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Determination of acceptor concentration in GaN from photoluminescence

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The concentration of the acceptor responsible for the yellow luminescence (YL) band at about 2.2 eV in GaN is determined from photoluminescence. The YL band intensity increases linearly with excitation power density and partially saturates above some critical value. The dependence is quantitatively described within a phenomenological model accounting for recombination statistics in GaN layer and saturation of acceptors with photogenerated holes. The incomplete saturation of the YL intensity at high excitation intensities is explained by gradual saturation of acceptors at different distances from the sample surface. The identity of deep and shallow acceptors in GaN is discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2204835]

Gallium nitride has gained unprecedented attention due to its applications in emitters [green, blue, and ultraviolet light emitting diodes (LEDs) and laser diodes], optical detectors, and high-power amplifiers. However, even the best-quality GaN contains many point defects reducing the efficiency and lifetime of electronic and optical devices. To date, the majority of point defects in GaN remain unidentified and insufficiently studied.[1] In particular, in undoped GaN grown by any technique a yellow luminescence (YL) band is commonly observed near 2.2 eV that is attributed to transitions from the shallow donors or conduction band to an unidentified deep acceptor.[1] The main candidate for the deep acceptor is the gallium vacancy-oxygen complex ($V_{Ga}O_N$) that is abundantly formed in *n*-type GaN during growth.[2,3] In particular, the YL and green luminescence bands in high-quality freestanding GaN templates were assigned respectively to $2-/-$ and $-/0$ charge states of $V_{Ga}O_N$.[4] However, there remains a controversy over the identification of the YL band in less pure material.[1] In particular, Armitage *et al.*[5] proposed that the carbon impurity in C-doped GaN and V_{Ga}-related defects in undoped GaN cause YL bands very similar in shape and position.

The main difficulty in the identification of the YL band in GaN is associated with the common failure to determine the concentration of the related acceptor and compare it with the concentrations of the dominant impurities and vacancy-related defects. The omnipresent method to determine the relative concentration of the acceptor from the relative intensity of the YL band in different samples is unacceptable since the photoluminescence (PL) intensity from a particular defect depends on many factors.[6] Previously we proposed a method of how to determine the concentration of radiative acceptors in GaN from the analysis of the dependence of PL intensity on excitation intensity.[6] However, at that time we could not explain satisfactorily the incomplete saturation of this dependence at excitation power densities corresponding to the saturation of the radiative acceptors with photogenerated holes. In this work we give an explanation of the incomplete saturation and determine the concentration of radiative acceptors in a GaN sample.

A 1.9-μm-thick unintentionally doped GaN layer was grown by metal organic chemical vapor deposition method on *c*-plane sapphire substrate by EMCORE Corporation and studied by several research groups within the Wood-Witt Initiative "Defects in GaN" (Sample No. EM1256 for internal reference). Concentration of Si, C, and O in this sample has been estimated as about 3×10^{16}, 4×10^{16}, and 5×10^{16} cm^{-3}, respectively, by the secondary ion mass spectrometry.[7] Concentrations of free electrons at room temperature, n_0, shallow donors, N_D, and all compensating acceptors, ΣN_A, have been estimated as 2×10^{16}, 6×10^{16}, and 4×10^{16} cm^{-3}, respectively, from the analysis of the temperature-dependent Hall effect.[8] Steady-state PL was excited with unfocused He–Cd laser (55 mW, 325 nm), dispersed by a 1200 rules/mm grating in a 0.3 m monochromator, and detected by a cooled photomultiplier tube. Calibrated neutral-density filters were used to attenuate the excitation power density (P_{exc}) over the range of 1×10^{-5}–0.3 W/cm^2. Time-resolved PL was excited with a pulsed nitrogen laser (337 nm) and analyzed with an oscilloscope. A closed-cycle optical cryostat was used for temperatures between 10 and 320 K.

