

Evidence of compensating centers as origin of yellow luminescence in GaN

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The dependence of the near-band edge and the yellow luminescence in *n*-type GaN grown by organometallic vapor-phase epitaxy is investigated as a function of doping concentration. The band edge and yellow luminescence intensity increase as the doping concentration is increased. However, the band-edge-to-yellow luminescence ratio does not change significantly as the doping concentration is increased by two orders of magnitude. A theoretical model based on rate equations is developed for the band-edge-to-yellow intensity ratio. Analysis of the experimental data in terms of the model reveals that the concentration of the level causing the yellow luminescence increases linearly with doping concentration. This dependence shows that the yellow luminescence is due to a compensating center. © 1997 American Institute of Physics. [S0003-6951(97)00248-9]

The dominant optically active defect in GaN causes an optical transition at 2.2 eV which is in the yellow part of the visible spectrum. The yellow luminescence is commonly found in GaN grown by organometallic vapor-phase epitaxy (OMVPE).¹⁻⁴ Although, luminescence measurements reveal a distinct optical signature of the defect, the microstructure and chemical nature of the defect has not been identified. Recently, Neugebauer and Van de Walle⁵ proposed that a native defect, namely, the Ga vacancy, is the microstructural origin of the yellow luminescence. Their calculations suggest that the Ga vacancy is a triply-charged acceptor level whose abundance increases with the third power of the doping concentration. Thus, the calculations suggest that the center is a compensating native defect which occurs predominantly in *n*-type GaN. Other models^{6,7} propose that the yellow luminescence is due to C acceptors, double donors, iron impurities, and intrinsic defects related to dislocations.

In this publication, the UV and yellow luminescence transitions in Si-doped GaN epitaxial films are investigated as a function of the doping concentration. The comparison of a theoretical model with experimental results yields the dependence of the defect concentration on the doping concentration. This dependence can reveal the critical signature of compensating defects which are known to increase with doping concentration according to a power law.⁸⁻¹⁰

The Si-doped GaN samples were grown by OMVPE on the *c* plane of a sapphire substrate at a temperature of 1100 °C. A growth rate of 2 μm/h was employed. The flow of the diluted silane (SiH₄) doping precursor was systematically varied to achieve doping densities in the range 5 × 10¹⁶ to 7 × 10¹⁸ cm⁻³. The room-temperature photoluminescence measurements were performed using an 80 mW HeCd laser emitting at 325 nm. The excitation density was adjusted to 3 W/cm⁻². The luminescence was dispersed in a 0.75 m spectrometer, detected by a GaAs photomultiplier using low-noise phase-sensitive “lock-in” amplification.

The room-temperature photoluminescence spectrum of an *n*-type GaN sample grown by OMVPE is shown in Fig. 1.

The spectrum displays two features namely the near-band-edge transition at 3.4 eV and the broad emission band centered at 2.2 eV. The two transitions will be referred to as the *ultraviolet* (UV) and *yellow* transition for the 3.4 and 2.2 eV transition, respectively. The broad yellow band exhibits a periodic intensity modulation attributed to microcavity effects.¹¹

The inset of Fig. 1 shows the two transitions in terms of the band diagram. The yellow transition involves a Shockley–Read type transition with a single deep level located within the bandgap. This deep level is broadened to account for the substantial linewidth of the yellow luminescence band. Either one of the two transitions labeled as “1” and “2” in the inset is radiative. The band diagram with a single deep level, as shown in the inset, was used to successfully model the excitation-density dependence of the UV and yellow luminescence.¹²

Photoluminescence spectra of the four samples with different doping concentration are shown in Fig. 2. The excita-

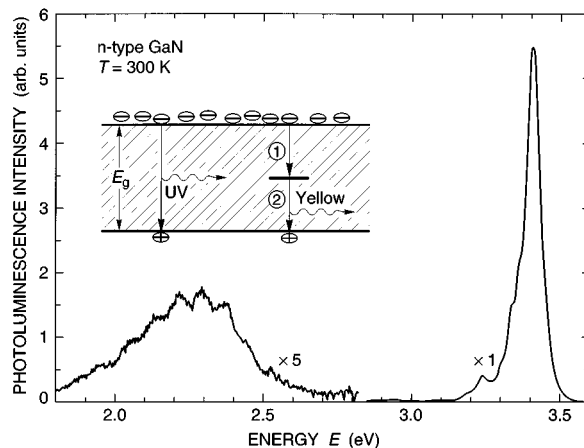


FIG. 1. Room-temperature photoluminescence of *n*-type GaN. The inset schematically shows the near-band edge and the yellow transition occurring at 3.4 and 2.2 eV, respectively.

