2002

Two charge states of dominant acceptor in unintentionally doped GaN: Evidence from photoluminescence study

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Reshchikov, M.A., Morkoç, H., Park, S.S., et al. Two charge states of dominant acceptor in unintentionally doped GaN: Evidence from photoluminescence study. Applied Physics Letters, 81, 4970 (2002).

Two charge states of dominant acceptor in unintentionally doped GaN: Evidence from photoluminescence study

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(Received 23 May 2002; accepted 30 October 2002)

Photoluminescence of the dominant deep-level acceptor in high-purity freestanding GaN is studied over a wide range of excitation intensities. A yellow luminescence (YL) band at about 2.2 eV saturates with increasing excitation intensity, whereas a green luminescence (GL) band at about 2.5 eV increases as a square of the excitation intensity. The YL and GL bands are attributed to two charge states of the same defect, presumably a gallium vacancy-oxygen complex. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1531227]

Recent advances in growth techniques and remarkable breakthroughs in developing GaN-based optoelectronic and high-temperature/high-power devices stimulated efforts to grow GaN crystals of superior quality. At present, freestanding GaN templates grown in the Samsung Advanced Institute of Technology exhibit high-quality crystal structures with the lowest concentrations of point defects.[1] In common with undoped GaN grown by any technique, the dominant radiative defect in these crystals is a deep-level defect responsible for the omnipresent yellow luminescence (YL) band centered near 2.2 eV. After hot debates about the origin of this luminescence band, most investigators agreed that it is caused by transitions from the conduction band or a shallow donor to a deep acceptor.[2–4] The main candidates for the deep acceptor are a gallium vacancy (V_{Ga}) and a gallium vacancy-oxygen complex ($V_{Ga}O_N$) that are abundantly formed in *n*-type GaN during growth.[5,6] Recent studies of the positron annihilation in the oxygen-rich bulk GaN confirmed that the dominant point defect in these samples is not the isolated V_{Ga} but the V_{Ga}-containing complex, presumably $V_{Ga}O_N$.[7] The $V_{Ga}O_N$ complex should act as a double acceptor with its $-/2-$ and $0/-$ levels that are, respectively, close to the $2-/3-$ and $-/2-$ levels of the isolated V_{Ga} in GaN.[5,6] In *n*-type GaN, the $V_{Ga}O_N$ acceptor is fully occupied with electrons and in equilibrium its charge state is $2-$. If the concentration of the $V_{Ga}O_N$ acceptors is very low and the lifetime of the acceptor-related luminescence is long enough, one may expect saturation of the $-/2-$ level with photogenerated holes, so that the complex starts capturing a second hole, thus switching to its neutral charge state ($0/-$ level).

In this letter, we analyze dependence of the photoluminescence (PL) intensity on excitation density in high-purity GaN. Saturation of the YL band and superlinear emergence of the green luminescence (GL) band with excitation power are quantitatively explained by existence of two charge states of the $V_{Ga}O_N$ complex dominating in undoped GaN.

Thick GaN layers were grown by hydride vapor phase epitaxy (HVPE) on the *c*-plane of sapphire substrate and then thermally separated from the substrate by a laser beam. The Ga face of the 200-μm-thick freestanding template was polished and dry etched to a smooth ''epi-ready'' surface. The concentration of free electrons (n_0) and their mobility, obtained from the Hall effect measurements at room temperature, are 1.3×10^{16} cm^{-3} and 1200 cm^2 V^{-1} s^{-1}, respectively. PL was excited with a He–Cd laser (55 mW, 325 nm), dispersed by a SPEX500M grating monochromator and detected by a Hamamatsu R955-P photomultiplier tube. Neutral density filters were used to attenuate the excitation density (P_{exc}) over the range 3×10^{-5}–0.3 W/cm^2.

