (±0.05) ns for the GaN/Al₂O₃, HNPS GaN, and GaN/Si samples, respectively (table 3). In TRPL measurements, excited carriers recombine either radiatively or nonradiatively, both contributing in parallel to the effective lifetime [36]:

\[ \tau_{eff} = \tau_{rad}^{-1} + \tau_{nonrad}^{-1} \]

where τ_{nonrad} is the nonradiative lifetime. Nonradiative lifetimes of 378 (±13), 240 (±12), and 20 (±1) ps for the GaN/Al₂O₃, HNPS GaN, and GaN/Si samples were derived, respectively (table 3). The A and B coefficients can be extracted via [37]:

\[ A = \frac{1}{\tau_{nonrad}} \]  \[ B = \frac{1}{\tau_{rad}(n_0 + \Delta n)} \]

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where $\Delta n$ was $1.6 \times 10^{17}$ cm$^{-3}$. A coefficients for the GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples were thus calculated to be $2.6 \pm 0.1 \times 10^9$, $4.2 \pm 0.2 \times 10^9$, and $4.9 \pm 0.5 \times 10^{10}$ s$^{-1}$, respectively. B coefficients for the GaN/Al$_2$O$_3$, HNPS GaN, and GaN/Si samples were calculated to be $9.7 \pm 0.3 \times 10^{-10}$, $9.2 \pm 0.5 \times 10^{-10}$, and $1.4 \pm 0.1 \times 10^{-10}$ cm$^3$ s$^{-1}$, respectively. The experimentally determined B coefficient for the GaN/Al$_2$O$_3$ and HNPS GaN samples are higher than the B coefficient for GaN calculated from first principles via Fermi’s golden rule ($\sim 1 \times 10^{-10}$ cm$^3$ s$^{-1}$) [38]. However, they are closer to a theoretically determined B coefficient of $7 \times 10^{-10}$ cm$^3$ s$^{-1}$ for a coupled exciton free-carrier system with Coulomb correlation considered [39]. The calculated B coefficient for the GaN/Si sample is roughly 6 times lower than for the other two samples, though in reality is significantly smaller due to the overestimation of $\eta_{\text{IQE}}$. Table 3 summarizes all the optical data.

4. Discussion

Comparing A coefficients between samples, the A value for the HNPS GaN sample is almost 2 times as high as the GaN/Al$_2$O$_3$ sample ($2.6$ vs $4.2 \times 10^9$ s$^{-1}$) despite an over 10-fold reduction in TDD and a nearly two orders of magnitude lower carbon content. This suggests that threading dislocations and carbon are not responsible for the high A coefficient in this sample. A possible culprit is V$_{Ga}$ point defects, which based on the high YL intensity observed in the room-temperature photoluminescence spectra, may be present in high concentration [16]. It would appear that TDD in the range $10^7$–$10^8$ cm$^{-2}$ does not significantly affect the A coefficient. This agrees with the literature [7, 29], which reported that the gross concentrations of V$_{Ga}$ point defects and complexes determined the nonradiative lifetime and A coefficient of GaN [7]. Beyond a TDD of $10^8$ cm$^{-2}$, however, TDD begins to dominate the A coefficient behavior, as evidenced by the large increase in the A coefficient for the GaN/Si sample with TDD $> 10^{10}$ cm$^{-2}$[6].

