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Temperature quenching of photoluminescence intensities in undoped and doped GaN

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This work discusses the temperature behavior of the various photoluminescence (PL) transitions observed in undoped, *n*- and *p*-doped GaN in the 9–300 K range. Samples grown using different techniques have been assessed. When possible, simple rate equations are used to describe the quenching of the transitions observed, in order to get a better insight on the mechanism involved. In undoped GaN, the temperature dependence of band edge excitonic lines is well described by assuming that the *A* exciton population is the leading term in the 50–300 K range. The activation energy for free exciton luminescence quenching is of the order of the *A* rydberg, suggesting that free hole release leads to nonradiative recombination. In slightly *p*-doped samples, the luminescence is dominated by acceptor related transitions, whose intensity is shown to be governed by free hole release. For high Mg doping, the luminescence at room temperature is dominated by blue PL in the 2.8–2.9 eV range, whose quenching activation energy is in the 60–80 meV range. We also discuss the temperature dependence of PL transitions near 3.4 eV, related to extended structural defects. © *1999 American Institute of Physics.* [S0021-8979(99)05619-4]

I. INTRODUCTION

GaN is the base of a family of compounds (Al,Ga,In)N which during the last decade has gained a lot of attention due to their present or future applications such as, for instance, light emitting diodes,[1] laser diodes,[1] ultraviolet photodetectors[2,3] and high temperature, high power electronic devices.[3,4] These developments are due to tremendous improvements in the crystal growth of these alloys. Concomitantly, the understanding of the basic properties of GaN and its alloys has been increasing, and optical studies such as photoluminescence (PL) have been widely used to this end (see for instance Refs. 5–12). However, there are still some problems that are unresolved, for instance, the nature of the residual acceptor and the optical depth of Mg acceptors,[13–15] the identification of some bound exciton lines[16,17] etc. Recently, Monemar[18] has reviewed the difficulties that remain regarding the optical properties of GaN, and his remarks are still up-to-date. The present work studies the temperature (T) dependence of the various PL transitions observed in undoped and doped GaN in the 9–300 K range. A particular emphasis is given to the quenching of these transitions, and an explanation in terms of simple rate equations is given when possible. Our aim is to get a deeper understanding on the mechanisms involved in the temperature induced reduction of the quantum efficiency of GaN. We show that it is possible in some cases to get general rules for the quenching of PL intensities, and point cases where it is not (for instance highly *p*-doped samples). This article is organized as follows: Sec. II will present the experimental details and some generalities about the temperature dependent PL spectra of GaN. Section III will discuss the temperature dependence of band edge PL intensities in undoped and *n*-doped GaN. Section IV is devoted to *p*-doped GaN. Conclusions are given in Sec. V.

II. EXPERIMENTS AND GENERALITIES

The samples were grown by metal-organic vapor phase epitaxy (MOVPE), molecular beam epitaxy (MBE) using NH_3 as nitrogen precursor, and halide vapor phase epitaxy (HVPE). The substrates are *c* plane sapphire in each case. Typical thicknesses for the samples used in the present study are in the 2–4 μm range for MOVPE- or MBE-grown ones, and much larger for HVPE-grown ones ($\geqslant 20$ μm). Details on the growth procedures can be found in Ref. 19 and 20 for MOVPE and MBE, respectively. Typical residual *n*-type doping are about 5×10^{16}, 5×10^{16}, and $5\times10^{17}\,\mathrm{cm}^{-3}$, and mobilities 500, 150, and 150 $\mathrm{cm}^2/\mathrm{V\,s}$ for our MOVPE-, MBE-, and HVPE-grown samples, respectively. Intentional *n*-type doping is achieved using SiH_4 or elemental Si for MOVPE and MBE growth, respectively. In MOVPE growth, *p*-type doping is achieved using bismethylcyclopentadienylmagnesium, and acceptor activation is obtained through annealing under N_2 atmosphere.[1,19] Elemental Mg is used for *p* doping in MBE growth, and no postgrowth annealing is necessary in this case.[21] For PL experiments, the samples were placed in a closed cycle He cryostat. PL was excited with a 10 mW HeCd laser working at 325 nm (maximum excitation intensity$\approx 15\,\mathrm{W/cm}^2$) and was detected through a Jobin Yvon HR 640 monochromator using a cooled GaAs photomultiplier and conventional lock-in techniques. For undoped or slightly *n*-doped samples, the energy positions of the free *A*, *B*, and *C* excitons were measured by reflectivity,[22] in order to ascertain the identification of near edge PL transitions. However, reflectivity spectra proved to be featureless in *p*-type samples, or in *n*-type samples with doping larger than $10^{18}\,\mathrm{cm}^{-3}$.

