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Transient photoluminescence of defect transitions in freestanding GaN

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Deep level defects responsible for the 2.4 eV photoluminescence (PL) band in a freestanding GaN template were studied by transient photoluminescence. A nonexponential decay of PL intensity observed at low temperature is attributed to a donor–acceptor pair recombination involving a shallow donor and a deep acceptor. At room temperature, a single-exponential PL decay with a lifetime of 30 μs was observed at the high-energy side of the band, whereas the second component with a lifetime of about 750 μs was detected at the low-energy side of the band. The PL decay and transformation of the PL spectrum at room temperature can be explained by transitions from the conduction band to two deep acceptors. Electron-capture cross section has been estimated as 4×10^{-21} and 10^{-19} cm^2 for the yellow and green bands, respectively, contributing to the broad 2.4 eV band. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1370119]

Yellow luminescence (YL) remains the most controversial object affecting optical properties of GaN. YL is a broad band with a maximum at about 2.1–2.4 eV, which is universally observed in *n*-type wurtzite GaN. The exact position of this band and its full width at half maximum (FWHM) differ slightly in numerous publications. Several attempts to describe this band as a point defect subject to strong electron–phonon coupling have been made.[1–3] However, variation of position and shape of the YL band in different studies suggests that several point defects can contribute to this emission. Transient photoluminescence (PL) is helpful in the determination of defect properties and sometimes it provides a key for defect identification. There is major controversy between the transient PL decay times measured by different research groups for YL. For example, Hoffman *et al.*[4] and Korotkov *et al.*[5] reported nonexponential decay of the YL in the range 10^{-1}–10^3 μs at cryogenic temperatures. This decay was quantitatively described in the Thomas–Hopfield model[6] of the donor–acceptor pair (DAP) recombination. A very long lived emission with maximum at 2.35 eV and decay time of about 300 ms at 10 K has been observed by Seitz *et al.*[7] In contrast, very fast decay of the YL has been reported in Refs. 8 and 9. A decay time of about 1 ns was observed at 2 K and related to strong contribution of free-to-bound transitions.[8] Even a faster decay at room temperature, 20 ps, has been reported by Haag *et al.*[9] and attributed to the DAP recombination.

In this letter, we report on a study of time-resolved PL in a freestanding GaN with very low concentration of point defects. The decay of the broad PL band with a maximum at about 2.4 eV has been analyzed at different temperatures and several recombination mechanisms were considered.

Thick GaN layers were grown by hydride vapor phase epitaxy on *c*-plane sapphire substrate and then thermally separated from the substrate by a laser beam. The N face of the freestanding template (forming the interface with sapphire) was only mechanically polished, whereas the Ga face was polished and dry etched to a smooth ''epiready'' surface. The thickness of the GaN template was about 200 μm. The concentration of free electrons (n_0) and their mobility (μ_n), obtained from the Hall effect measurements at room temperature, are 1.3×10^{16} cm^{-3} and $\sim$1200 cm^2 V^{-1}s^{-1}, respectively. PL was excited either with a cw He–Cd laser (photon energy 3.81 eV) or a pulsed nitrogen laser (4 ns pulses with 20 Hz repetition and photon energy of 3.68 eV). The spectra were analyzed with a SPEX grating monochromator with a Hamamatsu photomultiplier tube R955. Neutral density filters were used to attenuate the excitation density. The pump density was in the range of 10^{-3}–1 W/cm^2 for cw excitation and $\sim10^2$–10^4 W/cm^2 for pulsed excitation. The temperature of the sample investigated varied from 15 to 295 K with the aid of a closed cycle cryostat.