Comparing B coefficients between samples, the B coefficient for the GaN/Si sample is severely reduced by a factor of six compared to the higher quality and less-doped GaN/Al$_2$O$_3$ and HNPS GaN samples, where the B coefficients were the same. High doping levels can significantly reduce the B coefficient via screening of the B coefficient for the GaN/Al$_2$O$_3$ and HNPS GaN samples were calculated to be $9.7 \pm 0.3 \times 10^{-10}$, $9.2 \pm 0.5 \times 10^{-10}$, and $1.4 \pm 0.1 \times 10^{-10}$ cm$^3$ s$^{-1}$, respectively. The experimentally determined B coefficient for the GaN/Al$_2$O$_3$ and HNPS GaN samples are higher than the B coefficient for GaN calculated from first principles via Fermi’s golden rule ($\sim 1 \times 10^{-10}$ cm$^3$ s$^{-1}$) [38]. However, they are closer to a theoretically determined B coefficient of $7 \times 10^{-10}$ cm$^3$ s$^{-1}$ for a coupled exciton free-carrier system with Coulomb correlation considered [39]. The calculated B coefficient for the GaN/Si sample is roughly 6 times lower than for the other two samples, though in reality is significantly smaller due to the overestimation of $\eta_{\text{IQE}}$. Table 3 summarizes all the optical data.

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5. Conclusion

In summary, GaN samples grown by MOCVD, HNPS, and HVPE methods on different substrates were experimentally studied to compare the A and B recombination coefficients. XRD, Hall Effect, and SIMS were used to quantify defect and impurity densities. Power-dependent photoluminescence revealed mixed free-exciton and band-to-band recombination in the GaN NBE emission of all samples and revealed unsaturated luminescence from defects in the GaN/Si sample. Time-resolved and temperature-dependent photoluminescence techniques were then used to extract carrier lifetimes, internal quantum efficiencies, and the A and B recombination coefficients. It is observed that even when the TDD is lowered by three orders of magnitude from $10^7$ cm$^{-2}$, the A coefficient in GaN remains on the order of $10^9$ s$^{-1}$ due to nonradiative recombination at point defects, indicating that further performance gains for devices must focus on point defect reduction through optimized growth conditions. In addition, the GaN/Si sample was found to have a B coefficient six times lower than the other samples due to high defectivity and doping (TDD $> 10^7$ cm$^{-2}$ and free electron concentration > $5 \times 10^{18}$ cm$^{-3}$). The GaN/Al$_2$O$_3$ and HNPS GaN samples, which had lower TDD in the range $10^7$–$10^8$ cm$^{-2}$ and doping $\sim 10^{17}$ cm$^{-3}$, exhibited a similar B coefficient of $\sim 9.5 \times 10^{-10}$ cm$^3$ s$^{-1}$, indicating that the B coefficient is constant in higher-quality and lower-doped GaN.

