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Optically-generated giant traps in high-purity GaN

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Abstract

An unusual temperature dependence of the photoluminescence lifetime for the green luminescence (GL) band in GaN is explained. This GL is caused by an internal transition of electrons from an excited state to the ground state of the 0/+ transition level of the isolated C_N defect. The excited state appears only after the C_N defect captures two photogenerated holes. The electron capture by the excited state is nonradiative, yet the lifetime of such can be probed by the temperature variation of the GL lifetime, whose temperature dependence shows a classic case of electron capture by a giant trap.

Keywords: GaN, luminescence, defects, giant traps, Lax model, cascade capture

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Giant traps in semiconductors are point defects with enormous capture cross-sections for electrons or holes, where the cross-section may be as large as 10^2-10^4 nm^2 at liquid He temperatures [1-3]. These attracted considerable interest among researchers in the 1960s-1990s [1-10]. Lax [10] was the first to explain the enormous capture cross-section of attractive centers in Ge and Si by noticing a close analogy between electron or hole capture by attractive centers and the Thomson theory [11] of positive-negative ion recombination in gases.

According to the Lax model (often referred to as the cascade capture model), free electrons are captured into a series of Coulomb excited states of a positively charged defect. The electrons lose energy by a cascade of one-phonon transitions between the excited states. A distinctive feature of the cascade capture by giant traps is that the capture cross-section is inversely proportional to the third power of the temperature (when acoustic phonons are emitted) [2]. The significant decrease of the capture cross-section with temperature is attributed to the thermal ejection of the trapped electrons from the ladder of excited states back to the conduction band. It should be noted that the electron-capture cross-sections for giant traps in Ge and Si were calculated from the lifetimes of free electrons in photoconductivity experiments [9], with the assumption that the measured lifetime of nonequilibrium electrons is related to a particular defect, but the defect was not directly probed. To the best of our knowledge, giant traps were neither found in wide-bandgap semiconductors nor detected by optical methods such as photoluminescence (PL). However, it is of great importance to investigate point defects with unusual properties in wide-bandgap semiconductors, since they are currently attracting significant attention, in particular due to their potential applications in quantum cryptography (e.g., the VN center in diamond) [12]. In this work, we report on excited

states of the C_N defect in GaN, which appear only under UV illumination, behave as a classic giant trap for electrons, and can be revealed in time-resolved PL experiments.

A dominant defect-related PL band in high-purity GaN grown by hydride vapor phase epitaxy (HVPE) is the green luminescence (GL) band with a maximum at 2.40 eV [13]. While in early works the GL band was attributed to one of the charge states of the $V_{Ga}O_N$ complex [14], recent first-principles calculations indicate that carbon in a nitrogen site (C_N) is a superior candidate [15]. According to these calculations, the C_N defect is expected to have two transition levels: the –/0 level at 1.04 eV and the 0/+ level at 0.48 eV above the valence band maximum. In *n*-type GaN, the recombination of free electrons with a photogenerated hole at the –/0 level causes the yellow luminescence (YL) band with a maximum at 2.1-2.2 eV. At high excitation intensity, the –/0 level of nearly all C_N defects is occupied with a hole (the C_N^0 state), and the capture of a second hole becomes possible (C_N^+). When this occurs, the GL band emerges. The intensity of the GL band is proportional to the square of the excitation intensity, because the capture of two photogenerated holes by the C_N defect is essential for the GL band to occur. While previously the GL band was thought to be caused by electron transitions *from the conduction band* to the 0/+ level of C_N [15], we will show in this work that in fact the GL band is caused by *an internal transition* between the excited and ground state of the 0/+ transition level. The theoretical model suggested in Ref. 15 was able to explain almost all the experimental findings, including the thermal quenching of the GL band at temperatures above 280 K with an activation energy of 0.54 eV, corresponding to the thermal emission of holes from the 0/+ level of the C_N defect to the valence band. However, one puzzle, namely a very unusual temperature dependence of the PL lifetime, remained unsolved.