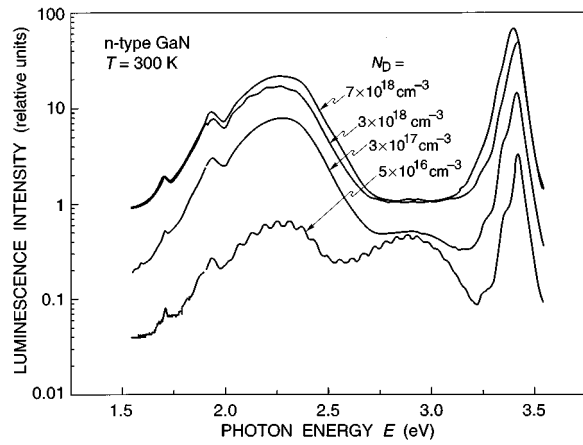


FIG. 2. Room-temperature photoluminescence spectra of *n*-type GaN for different doping concentrations.

tion density is 3 W/cm^2 for all spectra. Inspection of Fig. 2 reveals that the UV intensity increases with the doping concentration. The linewidth of the UV peak is about $2 \times kT$. In addition, the spectra display a strong yellow luminescence line. The intensity of the yellow line also increases with the doping concentration. All spectra exhibit another weak luminescence band around 2.9 eV which is probably due to a band-to-acceptor transition.

Next, a theoretical model will be developed which allows one to deduce the *concentration* of the defect causing the yellow luminescence as a function of doping concentration. The model takes into account the dominant optical transitions in GaN, namely, the near-band edge and the yellow luminescence transition. The model presented here is based on these two transitions. It is assumed that the semiconductor has *n*-type conductivity with $n = N_D$. Under low-density photoexcitation, the free electron and hole concentrations are $n \approx N_D$ and $p \gg p_0$, respectively. Assuming that the charge state of the deep level is either neutral or negative, the total deep level concentration is given by $N_T = N_T^0 + N_T^-$, where N_T^0 and N_T^- is the concentration of neutral and negatively charged deep levels, respectively.

Next, rate equations for the UV and yellow transitions will be derived. Using these rate equations, it will be shown that the comparison between theoretical and experimental results allows one to deduce the dependence of the deep level concentration on the doping concentration. The intensity of the UV transition can be expressed by the bimolecular recombination coefficient B , i.e.,

$$I_{\text{UV}} = Bnp = BN_D p. \quad (1)$$

The deep level transition consists of two sequential transitions, namely the conduction-band-to-deep-level transition with rate I_1 , and the deep-level-to-valence-band transition with rate I_2 . The two transition rates are given by

$$I_1 = C_1 n N_T^0 = C_1 N_D N_T^0, \quad (2)$$

$$I_2 = C_2 N_T^- p, \quad (3)$$

where C_1 and C_2 are constants. The two transitions are sequential and therefore the rate I_1 is equal to I_2 under steady-

state conditions. This condition along with $N_D \gg p$ leads to the inequality $N_T^- \gg N_T^0$. That is, most of the deep centers are *occupied* at low excitation levels

$$N_T = N_T^0 + N_T^- \approx N_T^-. \quad (4)$$

This result can also be obtained by considering that the trap levels are *below* the Fermi level and therefore they are mostly occupied.

The *ratio* of the UV and yellow luminescence intensity can be obtained by dividing Eq. (1) by Eq. (3). Using $I_{\text{yellow}} = I_2$, one obtains

$$\frac{I_{\text{UV}}}{I_{\text{yellow}}} = \frac{BN_D p}{C_2 N_T p} = \frac{BN_D}{C_2 N_T} \propto \frac{N_D}{N_T}. \quad (5)$$

Thus the UV-to-yellow ratio is proportional to N_D/N_T if the deep level concentration is independent of the doping concentration. On the other hand, since the UV-to-yellow ratio and N_D is known, the dependence of N_T on the doping concentration can be deduced.