A room-temperature PL spectrum of the GaN template (from Ga face) contains a near-band-edge emission peaking at 3.408 eV and a broadband, the maximum of which shifts from about 2.22 to 2.47 eV with increasing excitation intensity (Fig. 1). In contrast to monotonic shift of the PL band with excitation intensity, typical for a deep donor–acceptor-pair band,[8] we observed rapid shift of the band maximum between 1 and 10 mW/cm^2 (Fig. 1). Self-consistent deconvolution of the broadband at different excitation intensities[9] revealed that it is composed of two bands: (i) a nearly Gaussian-shaped YL band with a maximum at 2.22 eV and full width at half maximum (FWHM) of about 0.58 eV and (ii) slightly asymmetric GL band with a maximum at 2.48 eV and FWHM of about 0.53 eV. Examples of the deconvolution for two excitation intensities are shown in Fig. 2. With increasing P_{exc}, the YL intensity increases linearly and saturates above $P_{exc}=1$ mW/cm^2, whereas the GL intensity is approximately quadratic in P_{exc} at low excitation density and linear in P_{exc} above ~10 mW/cm^2 (Fig. 3). Below we will show that the above behavior of the defect-related PL is a signature of two charge states of the dominant defect in the studied GaN sample.

Following the phenomenological approach presented in Ref. 10, let us consider the balance equations for electrons in the conduction band ($n=n_0+\delta n$) and holes in the valence band ($p=\delta p$) in *n*-type semiconductor, containing a double acceptor with concentration N_A in conditions of steady state PL

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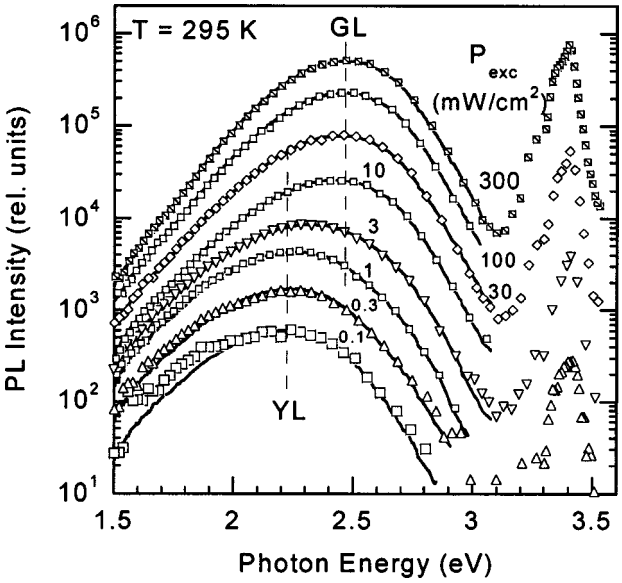

FIG. 1. Room-temperature PL spectrum of a freestanding GaN template (Ga face) at different excitation densities. Points are experimental data (only every tenth point is shown for clarity); solid curves—fit using modeled YL and GL bands with their relative contribution given in Fig. 3.

$$\frac{\partial n}{\partial t} = G - C_{n1} N_A^- n - C_{n2} N_A^0 n - Bpn = 0, \tag{1}$$

$$\frac{\partial p}{\partial t} = G - C_{p1} N_A^{2-} p - C_{p2} N_A^- p - Bpn = 0. \tag{2}$$

Here, G is the electron-hole pair generation rate; N_A^{2-}, N_A^-, and N_A^0 are concentrations of doubly charged, singly charged, and neutral acceptors, respectively ($N_A^{2-} + N_A^- + N_A^0 = N_A$); C_{n1} and C_{n2} are electron-capture coefficients and C_{p1} and C_{p2} are hole-capture coefficients for the acceptor states

