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Tunable thermal quenching of photoluminescence in Mg-doped *p*-type GaN

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We have studied the thermal quenching of the ultraviolet luminescence band with a maximum at about 3.25 eV in *p*-type Mg-doped GaN. The characteristic temperature of the thermal quenching of photoluminescence (PL) gradually shifted to higher temperatures with increasing excitation intensity. This effect is explained by a population inversion of charge carriers at low temperatures, which suddenly converts into a quasiequilibrium population as the temperature increases above the characteristic value. Tunable quenching of PL has been observed only in some of the GaN:Mg samples. The absence of the tunable quenching of PL in another group of GaN:Mg samples is preliminarily attributed to different types of dominant nonradiative defects in the two groups of samples.

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Recently, an abrupt and tunable thermal quenching of photoluminescence (PL) was discovered for high-resistivity Zn-doped GaN and was attributed to certain properties of the nonradiative defects in this material.[1,2] The intensity of the Zn-related blue luminescence (BL^{Zn}) band with a maximum at 2.9 eV decreased by several orders of magnitude in a narrow range of temperatures, and the characteristic temperature of the quenching T^* (or T_0) (Ref. 3) increased with increasing excitation intensity; i.e., the quenching was tunable. We predicted that this interesting PL behavior should be a general phenomenon that could be observed for high-resistivity or *p*-type semiconductors, in particular, for Mg-doped GaN.[1] However, to the best of our knowledge, there are no reports about the tunable quenching of PL in Mg-doped GaN. Since Mg is the only dopant that enables one to obtain reliable *p*-type GaN, understanding and explaining the properties of point defects in this material, especially nonradiative defects, is crucial for improving the efficiency and longevity of GaN-based light-emitting devices.

In the PL spectrum of Mg-doped GaN, either an ultraviolet luminescence (UVL) band with a maximum at about 3.2–3.3 eV or a broad blue luminescence (BL) band with a maximum at 2.7–3.0 eV (the exact position depends on doping and on excitation intensity) dominate in the PL spectrum. The UVL and BL bands are commonly assigned to donor-acceptor pair transitions involving the shallow Mg_{Ga} acceptor and a shallow donor (for the UVL band) or a deep donor (for the BL band).[4–8] Alves *et al.*[9] noted that, for high concentrations of Mg, the BL band dominates in *p*-type GaN grown by metal-organic chemical-vapor deposition (MOCVD), whereas, the UVL band dominates in GaN grown by molecular-beam epitaxy (MBE) and explained it by a lower concentration of deep donors formed in the latter method. However, recent experimental papers show that two or even three acceptor states may be formed in Mg-doped GaN.[10,11] Additionally, new first-principles calculations apparently call for the revision of old models.[12,13] According to Lany and Zunger,[12] the effective-mass state and localized deep state of the Mg_{Ga} acceptor have binding energies of 0.15 and 0.18 eV, respectively. On the other hand, Lyons *et al.*[13] proposed that two levels at 0.26 and 0.13 eV above the valence-band maximum are due to the Mg_{Ga} acceptor and Mg-H complex, respectively. Thus, defect-related PL in Mg-doped GaN should be examined more closely. In this paper, we report on the discovery of tunable thermal quenching of the UVL band in Mg-doped GaN.

The samples studied in this paper were grown by MBE in two steps. First, 350–500-nm-thick layers of undoped GaN were grown on 5- to 6-μm-thick GaN(0001) templates, which were grown by MOCVD on Al_2O_3. On top of that, 750–800-nm-thick *p*-type GaN:Mg layers were grown. The concentration of free holes p and their mobility μ were estimated from an analysis of the Hall-effect data at room temperature and were in the ranges of (6–11) $\times$ 10^{17} cm^{-3} and 9–13 $cm^2\,V^{-1}\,s^{-1}$, respectively. The concentration of Mg in these samples, measured by secondary ion-mass spectrometry varied between 2.3 $\times$ 10^{19} and 4.9 $\times$ 10^{19} cm^{-3}. Steady-state PL was excited with a continuous-wave He-Cd laser (40 mW). Other details of the PL measurement can be found in Ref. 1. The absolute internal quantum efficiency of PL η is defined as $\eta = I^{PL}/G$, where I^{PL} is the integrated PL intensity from a particular PL band and G is the concentration of electron-hole pairs created by the laser per second in the same volume. To find η, we compared the integrated intensity of the UVL band with PL intensity obtained from a calibrated GaN sample.[1,14] All of the measurements were performed under identical conditions with calibrated excitation power density P_{exc}.

