Long-lasting photoluminescence in freestanding GaN templates

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We studied time-resolved photoluminescence (PL) over a temporal range 10^{-6}–10^{3} s in high-purity freestanding GaN templates. Red, yellow, green, blue, and shallow donor–acceptor emission bands can be resolved in the PL spectrum. Observation of luminescence long after the excitation is switched off is a striking feature of our study. The persistent PL observed for all above bands, except for the green band, is primarily attributed to the donor–acceptor-pair-type recombination. An unusually slow, nonexponential decay of radiative transitions from the conduction band to the shallow acceptor was also observed, pointing to some additional mechanism for the persistent PL. Possible role of the surface states in this effect is discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1589194]

In recent years, significant progress has been made in the growth of high-purity freestanding GaN templates that can be used as substrates for GaN epitaxial layers and devices of superior quality.[1] However, little is known about carrier recombination mechanisms in these materials. Photoluminescence (PL), and in particular time-resolved PL (TR-PL), is a strong tool for the study of recombination dynamics involving point defects in semiconductors. Although numerous publications have been devoted to this issue, the results of TR-PL in GaN are very controversial.[2] In the present work, we have studied PL decay and transformation of PL spectra over a very wide temporal range, extending from microseconds to as long as several minutes in freestanding GaN templates having a very low concentration of point defects. We demonstrate that the unusually slow decay of the PL in these samples is largely related to the donor–acceptor-pair (DAP) recombination mechanism.

Thick GaN layers were grown by hydride vapor phase epitaxy on the *c*-plane of sapphire substrates that were thermally separated from the substrate by a laser beam. Concentrations of shallow donors (N_D) and compensating acceptors (N_A) were estimated as 1.8×10^{16} and 2.4×10^{15} cm^{-3}, respectively, from analysis of the Hall data.[3] PL was excited either with a cw He-Cd laser (photon energy 3.81 eV) or a pulsed nitrogen laser (5-ns pulses with repetition frequency 5–30 Hz and photon energy 3.68 eV), dispersed with a SPEX 500M grating monochromator and detected by a Hamamatsu photomultiplier tube R955-P. Neutral density filters were used to attenuate the excitation density in the range 10^{-4}–0.3 W/cm^2 for the cw excitation and 10–10^4 W/cm^2 peak power for the pulsed excitation. Short time (10^{-6}–10^{-1} s) PL transients were detected with the aid of a digital oscilloscope. Slow PL decays ($\sim10^{-1}$–10^{3} s) were measured in the photon counting mode. The sample was attached to a cold finger in a closed-cycle cryostat cooled to a nominal temperature of 6 K. The actual sample temperature is estimated to be 15 K from careful calibration experiments.

The steady-state PL (SS-PL) spectrum measured at 15 K contained a set of sharp peaks in the excitonic region with the strongest peak at 3.471 eV, having full width at half-maximum (FWHM) of 1 meV. A comprehensive analysis of the exciton-related PL spectrum in the studied freestanding GaN templates can be found elsewhere.[4] In the present work, we concentrate on PL at photon energies below 3.4 eV, corresponding to recombination via point defects. We observed the shallow DAP band with the main peak at about 3.26 eV, followed by a few LO phonon replicas, a broad yellow-green band whose position and shape depended on excitation intensity,[5] and a weak shoulder at about 1.7–1.8 eV corresponding to red luminescence (Fig. 1).

For short times following pulsed excitation, the green luminescence (GL) band with a maximum at about 2.45 eV dominated the PL spectrum at 15 K (Fig. 1). Similar to the earlier reported results,[6] the shape and position of the GL band remained nearly unchanged up to about 10 μs. However, at longer delay times the GL band disappeared, giving way to the yellow luminescence (YL) band peaking at 2.2 eV. In addition, the red luminescence (at about 1.8 eV) and the blue luminescence (at about 2.9 eV) could be seen as shoulders of the YL band and the shallow DAP band at long delay times (Fig. 1). Transformation of the shallow DAP band with time delay is shown in Fig. 2. The zero-phonon line gradually shifts from 3.265 to 3.253 eV in a time interval from 10^{-6} to 10 s after pulsed excitation. This shift can be explained within the Thomas–Hopfield model for DAPs,[7] according to which at short times recombination in nearby pairs, experiencing stronger Coulomb interaction, dominates. Besides the shallow DAP peaks, we observed transitions from the conduction band to the same shallow acceptor (e–A transitions). As can be better seen from the SS-PL spectrum obtained under excitation with pulsed nitrogen laser and from TR-PL spectra at delays in the range of a few seconds