More than ten undoped 10-30 μm-thick GaN films were grown by HVPE on c-plane 2-inch sapphire substrates. The room-temperature concentration of free electrons in these samples is between 2×10^{16} and 4×10^{17} cm^{-3}, as was determined from the analysis of the temperature-dependent Hall-effect measurements. The GL band could be detected in almost all of the HVPE-grown GaN samples. The time-resolved PL was excited with a pulsed nitrogen laser (1 ns pulses with repetition frequency of 6 Hz and 337 nm wavelength). Other experimental details can be found in Ref. 16.

The temperature dependence of the PL lifetime for the GL band in two HVPE-grown GaN samples with different concentrations of free electrons, n, ($n \approx 2\times10^{16}$ cm^{-3} in sample RS280 and $n \approx 2\times10^{17}$ cm^{-3} in sample H201 at room temperature), is shown in Fig. 1. For comparison, the temperature dependence for the ultraviolet luminescence (UVL) band with the main peak at 3.26 eV is also shown. At temperatures above ~40 K,

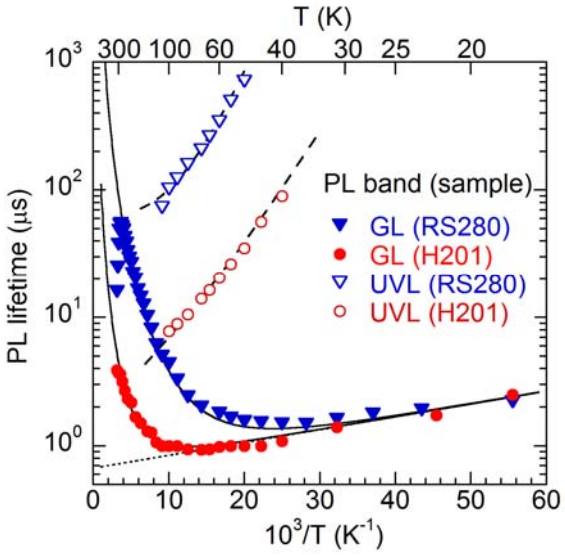

FIG. 1. (color online) Temperature dependence of the PL lifetime for the GL band and the UVL band in two HVPE GaN samples. The solid lines are fit with the dependence $\tau(T) = \tau_1 + \tau_2$ calculated using Eqs. (5) and (6), with a = 3.1 and $\tau_1(100\text{ K}) = 3$ μs (upper curve); a = 2.8 and $\tau_1(100\text{ K}) = 0.17$ μs (lower curve); $\tau_{20} = 0.67$ μs, E_2 = 2 meV (both curves). The dotted line is τ_2 given with Eq. (5). The dashed lines are calculated using Eq. (1) with $C_{nA} = 3\times10^{-12}$ cm^3/s for the UVL band.

the UVL band is caused by transitions of electrons from the conduction band to an unknown shallow acceptor [13]. It is well known that the PL lifetime, τ, for such transitions in an *n*-type semiconductor is inversely proportional to *n* [16]:

$$\tau^{-1} = C_{nA} n \,. \tag{1}$$

Here C_{nA} is the electron-capture coefficient, which is proportional to the defect capture cross-section, σ_{nA}; i.e., $C_{nA} = \langle v_n \rangle \sigma_{nA}$, where $\langle v_n \rangle$ is the mean thermal velocity of electrons in the conduction band (1.3×10^7 cm/s for GaN at 100 K). For a majority of defect-related PL bands in GaN, including the UVL band, the coefficient C_{nA} is temperature-independent, and the PL lifetime decreases with increasing temperature [13,16], in agreement with the temperature-induced increase in *n* (Fig. 1). The GL band is the only defect-related PL band in GaN, for which the PL lifetime markedly *increases* with increasing temperature (Fig. 1). We are not aware of similar observations for other defects in GaN or other semiconductors.

From the analysis of the temperature dependence of the GL lifetime and the concentration of free electrons in several HVPE GaN samples, we have found that the PL lifetime for the GL band is inversely proportional to *n* at any given temperature above ~100 K. This means that Eq. (1) is valid for the GL lifetime in this temperature region. The unusual rise of the GL lifetime can in fact be explained by a temperature dependence of C_{nA} for the defect participating in the GL. From Eq. (1), the temperature dependence of C_{nA} can be found, where *n* is found from temperature-dependent Hall effect measurements (Fig. 2).