The PL spectra and their evolution with increasing temperature from 20 to 200 K for two characteristic samples are shown in Fig. 1. The dominant PL band at low temperatures is the UVL band which extends from 2.8 to 3.3 eV and has a main maximum at about 3.25 eV. The exciton emission is weak, peaking at 3.465 eV at 20 K. A defect-related band with a maximum at 2.36 eV [the high-energy tail of which could be seen in Fig. 1(b) at temperatures above 120 K] is probably the GL2 band,[5] and its study is beyond the scope of this paper. We have not observed the BL band in these samples. The studied samples can be divided into two groups according to their different temperature behaviors of PL: group A (representative sample 9600 with $p = 6 \times 10^{17}$ cm^{-3}) and group B (samples 9591 and 9599 with $p \approx 1 \times 10^{18}$ cm^{-3}).

For the samples from group A, the UVL band is quenched above 60 K with an activation energy of only about 30 meV.

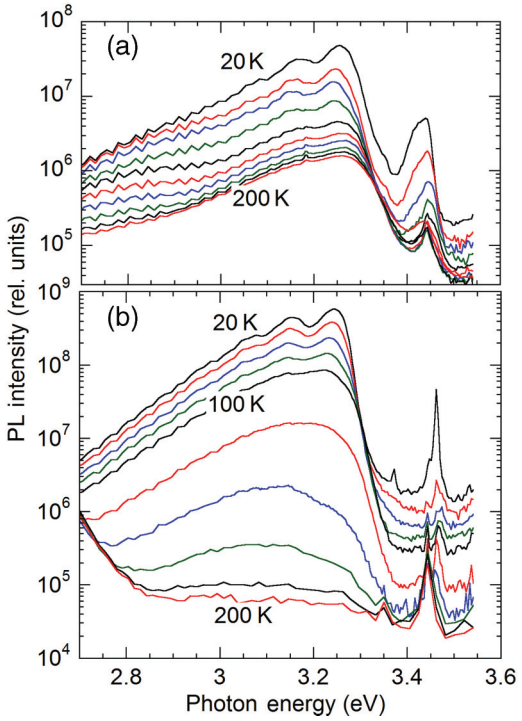

FIG. 1. (Color online) Evolution of the PL spectrum in p-type Mg-doped GaN with increasing temperature from 20 to 200 K with a step of 20 K. (a) Sample 9600 (group A) and (b) sample 9591 (group B). $P_{exc} = 0.3$ W/cm^2. The weak oscillations with a period of about 35 meV are due to a Fabry-Pérot effect in the sapphire/GaN/air cavity, revealing the total thickness of the GaN layers (undoped and Mg doped) to be about 7 μm.

The total decrease in the UVL band intensity is about an order of magnitude in the temperature range of 20–200 K [Fig. 1(a)]. The intensity of the UVL band in samples of group B decreases slowly as the temperature increases from 20 to 100 K, and its shape transforms into a structureless band [Fig. 1(b)]. This changing shape can be explained by potential fluctuations due to a random distribution of charged centers in a heavily doped semiconductor.[4,15,16] A remarkable feature is the abrupt quenching of the UVL band in these samples, which is observed in the temperature range of 100–180 K. At higher temperatures, the UVL band can hardly be resolved. Interestingly, the characteristic temperature T_0, at which the abrupt quenching begins, increases with increasing excitation intensity (Fig. 2). In contrast, T_0 in group A samples is much lower and apparently is independent of excitation intensity (Figs. 2 and 3).

The abrupt tunable quenching was previously observed in high-resistivity Zn-doped GaN and was attributed to a sudden transition of the system from a population inversion of charge carriers in the band gap at $T < T_0$ to a quasiequilibrium population at $T > T_0$.[1,2] When the value of $1/T_0$ is plotted as a function of the logarithm of excitation intensity, a linear dependence is observed for samples from group B (Fig. 3). This dependence can be described with the following expression:[1]