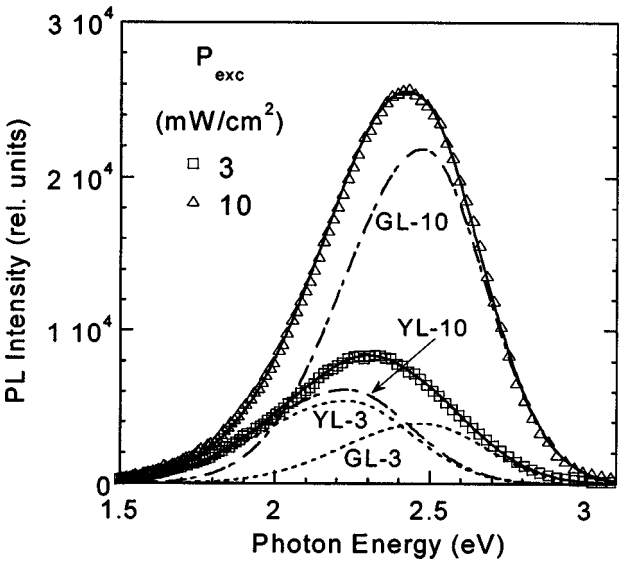

FIG. 2. Simulation of the PL spectrum at two excitation densities with two modeled bands: the YL band with a maximum at 2.22 eV and FWHM of 0.58 eV and the GL band with a maximum at 2.48 eV and FWHM of 0.53 eV. Points are experimental data, broken and dotted curves are modeled spectra for the YL (YL-3 and YL-10 for 3 and 10 mW/cm^2) and GL (GL-3 and GL-10 for 3 and 10 mW/cm^2) bands and solid lines are their sum. The shape of the GL-10 curve is identical to the GL-3 one and the shape of the YL-10 curve is identical to the YL-3 one, only absolute intensities are different.

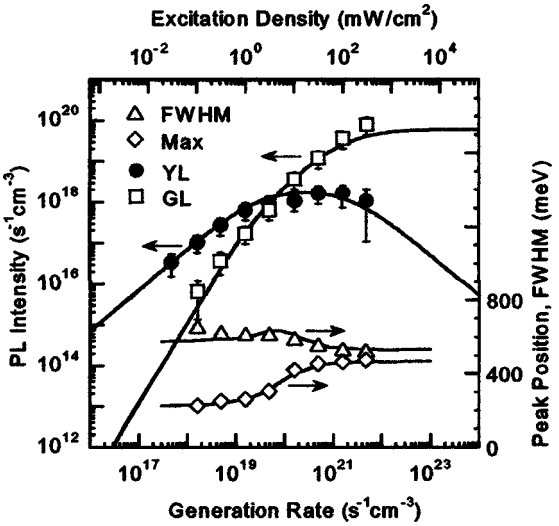

FIG. 3. Dependence of the integrated intensity of the YL and GL bands on excitation intensity. Points are experimental data obtained from deconvolution of the spectra shown in Fig. 1 onto two bands (YL and GL) similarly to an example shown in Fig. 2. Solid lines represent a fit by Eqs. (1)–(5) with the following parameters: $C_{n1} = 10^{-13}$ cm^3 s^{-1}, $C_{n2} = 2.5 \times 10^{-12}$ cm^3 s^{-1}, $C_{p1} = 3.3 \times 10^{-7}$ cm^3 s^{-1}, $C_{p2} = 1.5 \times 10^{-7}$ cm^3 s^{-1}, $B = 5 \times 10^{-7}$ cm^3 s^{-1}, $N_A = 1.5 \times 10^{15}$ cm^{-3}, $n_0 = 1.3 \times 10^{16}$ cm^{-3}. Also shown are the FWHM and position of maximum (after deduction of 2 eV for appearance) of the experimentally observed broadband (points) and the same values simulated by using the modeled shapes of the YL and GL bands and their relative contributions calculated from Eqs. (1)–(5) (solid curves).

$-/2-$ and $0/-$, respectively; and the rate coefficient B describes both band-to-band and exciton recombination.[10,11] The balance should take place for each recombination channel, implying

$$C_{n1} N_A^- n = C_{p1} N_A^{2-} p, \tag{3}$$

$$C_{n2} N_A^0 n = C_{p2} N_A^- p. \tag{4}$$

The condition for charge neutrality in n-type semiconductor can be expressed as

$$\delta n = N_A^- + 2N_A^0 + p, \tag{5}$$

where, as in Ref. 10, we assumed that shallow donors are ionized at room temperature in the GaN template[12] and their concentration $N_D^+ = n_0 + N_A$. The Fermi level is close to the conduction band and thus all acceptors are filled with electrons in dark ($N_A^{2-} = N_A$).

The system of coupled Eqs. (1)–(5) can be solved numerically and the dependencies of δn, p, N_A^- and N_A^0 on G can be calculated for the fixed parameters C_{n1}, C_{n2}, C_{p1}, C_{p2}, B, N_A, and n_0. As one would expect from a probability viewpoint, the concentrations of the acceptors binding one and two holes are respectively linear and quadratic functions of P_{exc} at low excitation intensity. Figure 3 demonstrates the fit of Eqs. (1)–(5) to the experimental data. In this fit[13] we used the hole-capture coefficient for the YL band C_{p1} found from its quenching behavior[10] and electron-capture coefficients for the YL and GL bands (C_{n1} and C_{n2}) found from the transient PL data.[14] C_{p2}, N_A, and B were the fitting parameters. We obtained $C_{p2} < C_{p1}$, as is expected for the hole capture by a less negatively charged acceptor and $N_A = 1.5 \times 10^{15}$ cm^{-3}. The latter value is in excellent agreement with the dominant acceptor concentration found from