To elucidate the mechanism of the radiative recombination and carry out a quantitative estimation of the radiative capture cross section, we analyzed the temperature dependence of the electron concentration and mobility. From the fit of the temperature dependence of the electron mobility, accounting for applicable scattering mechanisms, we have estimated[10] the upper limit of the total acceptor concentration to be 2.4×10^{15} cm^{-3}. The concentration of a shallow donor and its activation energy have been calculated as 1.6×10^{16} cm^{-3} and about 26 meV, respectively, from the temperature dependence of the free electron concentration. Note also that the electron concentration decreased from 1.3×10^{16} to $\sim10^{12}$ cm^{-3} as the sample temperature varied from 273 to 25 K, whereas the concentration of the shallow donor in neutral state, N_D, increased from about 5×10^{14} to 1.3×10^{16} cm^{-3} in this temperature range.[10] From these Hall effect data, we expect that the DAP-type transitions involving a shallow donor dominate at low temperatures due to the extremely low concentration of the equilibrium electrons in the conduction band. On the other hand, the free-to-bound

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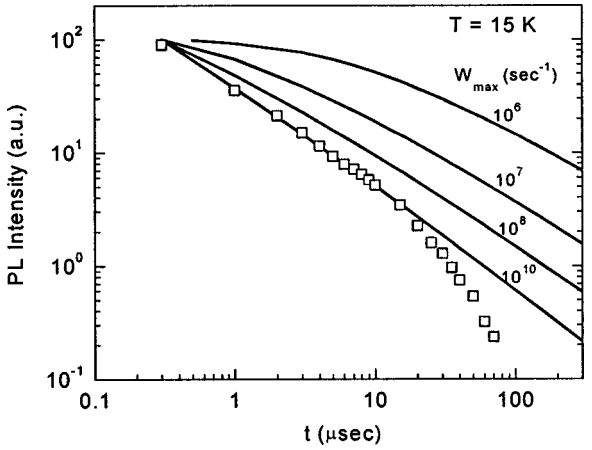

FIG. 1. Normalized intensity decay of the 2.4 eV band at 15 K. The solid curves are calculated using Eq. (2) with the following parameters: a_D=25 Å; $N_D=1.6\times10^{16}$ cm^{-3} and W_{max} as noted near the curves.

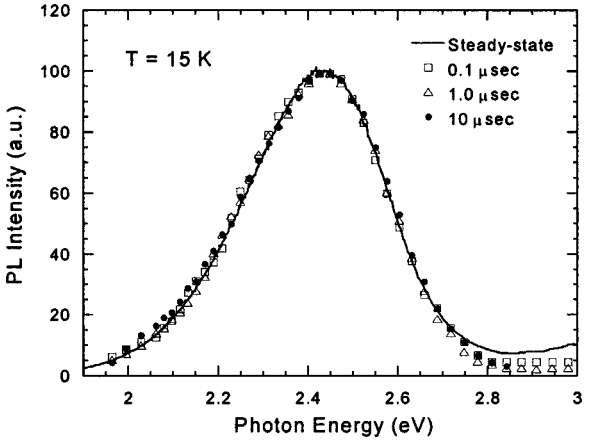

FIG. 2. Steady-state PL spectrum (solid curve) and transient PL spectrum (points) for time delays of 10^{-7}, 10^{-6}, and 10^{-5} s at 15 K. All spectra are normalized to their respective maxima.

transitions (*eA* transitions) may become dominant at room temperature since the concentration of free electrons substantially exceeds the concentration of the neutral donors.

Steady-state PL spectrum measured at 15 K exhibited a set of sharp peaks in the excitonic region with the highest peak being at 3.471 eV (FWHM=1.0 meV) and two defect-related bands. The excitonic transition has been attributed to a neutral shallow donor bound exciton. The two defect-related bands comprise a broad green band with a maximum at about 2.4 eV and the so-called shallow DAP band with the main peak at 3.255 eV. The shallow DAP band exhibited a transformation to the *eA* band in the temperature range 25–50 K, from which the ionization energy of the shallow donor has been estimated as 27.5 meV.[11]