$$T_0 \approx T^* = \frac{E_A}{k \ \ln(B/G)}, \tag{1}$$

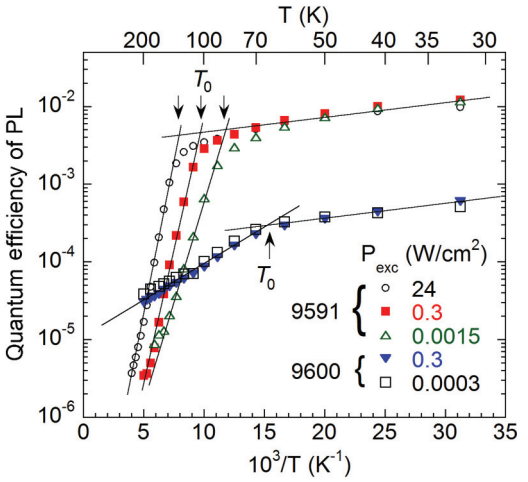

FIG. 2. (Color online) Temperature dependence of the quantum efficiency of the UVL band in p-type Mg-doped GaN for different P_{exc}'s. The lines are extrapolations of the low-temperature and high-temperature parts with an intersection at the characteristic temperature T_0. For sample 9591 (group B), T_0 shifts with increasing excitation intensity, whereas, for sample 9600 (group A), it does not.

with

$$B = C_{pA}\left(\eta_0^{-1} - 1\right)(N_A - N_D)N_v/2. \tag{2}$$

Here, E_A is the ionization energy of the acceptor A responsible for the abrupt quenching of PL, k is Boltzmann's constant, C_{pA} is the hole-capture coefficient for the acceptor, η_0 is the internal quantum efficiency of PL via the acceptor A at temperatures below T_0, N_A and N_D are concentrations of the acceptor and shallow donor, respectively, and N_v is the effective density of states in the valence band. By using the value of B, found from the fit (3×10^{34} cm^{-3} s^{-1}), C_{pA} estimated for the shallow acceptor responsible for the UVL band in GaN (10^{-6} cm^3/s),[5] $N_A \approx 4 \times 10^{19}$ cm^{-3} (assuming that $N_A \gg N_D$), and $N_v \approx 3 \times 10^{18}$ cm^{-3} at $T \approx 100$ K, we

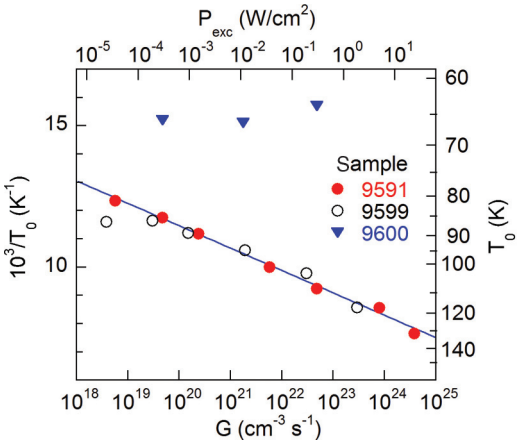

FIG. 3. (Color online) Dependence of the characteristic temperature T_0 on excitation intensity for the UVL band in three Mg-doped GaN samples. The line is calculated using Eq. (1) with $E_A = 250$ meV and $B = 3 \times 10^{34}$ cm^{-3} s^{-1}.

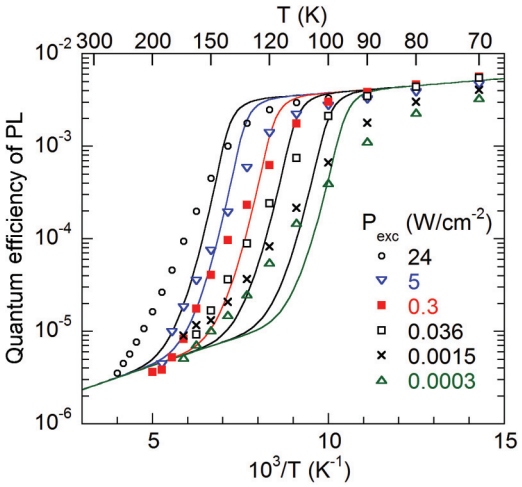

FIG. 4. (Color online) Temperature dependence of the quantum efficiency of the UVL band in p-type Mg-doped GaN (sample 9591) for excitation power densities between 3×10^{-4} and 24 W/cm^2. The solid lines are the numerical solution of Eqs. (7)–(12) from Ref. 1 with the following parameters: $N_S = 9 \times 10^{18}$, $N_A = 2 \times 10^{19}$, $N_D = 1 \times 10^{17}$ cm^{-3}, $C_{nD} = 8 \times 10^{-8}$, $C_{nS} = 10^{-6}$, $C_{pS} = 5 \times 10^{-6}$, $C_{pA} = 10^{-6}$, $C_{DA} = 10^{-11}$, $C_{nA} = 10^{-12}$ cm^3/s, $E_D = 10$, $E_A = 270$ meV, and $G = 1.6 \times 10^{23} \times P_{\text{exc}}$ cm^{-3} s^{-1}.

obtain $\eta_0 \approx 0.002$ from Eq. (2). This value is close to $\eta_0 \approx 0.005$ obtained from comparison of the integrated intensity of the UVL band with PL intensity from a calibrated GaN sample.