Before talking about luminescence quenching, it is useful to briefly present temperature dependent PL spectra and

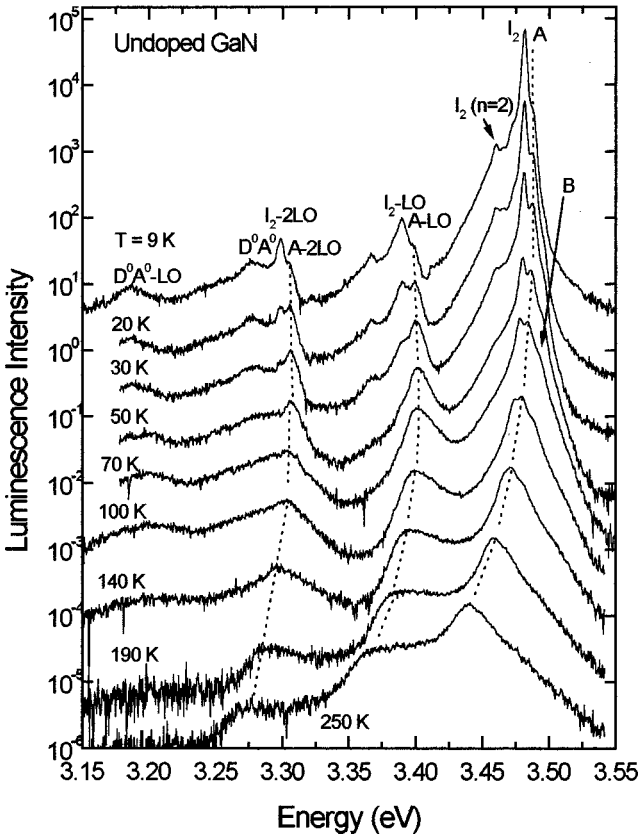

FIG. 1. Typical temperature dependence of the luminescence spectra of high quality undoped GaN. The spectra have been shifted vertically for clarity. The sample is grown by MOVPE.

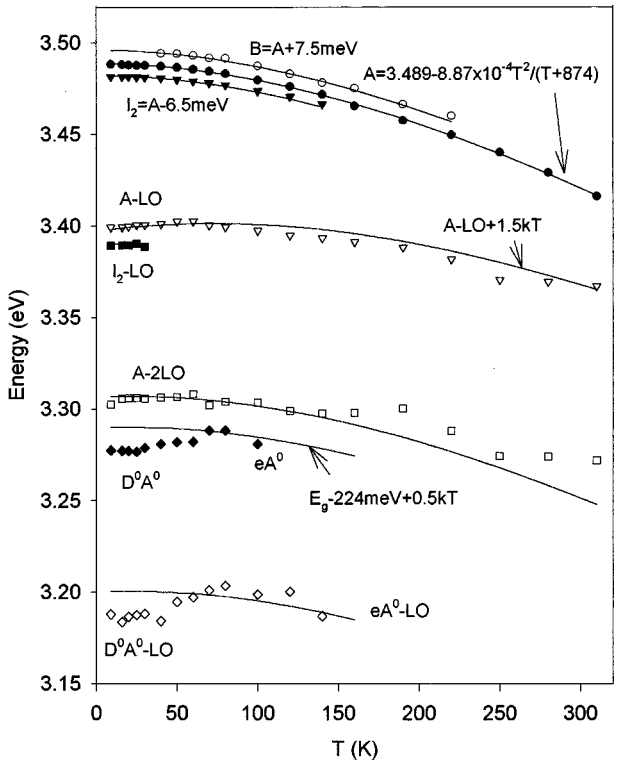

FIG. 2. Temperature dependence of the energy of the various transitions recorded in Fig. 1.