Next, two special cases will be considered. First, assume N_T does *not* depend on the doping concentration. In this case, it is $I_{\text{UV}}/I_{\text{yellow}} \propto N_D$ as deduced from Eq. (5). That is, the UV signal becomes stronger as the doping concentration is increased. In the second case, it is assumed that N_T *increases* with the doping concentration. This dependency applies to compensating defects whose abundance increases in highly doped semiconductors as shown by Baraff and Schlüter.⁸ If $N_T \propto N_D$, then the UV-to-yellow intensity ratio is *constant*, i.e., independent of the doping concentration, as inferred from Eq. (5).

Generally, if the deep level concentration depends on the doping concentration according to the power law

$$N_T \propto (N_D)^i \quad (i=0,1,2,\dots), \quad (6)$$

then the luminescence ratio deduced from Eq. (5) is given by

$$\frac{I_{\text{UV}}}{I_{\text{yellow}}} \propto N_D^{(1-i)}. \quad (7)$$

Using experimental results, the exponent $(1-i)$ can be determined and, by using Eq. (6), the dependence of the deep level abundance on the doping concentration.

The experimental UV-to-yellow luminescence intensity ratio is shown in Fig. 3. Both the peak ratio and the integrated ratio are shown in the figure. Figure 3 reveals that the doping concentration changes over more than two orders of magnitude, whereas the luminescence ratio changes by much less than one order of magnitude. Considering the large change in doping concentration and the relatively small change in the UV-to-yellow ratio, it is very reasonable to assume that the luminescence ratio is approximately constant, i.e., *independent* of the doping concentration. Using this experimental dependence, the exponent in Eq. (7) is given by $(1-i) = 0$ or $i = 1$. Thus the deep level concentration *increases linearly with doping concentration*, as deduced for $i = 1$ from Eq. (6).

The dependence $N_T \propto N_D$ obtained from the experimental data is the typical signature of acceptor-type impurities and for compensating native defects. Originally such defects have been proposed by Longini and Greene.¹⁰ Later the cal-

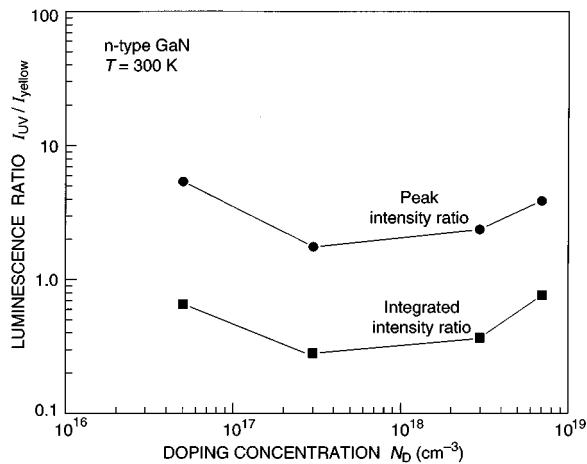


FIG. 3. Peak and integrated intensity ratio of the ultraviolet (UV) and yellow luminescence of *n*-type GaN as a function of doping concentration.

calculations of Baraff and Schlüter⁸ confirmed for GaAs that the abundance of native defects depends on the doping concentration. Recently, Neugebauer and Van de Walle⁵ performed first-principles calculations which provided evidence that Ga vacancies in GaN form a self-compensating acceptor level in *n*-type GaN. Based on the calculations, the Ga vacancy forms a level in the forbidden gap causing the yellow luminescence. Since the level is of the acceptor type, its formation energy decreases as the *n*-type concentration increases. The experimental results presented here confirm the predicted concentration increase.⁵

The trap level was postulated to have a dependence on the doping concentration according to the power law $N_T \propto N_D^3$.⁵ Careful inspection of the data shown in Fig. 3 displays some scattering, yielding a range of dependences of $N_T \propto N_D^i$ with $0.75 \leq i \leq 1.5$. Thus, a cubic dependence cannot be inferred from the experimental data. The data is consistent with a singly-charged acceptor level such as C in GaN.