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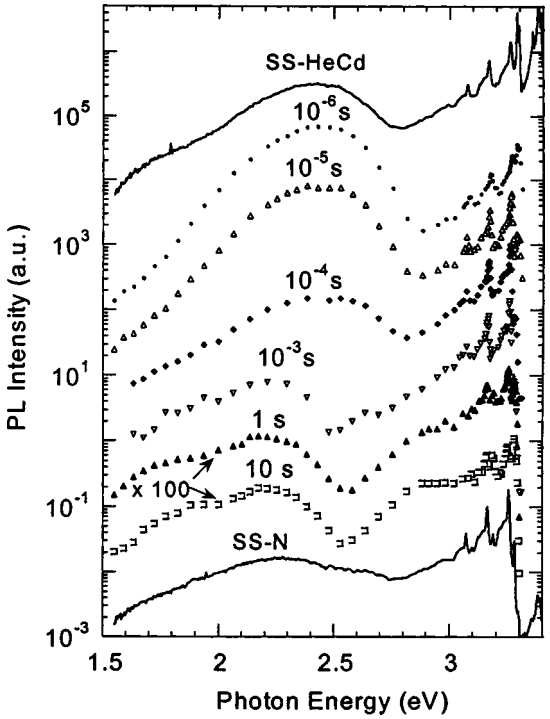

FIG. 1. Steady-state PL spectra (solid curves) obtained under excitation with pulsed nitrogen (SS-N) and cw He-Cd (SS-HeCd) laser, and TR-PL spectra at different time delays (points). $T=15$ K.

(Fig. 2), the e–A emission exhibits the zero-phonon line at about 3.282 eV, followed by at least two LO phonon replicas. A clear transformation of the DAP to e–A emission was observed in the temperature range from 25 to 50 K.

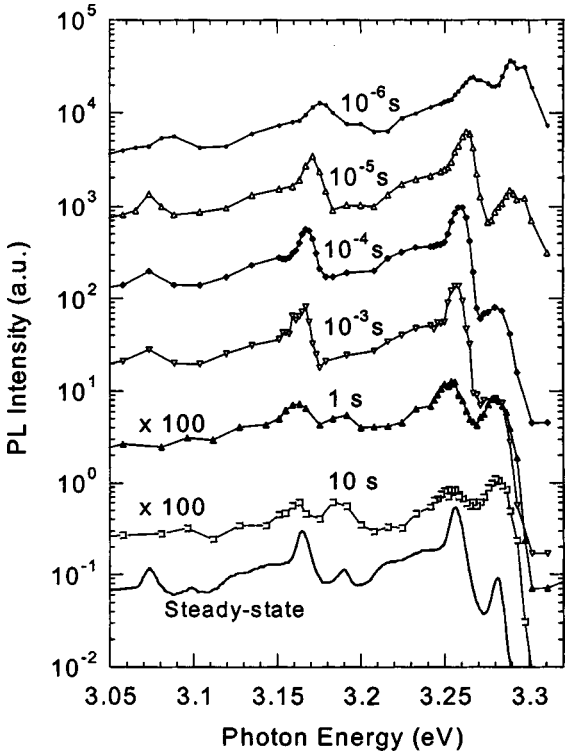

FIG. 2. Shallow DAP and e-A-related PL spectra excited with a pulsed nitrogen laser at 15 K. Solid curve: SS-PL spectrum. Points connected with a solid line show the TR-PL spectra at different time delays. The spectra for delays of 1 and 10 s were measured with lower resolution, resulting in artificial broadening of some peaks.