The temperature dependence of C_{nA} can be described with a power-law of the form T^{-b} with $b \approx 3$. Remarkably, this temperature dependence is typical for the capture

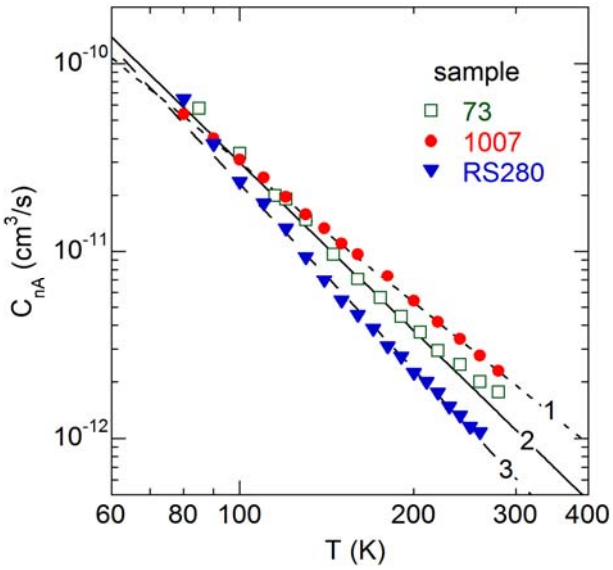

FIG. 2. (color online) The temperature dependence of the electron-capture coefficient for the GL band. The lines are calculated using Eq. (7) with $C_{n1}(100\ \mathrm{K}) = 3\times10^{-11}$ cm^3/s (curves 1 and 2) and 2.3×10^{-11} cm^3/s (curve 3); $b = 2.5$ (curve 1), 3.0 (curve 2), and 3.3 (curve 3).

of electrons by giant traps [2,10], but the known examples of giant traps are *nonradiative* defects. Moreover, the cascade capture mechanism is typical for relatively shallow attractive centers with weak electron-phonon coupling, as opposed to the multi-phonon recombination mechanism which is common for deep traps with strong electron-phonon coupling [8]. It appeared very surprising that in our PL experiments, the $C_{nA}(T) \propto T^{-3}$ dependence was observed for the GL band, a *radiative* recombination involving a deep defect. Note that no temperature dependence of the capture coefficients is expected for radiative transitions [17]. Below, we suggest a model explaining the observed behavior of the GL band.

We propose that the C_N^+ defect has an excited state near the edge of the conduction band (level 1 in Fig. 3). This state appears only after the defect captures two

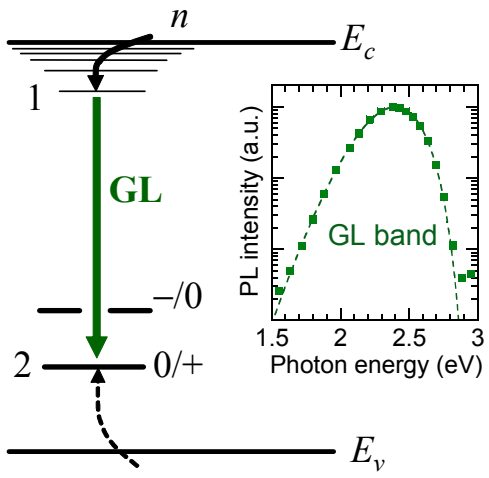

Fig. 3. (color online) Schematics of transitions associated with the GL band in GaN. The C_N acceptor becomes positively charged after capturing two holes (level 2). The capture of the second hole from the valence band to the 0/+ transition level is shown with a dashed arrow. In the electron-hole recombination, first, a free electron is captured at the excited state (level 1) by the Lax mechanism, a nonradiative process. Then, the internal transition from level 1 to level 2 causes the GL band. The PL lifetime in time-resolved PL experiments is dictated by the slower of these two processes. The inset shows the shape of the GL band at 30 K (note the log scale).