the temperature dependence of PL energies. Figure 1 shows the typical PL spectra of undoped GaN grown by MOCVD as a function of temperature. At low temperature, the spectra are dominated by neutral donor bound recombination (I_2 line). With increasing T, the I_2 line progressively quenches to the benefit of the A free exciton line. The free B exciton recombination can also be observed. Note that the assignment of the A and B lines to free excitons comes from temperature dependent reflectivity experiments. At high temperature, the spectra are dominated by free A excitons and their LO phonon replica. Other features appearing in the spectra shown in Fig. 1 are the phonon replica of donor bound excitons (I_2-LO), neutral donor acceptor pairs recombination (D^0A^0) near 3.27 eV and their LO phonon replica (D^0A^0-LO) near 3.18 eV, involving the usual residual acceptor in GaN, with a Huang–Rhys factor S of 0.7.[10] The line labeled $I_2(n=2)$ is the two electron replica of the donor bound exciton line, corresponding to a 29 meV deep donor.[22,23] We have observed a similar replica in intentionally Si doped samples[24] and tentatively identify this 29 meV donor to Si.[18,25] Figure 2 gives the temperature dependence of PL energies corresponding to Fig. 1. The A line is followed in the whole temperature range, and the fitting of its energy to a Varshni-type equation gives

$$E(T)(eV)=E(0)-8.87\times10^{-4}T^2/(T+874). \quad (1)$$

This relation gives a very satisfactory account of the excitonic energy variation in the μm thick GaN films on sapphire that we investigated. It is also in excellent agreement with that quoted in Ref. 26. The I_2 and B lines are shown to follow the A line. The position of the LO replica of the A line is compared to its expected temperature dependence deduced from its theoretical line shape[11,27] $I(A\text{-LO})\alpha E^{3/2}\exp(-E/kT)$. Some departure of the expected dependence can be due to point defect scattering, as discussed by Buyanova *et al.*[11] As Fig. 2 shows, for $T>50$ K, the D^0A^0 band progressively evolves towards a free electron–neutral acceptor band eA^0 due to donor ionization. The position of this last band points to a 223 ± 1 meV deep residual acceptor, in agreement with most findings.[8,10,13,18,22]

Under injection, the population governing a certain transition is given by

$$\partial n/\partial t=G-n/\tau_R-n/\tau_{NR}, \quad (2)$$

where n is the density of the minority carrier or exciton concerned, G is the generation rate, τ_R and τ_{NR} are radiative and nonradiative lifetimes. Nonradiative recombination rates are generally thermally activated (whether they correspond to level depopulation or to the activation of a nonradiative recombination center), i.e., $\tau_{NR}=\tau_0\exp(E_A/kT)$. Under steady state, and since PL intensities are proportional to n/τ_R, one obtains the familiar expression

$$I=I_0/[1+a\exp(-E_a/kT)] \quad (3)$$

with $a=\tau_R/\tau_0$. If for instance two nonradiative recombination channels are competitive, one gets

$$I=I_0/[1+a_1\exp(-E_{a1}/kT)+a_2\exp(-E_{a2}/kT)]. \quad (4)$$

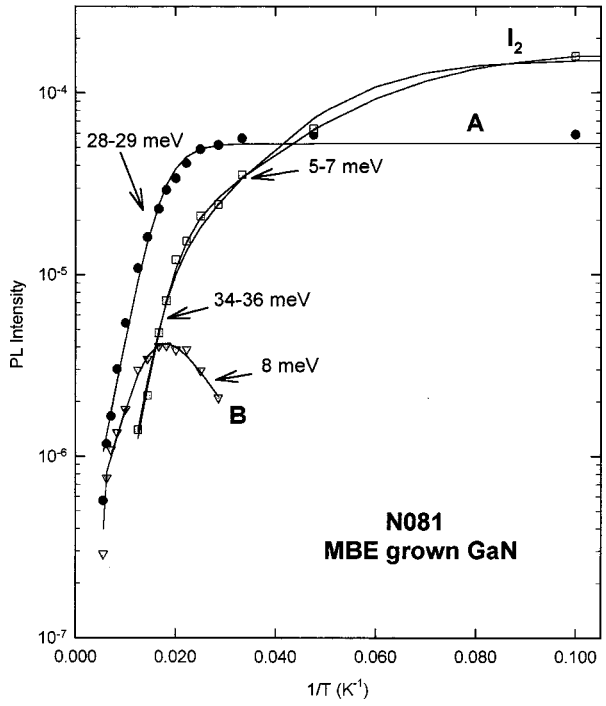

FIG. 3. Temperature dependence of the intensities of the main band edge luminescence lines in the case of an undoped MBE-grown GaN sample. Solid lines correspond to least square fits using the various expressions given in the text.