PL spectra of the GaN sample at different temperatures are shown in Fig. 1. At 10 K the spectrum contains a sharp line at 3.484 eV attributed to the annihilation of an exciton bound to a neutral shallow donor (DBE), followed by two LO phonon replicas, and a broad YL band with a maximum at 2.2 eV. With increasing temperature the DBE emission

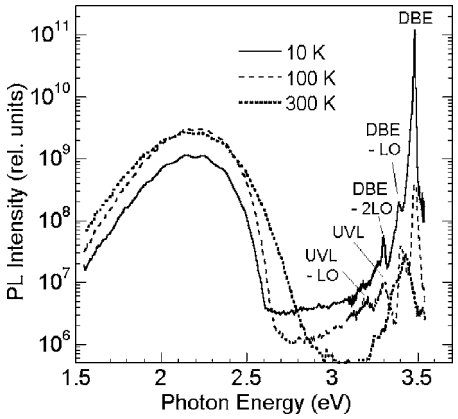

FIG. 1. PL spectrum from a GaN layer at different temperatures. The QE of different PL bands: $\eta_{exciton}$=8% at 10 K; η_{YL}=2% at 10 K and 4% at 100–300 K; η_{UVL}=0.01% at 100 K.

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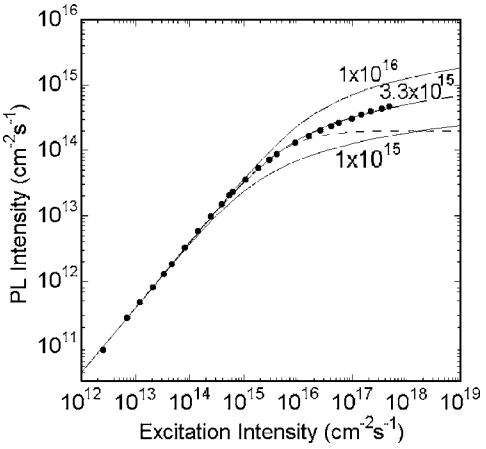

FIG. 2. Dependence of the YL intensity on excitation intensity at 300 K. Points—experimental data. Solid lines—calculated by using Eq. (6) with the following parameters: $\alpha=10^5$ cm^{-1}, $\tau=0.4$ ms, $\eta_{YL}^{exc}=0.04$, $N_{YL}=1\times10^{15}$, 3.3×10^{15} and 10×10^{16} cm^{-3}.

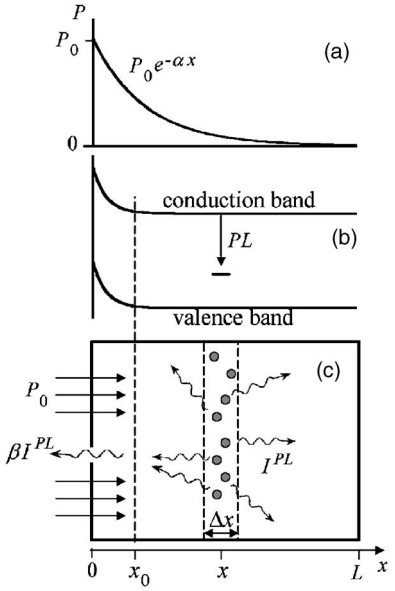

FIG. 3. Schematic of PL process. (a) Decrease of the excitation intensity inside GaN layer; (b) band diagram of the GaN layer having a depletion region between $x=0$ and $x=x_0$ due to upward band bending near the layer surface; (c) cross section of the GaN layer with selected thin layer Δx where acceptors with the density $\Delta N=N_i\Delta x$ are shown as dots which emit PL in all directions. A fraction β of the total PL intensity emitted from the layer is collected with a lens from the front side of the GaN layer.

quenches, giving way to the free exciton (FE) lines shifted by ~6 meV to higher energies. At temperatures close to 100 K, when the FE emission significantly quenches, a very weak ultraviolet luminescence (UVL) band could be detected, representing a peak at 3.27 eV followed by two LO phonon replicas (Fig. 1). At higher temperatures the UVL band quenches, and only the strong YL band and weak exciton band peaking at 3.428 eV could be seen at room temperature (Fig. 1).