holes; i.e., it is optically generated. The excited state behaves as a giant trap for the nonradiative capture of an electron. The trapped electron then recombines with one of the two holes localized at the C_N^+ defect. The transition from the excited state (level 1) to the ground state (level 2) is an internal transition causing the GL, whereby the charge of the defect remains unchanged. It appears that transitions of electrons from the conduction band directly to level 2 can be ignored, at least below room temperature. Otherwise, we would see a change in the temperature dependence of τ [from $\tau \propto T^3$ to $\tau = (C_{nA} n)^{-1} \propto \exp(-E_D / kT)$, where E_D is the ionization energy of shallow donors], but this was not observed in our experiments (Figs. 1 and 2). The radiative recombination of an electron, weakly localized at the excited state level, with a hole localized at the ground state level is followed by the relaxation of the crystal lattice near the defect, which causes

the emission of multiple phonons. The above two-stage model is able to explain quantitatively the unusual temperature behavior of the GL band as demonstrated below.

Let N_1^+ be the concentration of the C_N defect with two bound holes and an electron in the excited state (level 1), and N_2^+ be the concentration of the same defect with two bound holes only (level 2). Then, $N_1^+ + N_2^+ = N_A^+$, where N_A^+ is the total concentration of the C_N defect with two bound holes (with or without a trapped electron). After a laser pulse, intense enough to saturate the –/0 levels of the C_N defects with holes, the concentration of defects with two bound holes becomes $N_A^+(0)$ and decays in time due to an internal transition from level 1 to level 2, with a characteristic time τ_2; i.e.,

$$\frac{dN_A^+}{dt} = -\frac{N_1^+}{\tau_2}. \tag{2}$$

The concentration of defects with electrons in the excited state, level 1, increases due to the nonradiative capture of free electrons by this level and decreases due to internal radiative transitions from level 1 to level 2:

$$\frac{dN_1^+}{dt} = \frac{N_2^+}{\tau_1} - \frac{N_1^+}{\tau_2}. \tag{3}$$

Here, $\tau_1 = \left(C_{n1} n\right)^{-1}$, in agreement with Eq. (1). We neglect the change in the concentration of free electrons in the conduction band due to additional, photogenerated electrons. This is justified for temperatures above 100 K when the concentration of free electrons in dark exceeds 10^{16} cm^{-3}, and the concentration of photogenerated electrons is much lower. The system of Eqs. (2) and (3) has an analytical solution, which allows us to find the following expression for the decay of the GL intensity with time *t* after a laser pulse:

$$I^{PL}(t) = \frac{N_A^+(0)}{\tau_1 - \tau_2}\left(e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right) = I^{PL}(0)\left(e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right). \quad (4)$$

At low temperatures, the cascade capture of free electrons by the excited state (level 1) is very fast, so that $\tau_1 << \tau_2$, and Eq. (4) reduces to $I^{PL}(t) \approx I^{PL}(0)\exp(-t/\tau_2)$. With increasing temperature, τ_1 increases proportionally to T^3, whereas τ_2 is nearly independent of temperature. At high temperatures, when $\tau_1 >> \tau_2$, $I^{PL}(t) \approx I^{PL}(0)\exp(-t/\tau_1)$. Overall, at any temperature, the decay of PL is nearly exponential, with the characteristic lifetime equal to the longest of τ_1 and τ_2; i.e., $I^{PL}(t) \approx I^{PL}(0)\exp(-t/\tau)$, where $\tau \approx \tau_1 + \tau_2$. The slowest of the transitions determines the rate at which the GL intensity decays after a laser pulse.