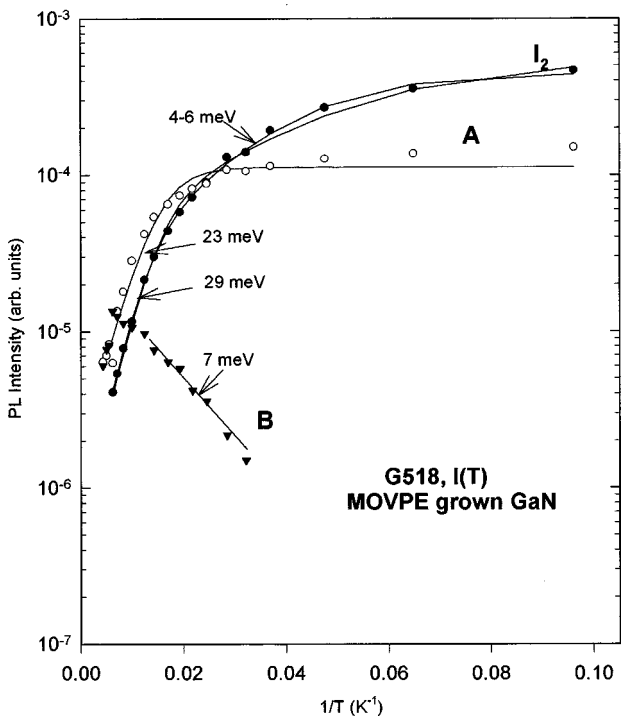

FIG. 4. Temperature dependence of the intensities of the main band edge luminescence lines in the case of an undoped MOVPE-grown GaN sample. Solid lines correspond to least square fits using the various expressions given in the text.

Equations (3) and (4) will be used in this work. They deserve some comments. A first one is that a quantum efficiency near unity is assumed at low T. The second is that the temperature dependence of radiative lifetimes is not taken into account. This variation is assumed to be weak in the temperature range where PL intensities are exponentially varying. Another comment is that apparent thermal depths are generally lower than optical ones, due for instance to the existence of excited states, of crystal field or spin orbit split levels.[28]

III. UNDOPED AND *n*-DOPED GaN

Figure 3 is an Arrhenius plot of the integrated intensities of the I_2, A, and B lines of an undoped MBE-grown sample. Figure 4 is the same for an undoped MOVPE-grown one. The solid lines are least square fits to their variations using Eq. (3) for the A exciton intensity, and Eq. (4) for the I_2 one. As Figs. 3 and 4 show, the A intensity is well described using a single activation energy, which amounts to 23 meV for the MOVPE sample and 28–29 meV for the MBE one. We emphasize that in all the samples studied, we measured activation energies in this range for the A exciton, with most values near the 25 meV range. This result is also in good agreement with Ref. 27 ($E_a = 26.7$ meV), and we note that the thermal activation energies so obtained for free exciton luminescence quenching is of the order of the A exciton Rydberg (reported to be in the 21–27 meV range[5,10,12,18,23,25,29]). The I_2 line first quenches with a weak activation energy in the range of 5–7 meV. This is in good agreement with the optical binding energy of donor bound excitons, ranging from 5.8 to 6.5 meV among the samples we have studied. As such we interpret the first decrease of the I_2 line to thermal detrapping towards the free exciton band, in agreement with other authors.[25] As a proof is the fact that in samples where I_2 luminescence is relatively very strong at low T, the quenching of the I_2 line is accompanied by an increase of the A line (not shown). At higher temperature, Figs. 3 and 4 show that a second activation energy is measured for the quenching of the I_2 line intensity. The overall behavior is well accounted for by an equation similar to Eq. (4). The second nonradiative path could be for instance the ionization of the neutral donor involved in the excitonic complex[25] (a similar activation energy should be observed in the case where unresolved free hole to neutral donor transitions are involved in the I_2 band). However, we remark that the second activation energy observed in the I_2 case is equal to the sum of the I_2 binding energy and of the activation energy for free exciton PL quenching. Moreover, the second high T nonradiative path for I_2 becomes effective at temperatures where the quenching of free exciton PL is also effective. As such, in Figs. 3 and 4, a second fit for the I_2 intensity variation is proposed, following the equation:

$$I(I_2) \alpha I(A)/[1 + a \exp(-E_a/kT)], \tag{5}$$

where $I(A)$ is the free A exciton PL intensity previously determined, proportional to the A exciton density. Equation (5) simply assumes that free excitons are the source for donor bound excitons. As Figs. 3 and 4 show, Eqs. (4) or (5) both account fairly well for the I_2 line quenching behavior, though we emphasize that Eq. (5) has two fitting parameters less than Eq. (4).