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References

[1] Binet F, Duboz J Y, Rosencher E, Scholz F and Harle V 1996 Appl. Phys. Lett. 69 1202–4
[2] DenBaars S P et al 2013 Acta Mater. 61 945–51
[3] Khan M R et al 2017 Solid. State. Electron. 136 24–9
[4] Bennett S E 2010 Mater. Sci. Technol. 26 1017–28
[5] Hsu J W P, Manfra M J, Chu S N G, Chen C H, Pfieffer L N and Molnar R J 2001 Appl. Phys. Lett. 78 3980–2
[6] Sugahara T, Sato H, Hao M, Naoy S, Kurasi S, Tottori S, Yamashita K, Nishino K, Romano I T and Sakai S 1998 Jpn. J. Appl. Phys. 37 398–400
[7] Chichibu S F, Uedono A, Onuma T, DenBaars S P, Mishra U K, Speck J S and Nakamura S 2009 Mater. Sci. Forum. 590 233–48
[8] Wang T, Shirahama T, Sun H B, Wang H X, Bai J, Sakai S and Misawa H 2000 Appl. Phys. Lett. 76 2220–2
[9] Porowski S 1996 J. Cryst. Growth 166 585–9
[10] Zhang J X, Qu Y, Chen Y Z, Uddin A and Yuan S 2005 J. Cryst. Growth 282 137–42
[11] Moram M A and Vickers M E 2009 Rep. Prog. Phys. 72 036502
[12] Liu R, McCormick C and Bayram C 2019 AIP Adv. 9 025306
[13] Huang Y M, Spence J C H and Sankey O F 1995 Phys. Rev. Lett. 74 3392
[14] Dai Q et al 2009 Appl. Phys. Lett. 94 111109
[15] Kawashima T, Yoshikawa H, Adachi S, Fujie S and Ohatsuka K 1997 J. Phys. D: Appl. Phys. 82 3528
[16] Lyons J L, Alkauskas A, Janotti A and Van de Walle C G 2015 Phys. Status Solidi B 252 900–8
[17] Armitage R, Yang Q and Weber E R 2005 J. Phys. D: Appl. Phys. 38 113524
[18] Reshchikov M A and Morkoc H 2005 J. Phys. D: Appl. Phys. 38 061301
[19] Kamytczyc P, Placzek-Popko E, Zytkiewicz Z R, Zielony E and Gumienny Z 2014 J. Phys. D: Appl. Phys. 47 115312
[20] Gregorzy I 2001 J. Phys. Condens. Matter 13 6875
[21] Liang F, Zhao D, Jiang D, Liu Z, Zhu J, Chen P, Yang J, Liu S, Xing Y and Zhang J L 2018 Nanomaterials 8 1026
[22] Schubert E F, Goepfert I D, Grieshaber W and Redwing J M 1997 Appl. Phys. Lett. 71 921–3
[23] Park B G, Saravana Kumar R, Moon M L, Kim M D, Kang T W, Yang W C and Kim S G 2015 J. Cryst. Growth 425 149–53
[24] Reimann K, Steube M, Frohlich D and Clarke S J 1998 J. Cryst. Growth 189–190 652–5
[25] Chen X B, Huso J, Morrison J L and Bergman L 2006 J. Phys. D: Appl. Phys. 39 046105
[26] Grieshaber W, Schubert E F, Goepfert I D, Karlicek R F, Schuman M J and Tran C 1996 J. Phys. D: Appl. Phys. 29 1561–20
[27] Shockley W and Read W T 1952 Phys. Rev. 87 835–42
[28] Hall R N 1952 Phys. Rev. 87 387
[29] Izumi T, Narukawa Y, Okamoto K, Kawakami Y, Fujita S and Nakamura S 2000 J. Lumin. 87 1136–8
[30] Ozgur U, Fu Y, Moon Y T, Yun F, Morko H, Everitt H O, Park S S and Lee K Y 2005 Appl. Phys. Lett. 86 232106
[31] Lakowicz J R 2006 Principles of Fluorescence Spectroscopy (Boston, MA: Springer US) pp 99 142
[32] Grundmann M 2016 The Physics of Semiconductors (Berlin: Springer) p 574
[33] Dai Q, Shan Q, Wang J, Chihade S, Cho J, Schubert E F, Crawford M H, Koleske D D, Kim M H and Park Y 2010 Appl. Phys. Lett. 97 133507
[34] Narukawa Y, Kawakami Y, Fujita S and Nakamura S 1999 Phys. Rev. B 59 10283
[35] Im J S, Moritz A, Steuber F, Harle V, Scholz F and Hangleiter A 1997 Appl. Phys. Lett. 70 631–3
[36] Chichibu S F, Uedono A, Kojima K, Ikeda H, Fujito K, Takashima S, Edo M, Ueno K and Ishihashi S 2018 J. Phys. D: Appl. Phys. 123 161131
[37] Liu W, Butt B, Dussainge A, Grandjean N, Deveaud B and Jacopin G 2016 Phys. Rev. B 94 195411
[38] Kioupakis E, Yan Q, Steihaa D and Van De Walle C G 2013 New J. Phys. 15 125006
[39] Brandt O, Wiinsche H J, Yang H, Klann R, Mullhauser I J and Ploog K H 1998 J. Cryst. Growth 189–190 790–3
[40] Matsy M, Mizcek M, Adamowicz B, Zytkiewicz Z R, Kamińska E, Piotrowska A and Hashizume T 2011 Acta Phys. Pol. A 120 73–7
[41] Yu J, Hao Z, Li L, Wang L, Luo Y, Wang J, Sun C, Han Y, Xiong B and Li H 2017 AIP Adv. 7 035321