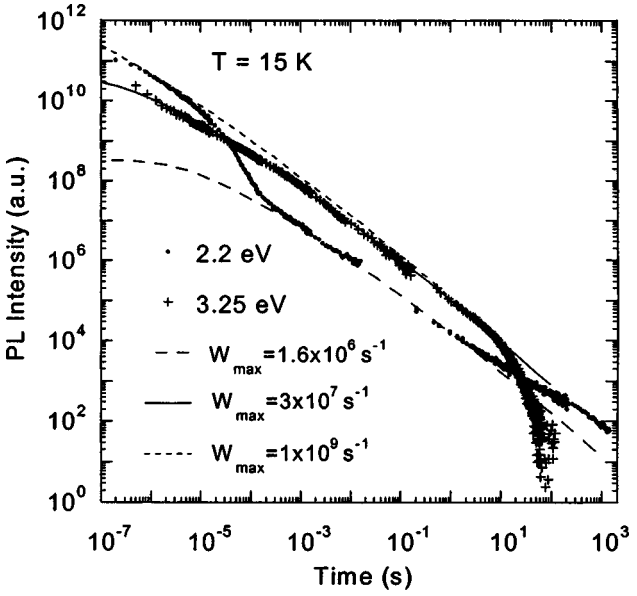

FIG. 3. PL intensity decay of the GL–YL (at 2.2 eV) and shallow DAP band (at 3.25 eV) at 15 K. The curves are calculated using Eq. (1) with the following parameters: $N_D=1.8\times10^{16}$ cm^{-3}, $a_D=2.4$ nm, and $W_{max}=1.6\times10^6$, 3×10^7, 1×10^9 s^{-1}, as shown in the figure.

A striking feature of the PL from the studied samples was a clearly visible (even with naked eye) persistence of light emission after the excitation was completely turned off. The PL intensity decays at two photon energies are shown in Fig. 3 on a log–log scale. Both decays are nonexponential, as expected for the DAP-type transitions in low-temperature PL of GaN.[2] The shallow DAP emission intensity decays as approximately t^{-1} over a wide time interval (from about 10^{-5} to 10 s). For longer times the intensity decays faster than t^{-1}. The time dependence of the emission at 2.2 eV exhibits a steep drop between 10^{-5} and 10^{-4} s, followed by a nonexponential decay, which is slower than t^{-1}. Recall that just in the same time interval the GL transforms into YL (see Fig. 1). It becomes clear that PL decays below and above 10^{-4} s at 2.2 eV are associated with two different emissions, namely GL and YL bands, respectively. Fast quenching of the GL band and very slow decay of the YL are consistent with the assignment of these bands to two charge states of the same defect, presumably $(V_{Ga}O_N)^{0/-}$ and $(V_{Ga}O_N)^{-/2-}$, respectively.[5] Red and blue luminescence also exhibited persistent behavior, as can be seen in Fig. 1.

Several mechanisms may lead to persistent PL. The most common ones among them are DAP-type transitions,[7] potential fluctuations,[8] and trapping-detrapping by shallow traps.[9] We may completely neglect potential fluctuations in the studied samples because concentration of impurities/defects and compensation ratio are very small. Furthermore, there is no experimental evidence of the shallow traps in GaN, and efficient emission from the known shallow donors seems quite questionable at 15 K. However, the DAP mechanism looks very attractive because in the studied high-purity samples the distances between donors and acceptors are expected to be large enough to provide very long-lived PL in conditions of very low concentration of free carriers at low temperature.

We attempted to fit the decay curves by the Thomas–Hopfield expression for the case of low compensation[7]

$$I(t) \propto \left[\int_0^\infty W(R) e^{-W(R)t} R^2 dR \right] \left\{ \exp\left[4\pi N_D \int_0^\infty (e^{-W(R)t} - 1) R^2 dR \right] \right\}. \quad (1)$$