the Hall effect data (the value of $N_A = 2.4\times10^{15}$ cm^{-3} [Ref. 12] is overestimated if the doubly charged acceptor dominates) and with the concentration of the vacancy-containing defects found from the positron lifetime experiments ($2.1 \pm 0.8\times10^{15}$ cm^{-3}).[15] The value of B (5×10^{-7} cm^3 s^{-1}) is higher than the calculated radiative recombination coefficient for GaN (7×10^{-10} cm^3 s^{-1} [Ref. 16] and 4.4×10^{-11} cm^3 s^{-1} [Ref. 17]) because in our calculations coefficient B includes not only band-to-band but also radiative and nonradiative recombination of excitons. Note that our value of B is close to the bimolecular recombination coefficient found experimentally in Ref. 18 (1.3×10^{-8} cm^3 s^{-1}). Attribution of the YL and GL bands to the $2-/-$ and $-/0$ states of the $V_{Ga}O_N$ complex is consistent with the obtained values of their capture cross sections for electrons and holes: electrons are much more likely captured by $(V_{Ga}O_N)^0$ than by $(V_{Ga}O_N)^-$, whereas the difference between $(V_{Ga}O_N)^{2-}$ and $(V_{Ga}O_N)^-$ for the capture of holes is not so important. Further, the predicted energy separation between the $2-/-$ and $-/0$ states of the $V_{Ga}O_N$ (0.45 eV)[6] is reasonably close to the difference in positions of the GL and YL bands (about 0.26 eV).

We observed similar transformation of the YL into GL band in several freestanding GaN templates, both at room and cryogenic temperatures, however it was never observed in thin undoped GaN layers grown by molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition. We explain the observation of the GL band by the high purity of the studied samples. Indeed, saturation of the acceptor-related PL is promoted by low concentration of the acceptor, long lifetime of the acceptor-related PL (which is inversely related to the shallow donor concentration) and high efficiency of radiative recombination (requiring low density of dislocations, perfect surface preparation, and large diffusion length).[10] All these parameters are at top level in the studied GaN.[1] Another explanation is that in less perfect GaN the $V_{Ga}O_N$ complexes are preferably bound to dislocations[19] that may affect the charge state and other characteristics of the defect. We should emphasize that in different GaN samples different defects may contribute to emission in the visible range. In particular, some investigators observed slow transformation of the blue band centered at about 3.0 eV to the YL band in real time and explained such behavior by metastable nature of the defect responsible for the YL.[20] We did not see any transformation of PL spectrum with time in the studied GaN samples at room temperature or at 15 K. However, in MBE-grown samples with special treatment of surface we observed irreversible bleaching of the blue luminescence in real time, which we attributed to photoinduced desorption of oxygen or the methastable nature of some surface defects.[21]

Previously, transformation of the YL into GL band in freestanding GaN templates has also been observed with variation of the excitation light wavelength.[22] In the framework of the current model, the experimental results presented in Ref. 22 can be easily explained. The YL band dominates at resonant excitation below 3.2 eV because the absorption coefficient is very small at these photon energies[22] and the acceptors cannot be saturated. The GL appears at higher photon energies and dominates above 3.3 eV if the excitation power is high enough because the absorption of GaN increases markedly in this range[22] and the defects can be saturated.

In conclusion, we have observed transformation of the yellow luminescence (2.22 eV) into green luminescence (2.48 eV) with increasing excitation power in high-purity freestanding GaN template, indicating that the dominant point defect in undoped GaN is a multiple-charge state acceptor. The yellow band saturates, while the green band increases as a square with excitation intensity, which is explained quantitatively by saturation of the $2-/-$ state of the $V_{Ga}O_N$ acceptor and its transformation into the $-/0$ state at high excitation level.

The authors would like to thank C. G. Van de Walle and K. Saarinen for valuable comments. The work was funded by AFOSR (Dr. G. L. Witt), NSF (Dr. L. Hess and Dr. U. Varshney), and ONR (Dr. C. E. C. Wood and Dr. Y. S. Park).

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