Now, let us return to the experimental data (Fig. 1). Closer inspection of the $\tau(T)$ dependence at temperatures below 50 K shows that the PL lifetime slowly decreases with increasing temperature in this region and can be fit with the following empirical expression (the dotted line in Fig. 1):

$$\tau(T) \approx \tau_2 = \tau_{20}\exp\left(E_2/kT\right), \quad (5)$$

where $\tau_{20} = 0.67$ μs and E_2 = 2 meV. The independence of the PL lifetime on n in different samples at low temperatures is consistent with our assumption that the transitions causing the GL band originate from an excited state; i.e., these are internal transitions [18]. Such an attribution is also supported by the fact that the PL decay for the GL band is exponential between 15 and 50 K. Conversely, for the majority of defect-related PL bands in *n*-type GaN, transitions from the conduction band to different defects are replaced by donor-acceptor-pair (DAP)-type transitions at T < 50 K due to the

freezing of free electrons at shallow donors [13]. DAP transitions cause a characteristic nonexponential decay of the PL, which is close to a power dependence, $I^{PL} \propto t^{-m}$, with $m \approx 1–2$ [19].

At higher temperatures ($T \approx 100 – 280$ K), the PL lifetime can be described with the following expression:

$$\tau(T) \approx \tau_1 = \tau_1(100\ \mathrm{K})\left(\frac{T}{100\ \mathrm{K}}\right)^a, \tag{6}$$

where the parameter $\tau_1(100\ \mathrm{K})$ is inversely proportional to the concentration of free electrons (i.e., sample-dependent) and $a \approx 3$. The PL lifetime at these temperatures is governed by the cascade capture of electrons by the excited state acting as a giant trap. The corresponding capture coefficient has the following temperature dependence:

$$C_{n1}(T) = C_{n1}(100\ \mathrm{K})\left(\frac{100\ \mathrm{K}}{T}\right)^b, \tag{7}$$

with the power *b* close to 3. The insignificant difference in powers *a* and *b* in Eqs. (6) and (7) is due to a weak temperature dependence of *n* in Eq. (1). For a wide range of temperatures (from 15 to 280 K), the experimentally measured PL lifetime for the GL band represents the sum of two components: $\tau(T) = \tau_1 + \tau_2$. The solid lines in Fig. 1 show fits for two samples, while fits for several other samples (not shown) were equally good.

Finally, Eq. (4) predicts that the time dependence of the GL intensity after a laser pulse has a maximum at $t < \tau_1, \tau_2$. The magnitude of this maximum, called hereafter the peak intensity, $I_{\max}^{PL}$, depends on temperature through the temperature dependences of τ_1 and τ_2 . In our experiments, the initial increase of PL intensity could not be clearly observed, mostly because of a fast and strong parasitic signal from the intense near-band-

edge emission in the high-quality GaN samples studied in this work. In this case, $I_{\max}^{PL}$ was estimated as the initial value of the slow component in the decay kinetics (see inset to Fig. 4). Figure 4 compares the predicted (solid line) and experimentally measured (empty squares) $I_{\max}^{PL}(T)$ dependences. Both dependences slightly increase with increasing temperature from 20 to 40 K (due to the small decrease in $\tau \approx \tau_2$) and decrease markedly at higher temperatures (concurrently with the increase in $\tau \approx \tau_1$). On the other hand, the integrated-over-time PL intensity is expected, according to Eq. (4), to be independent of temperature until the thermal quenching of the GL band begins at $T > 280$ K, because it is determined only by the efficiency of the hole-capture by the C_N defect (assumed to be temperature independent). As observed in experiment, it is indeed independent of