With increasing excitation intensity, P_0, up to $\sim10^{15}$photons/cm^2 s, the YL intensity, I^{YL}, increases linearly, and at higher excitation intensities it partially saturates (Fig. 2). By fitting the $I^{YL}(P_0)$ dependence with the theoretical expression proposed in Ref. 6,

$$I^{YL}=P_0\left(\frac{P_0\tau_{YL}}{L_{eff}N_{YL}}+\frac{1}{\eta_{YL}}\right)^{-1}, \tag{1}$$

where τ_{YL} and η_{YL} are the lifetime and quantum efficiency (QE) of the YL, N_{YL} is the concentration of acceptors responsible for the YL band, and L_{eff} is "the effective thickness of the layer subject to excitation,"[6] we obtain $N_{YL}\approx8\times10^{15}$ cm^{-3} by ignoring the discrepancy between the theoretical and experimental dependencies above $P_0\approx1\times10^{16}$ cm^{-2} s^{-1} (Fig. 2). Note that for this evaluation the QE of the YL band ($\eta_{YL}=0.04$) has been estimated from the direct measurement of PL power with correction for the geometry of the PL registration optics.[6] However, it is well known that the upward band bending of about 0.8 eV exists near the surface due to the presence of negative charge at the surface of GaN.[9] In the sample with the concentration of uncompensated donors of 2×10^{16} cm^{-3} this band bending should create a 0.2-μm-thick depletion region near the surface from which the photogenerated carriers will be quickly swept out due to strong electric field, and the layer would be dead for PL. Therefore, the determined QE may be underestimated about ten times since the excitation intensity beyond the 0.2-μm-thick depletion region is reduced about ten times if the absorption coefficient α of GaN at 325 nm is about 10^5 cm^{-1}.[10] Note also that the depletion region remains almost unchanged in the whole range of the excitation intensities used in this work. Indeed, under continuous illumination with our He–Cd laser the band bending in GaN decreases by not more than 25% as compared to the dark.[11]

Below we develop a phenomenological model for calculating the concentration of acceptors in *n*-type semiconductors accounting for the depletion region near the surface and gradual saturation of defects located at different depths of the layer with arbitrary thickness L instead of using the effective thickness L_{eff}.

Let us consider a GaN layer with thickness L and depletion region width x_0 (Fig. 3). Laser intensity P_0 decreases inside the layer as exp $(-\alpha x)$. At distance x, the following intensity will be absorbed within a thin layer Δx:

$$\Delta P(x)=\alpha P_0e^{-\alpha x}\Delta x. \tag{2}$$

The number of acceptors related to the YL band in the thin layer of unit area is $\Delta N_{YL}=N_{YL}\Delta x$. Then the total intensity of the YL band emitted in the region from x_0 to L in all directions is

$$I^{YL}=\int_{x_0}^{L}\frac{\alpha P_0e^{-\alpha x}}{(\alpha\tau_{YL}P_0e^{-\alpha x}/N_{YL})+(1/\eta_{YL})}dx$$
$$=\frac{N_{YL}}{\alpha\tau_{YL}}\ln\left(\frac{P_0+P_1}{P_0+P_2}\right), \tag{3}$$

where $P_1=N_{YL}(\alpha\tau_{YL}\eta_{YL}e^{-\alpha x_0})^{-1}$ and $P_2=N_{YL}(\alpha\tau_{YL}\eta_{YL}e^{-\alpha L})^{-1}$. At $P_0<P_1$ the $I^{YL}(P_0)$ dependence is linear,

$$I^{YL}(P_0<P_1)=\eta_{YL}e^{-\alpha x_0}P_0=\eta_{YL}^{ext}P_0, \tag{4}$$

where η_{YL}^{ext} is the QE which can be found by direct measurements at low excitation intensity as $\eta_{YL}^{ext}=I^{YL}/P_0$. At $P_0>P_2$,