As Fig. 3 shows, the B exciton luminescence intensity temperature dependence can be fitted using

$$I(B)\alpha I(A)\exp(-E_{AB}/kT) \tag{6}$$

which accounts for both the increase and decrease with temperature of $I(B)$. E_{AB} is of the order of 7–8 meV, corresponding to the A-B energy splitting (which is slightly strain dependent[12]). The fact that Eqs. (5) and (6) can describe the thermal quenching of the I_2 and B lines, respectively, by using the A exciton density shows that the A exciton population governs the near edge PL in the 50–300 K range. At low T, excitons are trapped to neutral donors, but for T larger than about 20 K, they are significantly thermalized towards the A band (see also Ref. 30). Above 50 K the further quenching of I_2 is related to the depopulation of A, which is the source of donor bound excitons. Similarly, B excitons are created by thermal excitation of A excitons, and their thermal quenching is again due to the disappearance of A excitons. All this discussion is of course in agreement with the fact that the PL spectra of undoped GaN are dominated by A exciton recombinations from moderate temperature up to 300 K (see Fig. 1). Finally, it is worth reminding that we found an activation energy for A quenching close to the A Rydberg. Since undoped GaN is n type, this suggest that free hole release is a major nonradiative path in GaN. We think that free excitons being neutral are less sensitive to nonradiative centers than holes. As an origin for these nonradiative centers, dislocations should play a role. They are known to be nonradiative centers in GaN at room temperature,[31] and they are negatively charged,[32] i.e., attractive for holes. Moreover, we mention that the pre-exponential term a in Eq. (3) is equal to 300 for the MBE-grown sample of Fig. 3 and only 30 for the MOVPE-grown one in Fig. 4. These prefactors are inversely related to the nonradiative lifetimes, i.e., to the density of nonradiative centers, and the dislocation density is typically $5\times10^9\,\mathrm{cm}^{-2}$ in our MBE-grown samples (a value typical for GaN/Al_2O_3) whereas it is only about $5\times10^8\,\mathrm{cm}^{-2}$ in our MOVPE-grown ones.[33] Therefore our data indicate that dislocations may be at least partly responsible for hole recombination and PL quenching in undoped GaN.

As Fig. 1 shows, near 3.27 eV, transitions involving residual acceptors are observed. These are donor acceptor pairs (D^0A^0) recombinations at low T, transforming to electron acceptor (eA^0) recombination at higher T, typically 100 K, as Figs. 1 and 2 show. The residual acceptor involved has an optical depth of 222–224 meV.[13,22] We mention here that similar optical acceptor depths have been reported in slightly Mg doped GaN[14,22] (see also below) and in Si doped GaN.[34] The intensity of these acceptor related transitions is too weak in our MBE- and MOVPE-grown samples to allow the study of their temperature dependence. We then present results for HVPE-grown ones, where these transitions are more intense. Figure 5 gives the temperature dependence of PL intensities of a selected HVPE-grown sample, while the inset shows the corresponding 10 K PL spectrum. The edge excitonic band quenches with an activation energy of 5 meV, showing that it is primarily built from donor bound excitons, following the previous discussion. Also given is the temperature dependence of the integrated intensities of the D^0A^0, eA^0 and first phonon replica transitions involving the residual acceptor.