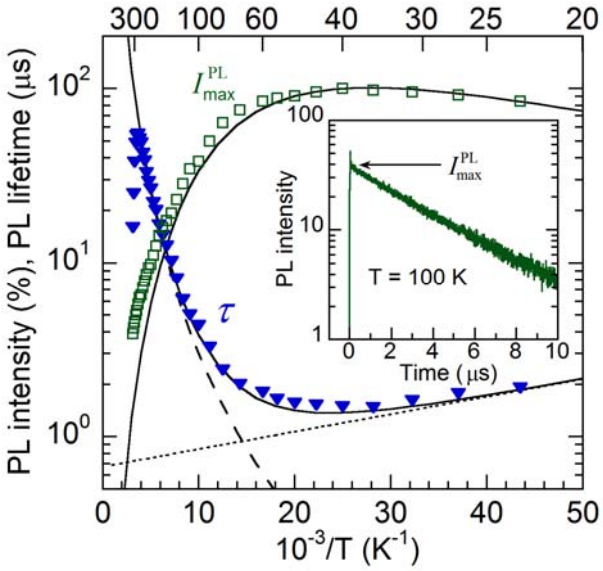

Fig. 4. (Color online) The temperature dependence of the PL lifetime (solid triangles) and the peak PL intensity after a laser pulse, $I_{\max}^{PL}$, (empty squares) for the GL band in GaN (sample RS280). The solid lines are $I_{\max}^{PL}(T)$ and $\tau(T) = \tau_1 + \tau_2$ calculated using Eqs. (4)-(6) with the parameters given in the caption to Fig. 1. The calculated τ_1 and τ_2 components of $\tau(T)$ are shown with the dotted and dashed lines, respectively. The measured and calculated $I_{\max}^{PL}(T)$ dependences are normalized to 100% at about 40 K. The inset shows the decay kinetics at 100 K.

temperature up to 280 K and decreases with an activation energy of about 0.5-0.6 eV at higher temperatures (concurrently with the decrease in τ and steady-state PL intensity). This decrease is explained by the thermal emission of holes from level 2 to the valence band and the related decrease in $N_A^+(0)$ in Eq. (4). The agreement between the experimental and theoretical dependences further supports the model suggested above.

The electron-capture cross-section for the C_N^+ center can be estimated as $\sigma_{nA} \approx 3\times10^{-18}$ and 10^{-19} cm^2 at T = 100 and 300 K, respectively. These values are at least two orders of magnitude smaller than those typically reported for giant traps in Ge and Si (between 10^{-17} and 10^{-14} cm^2 at 300 K) [2]. One reason for this discrepancy may be that photoconductivity measurements were used to determine the characteristic *time of escape*, τ_e, of photogenerated electrons from the conduction band, and the electron capture coefficient was determined from the relationship $\tau_e^{-1} = C_{nA}N_A$ [2]. This reason is two-fold. Namely, in our time-resolved PL measurements we determine the characteristic *time of capture*, τ, of photogenerated electrons by a particular defect, and derive C_{nA} from Eq (1). Also, N_A may be difficult to determine if several uncontrolled defects contribute to τ_e. Furthermore, for *deep* attractive centers, the successive one-phonon transitions of an electron through a ladder of excited states continue until the distance between the excited levels becomes larger than the highest phonon energy, after which multi-phonon transitions become more likely [9]. In our model of the C_N^+ center, one-phonon transitions end at level 1, and the transition of an electron from this level to the ground level 2 results in emission of a photon and the subsequent lattice relaxation via the multi-phonon mechanism (Fig. 3). Time τ_1, given by Eq. (6), is the characteristic time of

electron transition from the conduction band to level 1, and it may be much longer than the characteristic lifetime τ_e of photogenerated electrons in the conduction band. Finally, our experiments clearly reveal the strong temperature dependence of C_{nA} for the GL band in GaN, which is a fingerprint of attractive centers (as opposed to neutral centers for which the capture cross-section is expected to be insensitive to temperature). It is interesting to note that Lax in his pioneer work predicted that the last step in the cascade capture by a deep attractive center may be a radiative transition [1].

In summary, the unusual temperature-dependent behavior of the green luminescence in high-purity GaN is explained by the existence of an excited state of the C_N^+ defect. This state behaves as a classic giant trap, yet it appears only under UV illumination, after the C_N defect captures two holes. With increasing temperature, the capture rate of free electrons by this level decreases as the cube of the temperature, and this delay in the electron capture propagates into the measured PL lifetime for the GL band. The electron-hole recombination causing the GL band occurs in two steps: first, an electron is captured by a giant trap-like state via a cascade of one-phonon transitions; then a spontaneous recombination of the weakly localized electron with one of the holes localized at the C_N^+ defect produces the green luminescence band, which is broad because of multiphonon recombination. We predict that in *p*-type GaN the C_N^+ defects (if present) would behave as giant traps for electrons even in dark (e.g., in *p*-*n* junctions under forward bias).

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