$$I^{YL}(P_0>P_2)=\frac{N_i}{\tau_{YL}}(L-x_0). \tag{5}$$

Between P_1 and P_2 the $I^{YL}(P_0)$ dependence is sublinear with gradually reducing slope. In typical GaN layers with thick-

ness of more than 1 μm the transition region between P_1 and P_2 extends on several orders of magnitude of P_0, and the complete saturation cannot be observed in the typical range of excitation intensities. Moreover, at very high excitation intensity the $I^{YL}(P_0)$ dependence should become a square root dependence when the exciton emission becomes the dominant mechanism of recombination.[6] Thus, for not very thin GaN layers ($L>1$ μm) and not very high excitation power densities ($P_{exc}<100$ W/cm^2), Eq. (3) may be simplified to

$$I^{YL} = \frac{N_{YL}}{\alpha \tau_{YL}} \ln\left(1 + \frac{P_0}{P_1}\right), \tag{6}$$

consisting of the linear region at $P_0<P_1$ and incomplete saturation region at $P_0>P_1$.

The experimental $I^{YL}(P_0)$ dependence is fitted with Eq. (6) in Fig. 3. The lifetime of the YL at room temperature in the studied sample has been evaluated as 0.4 ms from the time-resolved PL study where a nearly exponential decay of the YL band intensity has been observed after pulse excitation. The value of η_{YL}^{ext} (0.04) was estimated from direct measurement of the QE by using a standard sample.[6] N_{YL} was the only fitting parameter, and the value of $N_{YL}=3.3\times10^{15}$ cm^{-3} was found. Note that the proposed method for estimation of the concentration of the radiative defects is relatively accurate (see the fits for $N_{YL}=10^{15}$ and 10^{16} cm^{-3} in Fig. 2) and does not require knowing the width of the depletion region. Note also that about twofold increase of the YL intensity with increasing temperature from 10 to 100 K (Fig. 1) favors the assumption that the QE of exciton emission is about 50% (at 10 K) and the real internal QE of the YL (η_{YL}) is close to 25% (at 300 K). The difference between $\eta_{YL}^{ext}=4\%$ and $\eta_{YL}=25\%$ is consistent with an assumption of a depletion region of about 0.1–0.2 μm in the studied GaN sample.

Unfortunately we are still unable to identify the defect responsible for the YL band in GaN. The value of $N_{YL}=3.3\times10^{15}$ cm^{-3} is about an order of magnitude smaller than the total concentration of acceptors or major impurities, including C and O, in the studied sample. Remarkably, we can estimate also the concentration of the shallow acceptor responsible for the UVL band in this sample, N_{UVL}. Indeed,[6]

$$N_{UVL} = N_{YL} \frac{I^{UVL}}{I^{YL}} \frac{C_{YL}}{C_{UVL}}, \tag{7}$$

where the hole capture coefficients for two acceptors can be taken as $C_{YL}=3\times10^{-7}$ and $C_{UVL}=1\times10^{-6}$ cm^3 s^{-1} and the ratio of the integrated PL intensities between the YL and UVL bands at 100 K is 400. This gives $N_{UVL}\approx3\times10^{12}$ cm^{-3}. The result calls into question the possibility for C_N to be likely formed in GaN (Ref. 12) and be responsible for the UVL band.[13,14]

In conclusion, we have developed a new method for estimation of the radiative defects in semiconductors from the analysis of photoluminescence. Application of this method to unintentionally doped *n*-type GaN allowed us to estimate the concentration of deep acceptors responsible for the strong yellow luminescence band in this sample as 3.3×10^{15} cm^{-3}. Concentration of the shallow acceptors in this sample is found to be 1000 times lower. The method is conceptually insensitive to the presence of depletion region near the surface of the semiconductor layer, which may significantly reduce the observed luminescence intensity.

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