The PL intensity decay of the 2.4 eV band at 15 K is shown in Fig. 1. It is nonexponential with an instantaneous lifetime increasing from about 1 to 20 μs with time delay. A very similar decay was observed when the excitation intensity was varied about 3 orders of magnitude. We have attributed the nonexponential decay of the DAP-type recombination as described in the Thomas–Hopfield model,[6] where the radiative recombination rate W depends on the donor and acceptor separation R,

$$W(R)=W_{\max}\exp\left(-\frac{2R}{a_D}\right), \tag{1}$$

where W_{max} is the transition rate in the limit $R\rightarrow0$ and a_D is the Bohr radius for the donor. We have estimated a_D=25 Å for the shallow donor in the effective mass approximation. Then the PL intensity decay $I(t)$ after the pulse excitation was fitted by the Thomas–Hopfield expression[6]

$$I(t)=4\pi N_D\left[\int_0^\infty W(R)e^{-W(R)t}R^2dR\right]\times\left\{\exp\left[4\pi N_D\int_0^\infty(e^{-W(R)t}-1)R^2dR\right]\right\}, \tag{2}$$

where N_D is the donor concentration and was taken to be 1.6×10^{16} cm^{-3}, and the only fitting parameter was W_{max}. The set of calculated curves with different W_{max} demonstrates that the best fit for a time delay below 15 μs is obtained with $W_{max}\approx10^{10}$ s^{-1} (Fig. 1), yet the decay in the range of 15–70 μs is still faster than the theory. The later may evidence that some alternative recombination mechanism contributes to the low-temperature emission. Note that W_{max} in our fit is much larger than that obtained for the YL band by Hoffman *et al.* (2.5×10^7 s^{-1}),[4] and Korotkov *et al.* (1.6×10^6 s^{-1}).[5]

To be sure that the obtained decay is related to one PL band only, we have measured the PL spectrum for time delays (t) up to 10 μs and compared it with the steady-state PL spectrum (Fig. 2). Evidently, the same band (green) contributes to the decay in the range of 0.1–10 μs. No energy shift of the band has been observed to an accuracy of 30 meV. This is consistent with the assertion that the DAP transitions involve a shallow donor.[12]

With increasing temperature, the decay curve approaches an exponential one and the PL lifetime increases. Finally, the room temperature decay is exponential up to 100 μs with a characteristic time of about 30 μs (Fig. 3). For longer time delays, we also observed a much slower second component of the PL decay (Fig. 3). The slow component could be detected at photon energies below ~2.5 eV and the spectrum for long time delays revealed the yellow band with the maximum at about 2.1 eV (Fig. 4). Previously, two bands with their maxima at about ~2.15 and 2.43 eV have been

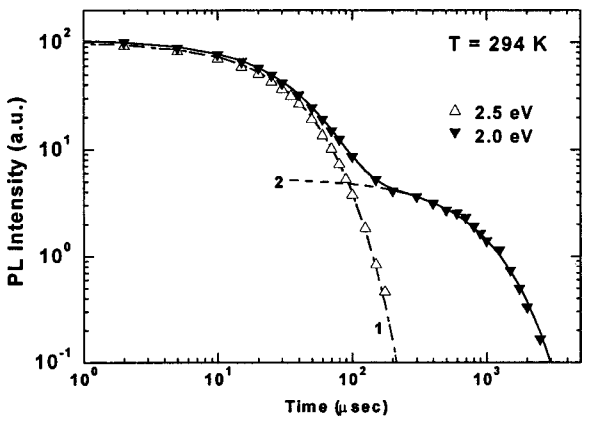

FIG. 3. Normalized PL intensity decay of the 2.4 eV band at room temperature at photon energies of 2.0 and 2.5 eV. The dashed-line fits are indicative of exponential decay with time constants of 30 μs (1) and 750 μs (2). The solid curve represents the sum of curves (1) and (2).