In order to quantitatively describe the temperature dependence of the PL intensity in group B samples, we will use a model involving three defects participating in the recombination of photoexcited charge carriers.[1] One defect is an acceptor A (presumably Mg_{Ga}), which is responsible for the UVL band. Another defect is a shallow donor D, which is possibly O_N or V_NH.[17] The transition of electrons from this shallow donor to the acceptor is expected to be the main source of the UVL band, at least, at low temperatures. Finally, to account for less than 100% quantum efficiency of PL, we introduce a nonradiative defect S (a deep donor). This is the same set of defects that was used to explain the abrupt tunable thermal quenching of PL in high-resistivity Zn-doped GaN.[1] Note that the dominant nonradiative center may not be the same defect in these two materials. It is commonly accepted that a deep donor (presumably, the V_NMg_{Ga} complex) is involved in the optical transition responsible for the BL band in Mg-doped GaN.[5] However, the dominant nonradiative deep donor in our Mg-doped samples most likely has a different origin because the BL band was not observed at all.

Figure 4 shows the results of the fit of the experimental data with numerical solutions of Eqs. (7)–(12) from Ref. 1. The calculated dependencies reproduce the tunable quenching of the UVL band. In agreement with Eq. (1), the PL quenching shifts to higher temperatures with increasing excitation intensity (Fig. 4). The magnitude of the drop (about 3 orders of magnitude) is slightly smaller than in the case of Zn-doped GaN (4 to 5 orders of magnitude), and the drop in PL intensity is less abrupt. The slope of the thermal quenching region increases from 100 to 180 meV with increasing P_{exc} from 10^{-3} to 24 W/cm^2 (Fig. 2). The model predicts a more abrupt drop in PL. We attribute the discrepancy to a manifestation of the potential fluctuations in heavily doped or compensated semiconductors. Note that potential fluctuations rise with decreasing excitation intensity.[4,16]

The parameters of the model used in the fit shown in Fig. 4 may not ensure the best fit but rather are used to illustrate that the tunable behavior of PL can be reproduced with reasonable assumptions. The capture coefficients for the BL^{Zn} band in Zn-doped GaN (see Ref. 1) and the UVL band in Mg-doped GaN (given in the caption for Fig. 4) differ by not more than an order of magnitude. Concentrations of the A and S centers are much higher than for Zn-doped GaN, which is consistent with the high level of doping in GaN:Mg. The ionization energy of the acceptor obtained from a simple fit with Eq. (1) and from numeric calculations is about 250–270 meV, which is slightly larger than the ionization energy of the Mg_{Ga} acceptor [150–200 meV (Ref. 5)]. This discrepancy can also be caused by potential fluctuations in Mg-doped GaN.

According to the model, the tunable quenching of PL implies that, at low temperatures ($T < T_0$), the nonradiative S centers are saturated with electrons when the sample is illuminated, which results in the accumulation of free electrons in the conduction band and in n-type conductivity. At higher temperatures ($T > T_0$), holes emitted from the shallow acceptor efficiently recombine with electrons at the S centers, which results in a sudden drop in the concentration of free electrons and, consequently, the reconversion of conductivity from n type to p type. It is interesting to note that the tunable quenching is observed only for some Mg-doped GaN samples (group B) and is not observed for others (group A) where the UVL band is quenched with a very low activation energy in a wide temperature range. The difference between groups A and B is attributed preliminarily to different types of dominant nonradiative centers in the different samples. More research is needed to establish which properties of the samples primarily cause the different PL behavior between groups A and B. Our preliminary study of p-type GaN:Mg samples grown by hydride vapor phase epitaxy gives similar results: Two types of the UVL band quenching can be distinguished that correspond to groups A and B discussed in this paper.

Until recently, the tunable quenching of PL was reported only for ZnS, ZnCdS, CdS, and GaP.[18–20] In all cases, the tunable quenching was observed in high-resistivity materials. This also agrees with the case of high-resistivity Zn-doped GaN where, not only tunable, but also very abrupt thermal quenching, was observed.[1] According to our model, the tunable quenching can also be observed in p-type semiconductors, provided that the acceptor level is not very shallow. The discovery of the tunable thermal quenching of PL in Mg-doped GaN is an important step in understanding the processes which contribute to the PL from defects in semiconductors. The detailed study of these processes may shed light on the origin and properties of nonradiative defects that may detrimentally affect GaN-based materials and light-emitting devices.

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