Here, the radiative recombination rate W in DAP depends on the donor–acceptor separation R as $W(R) = W_{\max} \exp(-2R/a_D)$, where $W_{\max}$ is the transition rate in the limit $R \to 0$ and $a_D = 24$ Å is the Bohr radius for the shallow donor. The calculated curves with three values of $W_{\max}$ are shown in Fig. 3 as typical examples rather than the best fit. The fitting parameters are reasonable and close to the parameters found earlier for DAP involving different acceptors in GaN.[10] As may be seen, the curve shape is not very sensitive to $W_{\max}$, especially for the values of $W_{\max}$ above 10^7 s^{-1}. Nevertheless, we may conclude that $W_{\max}$ for the shallow DAP band is larger than that for the YL band, consistent with previous results,[10] and that $W_{\max}$ for the GL is apparently very large, of the order of 10^8–10^{10} s^{-1}, as was already noted earlier.[6] Deviations of the shallow DAP and YL emission decays from the classical DAP-type decay at times above 10 s (Fig. 3) can be explained by redistribution of electrons thermally emitted to the conduction band. At long times, an electron may thermally escape from a particular shallow donor and be captured by another shallow donor. If the electron is captured by a donor located closer to a neutral acceptor, the recombination will occur faster. Otherwise, it will be emitted again to the conduction band and captured by another ionized donor. This is a reasonable explanation for the shallow DAP containing a simple acceptor. In contrast, the acceptor responsible for the YL band is negative when it binds a hole,[5] and this Coulomb potential would repel free electrons emitted from the donors. Thus we may expect slowing down of the YL recombination when the emission of electrons from the shallow donors becomes efficient (at times above 10 s). A comprehensive study of TR-PL at different temperatures is in progress to confirm this assumption.

A very surprising result of this work is that persistent PL is observed not only for DAP-type transitions, but also for the e–A transition involving the shallow acceptor, as clearly seen in Fig. 2. Note that even 1 s after the excitation pulse, a substantial number of the acceptors still binds the photogenerated holes. However, photogenerated free electrons are captured very rapidly by the shallow donors and the balance between the bound and free electrons would quickly approach the conditions of dark. According to the Hall data,[3] equilibrium concentration of free electrons is extremely small at 15 K, of the order of 10^9 cm^{-3}. Thus additional assumptions are needed to explain the existence of strong e–A recombination at long times.

One possible explanation for the presence of free electrons in the conduction band, at low temperature, long time after pulse excitation stems from the presence of surface states in GaN. Normally, we would expect accumulation of holes at the surface states due to strong upward band bending near the surface of undoped GaN.[11] However, nonequilibrium population of the surface states, including possible appearance of trapped electrons above the dark Fermi level, can be sustained for very long time after excitation pulse at sufficiently low temperature. These electrons may tunnel through the surface barrier and significantly increase concentration of free electrons in the conduction band. The nonexponential decay of the e-A emission (compare Figs. 2 and 3) may be indicative of energy distribution of the surface states, such that shallower states emit electrons to the conduction band at shorter time scales, while deeper surface states are emptied at longer time scales. Moreover, based on this experimental observation, we may reject an alternative model of a single shallow trap beyond depletion region that might emit electrons to the conduction band with long-lasting exponential transient. Another reason for the enhanced concentration of free electrons in the active bulk layer long time after pulse excitation at low temperature may be accumulation of photogenerated holes at the surface, resulting in saturation of the shallow donors with electrons.

Finally, we will comment on differences in SS-PL excited with cw He-Cd and pulsed nitrogen lasers (Fig. 1). Persistent emission from the red, yellow, blue, and shallow DAP (including shallow e–A) bands contributes much more to the PL spectrum excited with pulse nitrogen laser than in the case of cw excitation by the He-Cd laser. In the latter case, fast exciton recombination and relatively fast GL emission dominate the spectrum, whereas the channels of long-lasting PL are largely saturated.

In conclusion, we have studied PL decay and transformation of PL spectra for high-purity GaN at different time delays after pulse excitation over a very extended time period. The persistent PL could be seen even with the naked eye minutes after the excitation is completely turned off. Slow, nonexponential decay of the shallow DAP, blue, yellow, and red bands at 15 K is attributed to DAP-type recombination. Persistent PL due to transitions from the conduction band to the shallow acceptors (e–A) was also observed. The appearance of substantial amount of free electrons at times longer than 1 s after the excitation pulse is interpreted as manifestation of the surface states in GaN.

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