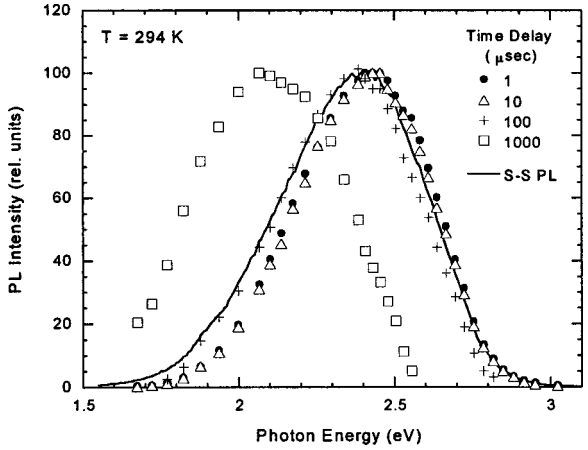

FIG. 4. Steady-state PL spectrum (solid curve) and transient PL spectrum (points) for time delays of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} s at 294 K. All spectra are normalized to their respective maximum.

revealed in a freestanding GaN template in experiments with varying excitation intensity and energy.[13]

We attribute the evolution of the PL decay with temperature to a change in the recombination mechanism. With increasing temperature, the concentration of free electrons increases, whereas the concentration of neutral donors decreases, and the DAP-type transitions give way to *eA*-type transitions. We can estimate the electron-capture cross section σ_n for the studied defects from the room-temperature decay of emission related to the yellow and green bands. Indeed,[14,15]

$$\sigma_n = (n \tau_R V_{\text{th}})^{-1}, \tag{3}$$

where n is the concentration of electrons in the conduction band, τ_R is the PL lifetime and $V_{\text{th}} = (8k_B T/\pi m^*)^{1/2}$ is the thermal velocity of electrons with the effective mass m^* in the conduction band. The exponential character of the PL decay and independence of τ_R on the excitation intensity in our experiments implies that τ_R is determined be equilibrium (dark) concentration of electrons in the conduction band, i.e., $n = n_0$. Taking $n = 1.3 \times 10^{16}$ cm^{-3} and $\tau_R = 30$ and 750 μs for the green and yellow bands, respectively, we have estimated $\sigma_n = 10^{-19}$ and 4×10^{-21} cm^2 for defects responsible for the green and yellow bands. The value of σ_n for the yellow band obtained in this work is very close to that in undoped GaN samples grown by metalorganic vapor phase epitaxy (2.7×10^{-21} cm^2) (Ref. 16) and it is much smaller than the cross section for the green band. This is consistent with our observation at 15 K that $W_{\max}$ for the green band in this work is much larger than that for the yellow band obtained in Refs. 4 and 5. Indeed, the parameters σ_n and $W_{\max}$ are linked since both describe the ability of the defect to capture an electron. For example, in the effective-mass approximation $\sigma_n V_{\text{th}} = \pi a_D^3 W_{\max}$ (Ref. 17).

The results of this and previous[13] investigations evidence that two deep defects contribute to the broad PL band with the combined maximum between ~2.1 and 2.4 eV in our freestanding GaN template. These defects have different concentrations and different capture characteristics. However, our data alone are not sufficient for identification of the defects responsible for the yellow and green bands in the studied sample.

In conclusion, the transient decay behavior of the broad PL band with a maximum at about 2.4 eV in freestanding GaN template at different temperatures was reported. At temperatures below 40 K, the decay is nonexponential and has been explained in the framework of the Thomas–Hopfield model for DAP-type recombination involving shallow donors. At elevated temperatures, the decay becomes exponential with two components revealing fast recombination (30 μs) of the green band and slow recombination (750 μs) of the yellow band. We attribute the room-temperature emission to transitions from the conduction band to two deep acceptors. The electron-capture cross section by acceptors responsible for the yellow and green bands was deduced to be about 4×10^{-21} and 10^{-19} cm^2, respectively.

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