The presence of additional nonradiative centers can be demonstrated on the basis of the overall improving radiative efficiency as the doping concentration increases. The luminescence intensity of the *n*-type GaN as a function of doping concentration is shown in Fig. 4. The peak and the integrated intensity clearly increase as the doping concentration is increased. The overall increase in quantum efficiency shows the relevancy of luminescence killers, in particular at low doping concentrations. Since the concentration of these luminescence killers is unknown, there is no benefit in taking them into account in our present model. However, the overall increases in luminescence efficiency argues against a super-linear increase of luminescence killers at high doping concentrations. Whereas the yellow luminescence defect is found to increase with the doping concentration, the overall concentration of luminescence killers does not increase with doping concentration.

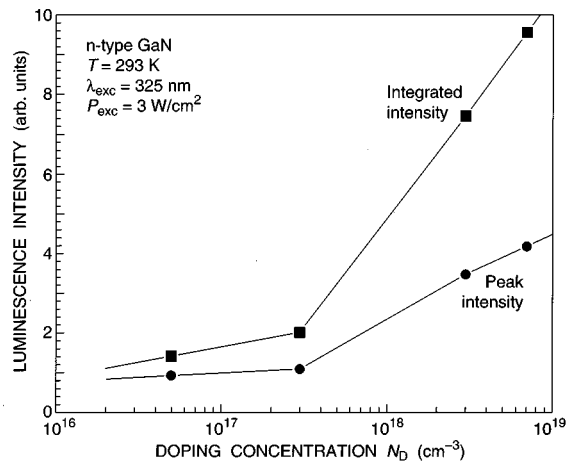


FIG. 4. Peak intensity and integrated intensity of the near-band-edge transition of *n*-type GaN as a function of doping concentration.

In conclusion, the UV-to-yellow luminescence ratio is investigated as a function of doping concentration for Si donor concentrations ranging from 5×10^{16} to $7 \times 10^{18} \text{ cm}^{-3}$. Experimental results show that this ratio is approximately constant in the low-excitation regime, i.e., independent of the doping concentration. A theoretical model based on rate equations is developed that allows for the deduction of the yellow luminescence defect concentration as a function of the doping concentration. The comparison of the model with experimental results reveals that the defect concentration increases approximately linearly with doping concentration. This dependence is consistent with compensating centers in semiconductors which could be either acceptor impurities such as carbon or compensating native defects as proposed by Neugebauer and Van de Walle.

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- ¹J. I. Pankove and J. A. Hutchby, *J. Appl. Phys.* **47**, 5387 (1976).
- ²D. H. Zhang, K. Radhakrishnan, and S. F. Yoon, *J. Cryst. Growth* **148**, 34 (1995).
- ³T. Ogino and M. Aoki, *Jpn. J. Appl. Phys.* **19**, 2395 (1980).
- ⁴D. M. Hofmann, D. Kovaler, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Hertz, T. Detchprom, H. Amano, and I. Akasaki, *Phys. Rev. B* **52**, 16702 (1995).
- ⁵J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **69**, 503 (1996).
- ⁶A. Hoffmann, L. Eckey, P. Maxim, J.-C. Holst, R. Heitz, D. M. Hofmann, D. Kovaler, G. Steude, D. Volm, B. K. Meyer, T. Detchprom, K. Hiramatsu, H. Amano, and I. Akasaki, *Solid-State Electron.* **41**, 275 (1997).
- ⁷E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. Asif Kahn, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, *Phys. Rev. B* **51**, 13326 (1995).
- ⁸G. A. Baraff and M. Schlüter, *Phys. Rev. Lett.* **55**, 1327 (1985).
- ⁹E. F. Schubert, *Doping in III-V Semiconductors* (Cambridge University, Cambridge, 1993).
- ¹⁰R. L. Longini and Greene, *Phys. Rev.* **102**, 992 (1956).
- ¹¹A. Billeb, W. Grieshaber, D. Stocker, and E. F. Schubert, and R. F. Karlicek, Jr., *Appl. Phys. Lett.* **70**, 2790 (1997).
- ¹²W. Grieshaber, E. F. Schubert, I. D. Goepfert, R. F. Karlicek, Jr., M. J. Schurman, and C. Tran, *J. Appl. Phys.* **80**, 4615 (1996).