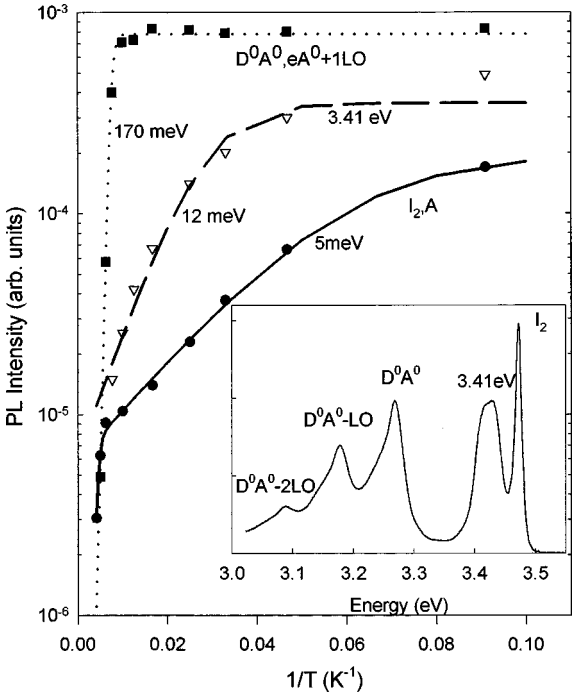

FIG. 5. Temperature dependence of the intensities of the main luminescence bands for an HVPE-grown GaN sample. The low temperature spectrum in the inset shows that this sample exhibits intense acceptor related luminescence and extended defect bound exciton luminescence.

The quenching is well described by Eq. (3), and the resulting activation energy is 170 meV. This value is equal to the Hall activation energy of Mg acceptors in GaN,[35] which is to date the only acceptor giving reliable p-type conductivity in GaN.

In an n-type sample, the densities of minority holes and neutral acceptors are governed by

$$\begin{aligned}\partial p/\partial t &= G - p/\tau - c_A N_A^- p + e_A N_A^0,\\ \partial N_A^0/\partial t &= -N_A^0/\tau_{DA} + c_A N_A^- p - e_A N_A^0,\end{aligned} \tag{7}$$

where p is the hole density, τ their lifetime, N_A^- and N_A^0 are the density of ionized and neutral acceptors, and τ_{DA} is the lifetime for acceptor related recombination. c_A and e_A are the hole capture and emission coefficients of the acceptors. They are related by detailed balance as $e_A=(N_v c_A/g)\times\exp(-E_A/kT)$, where E_A and g are the thermal acceptor depth and degeneracy, respectively, and N_v is the valence band effective density of states. The solution of Eq. (7) for steady state is

$$N_A^0=(c_A N_A^- G\tau)/[1/\tau_{DA}+c_A N_A^-\tau/\tau_{DA}+(N_v c_A/g)\times\exp(-E_A/kT)] \tag{8}$$

which, assuming that the lifetime of D^0A^0 pairs is long compare to the lifetime of free holes, and that in an n-type sample, $N_A^-\sim N_A$, reduces to

$$N_A^0=G\tau_{DA}/[1+(\tau_{DA}N_v/g)\exp(-E_A/kT)/\tau N_A]. \tag{9}$$

Equation (9) explains our experimental result, i.e., that in n-type GaN, the acceptor related PL is quenched with an activation energy corresponding to the thermal depth of the acceptor.

As the inset in Fig. 5 shows, the particular HVPE sample was not chosen only to study donor–acceptor pairs, but also because it displays a PL band around 3.41 eV that has been frequently reported in GaN.[36–39] Figure 5 shows that it has a low activation energy for quenching of 12 meV. Investigations of this 3.41 eV PL band in other samples show some scatter in the values for the activation energy, between 12 and 40 meV, but these values remain lower than an exciton escape energy (typically 60–70 meV). A model[39] has been proposed for this transition, assigning it to the recombination of an exciton bound to a I_1 type stacking fault in GaN. In this model, the stacking fault is similar to a cubic quantum well in wurtzite GaN. The electrons are trapped by the stacking fault and holes are in the wurtzite matrix (type II quantum well). The low activation energy for quenching corresponds to the escape of the electron. Our results are then in qualitative agreement with this model. The model was proposed by Albrecht *et al.*[39] from the observation of numerous I_1-type stacking faults in samples displaying strong PL at 3.41 eV. We have studied by transmission electron spectroscopy samples displaying this transition. The principal defects found are inversion domains, prismatic defects (i.e., stacking faults in the prismatic planes), and numerous I_1-type stacking faults. So both our PL and transmission electron microscopy studies are in agreement with the stacking fault model of the 3.41 eV PL band.[39]

We shall briefly discuss some results on intentionally Si-doped GaN. When doping with silicon, in a range lower than that necessary for metallic behavior (n typically lower than $1\times10^{18}\,\mathrm{cm}^{-3}$), one can observe a slight red shift of the band edge excitonic transitions.[22] This corresponds to a deepening of the main PL line relative to the A free exciton energy, as can be measured by reflectivity. This deepening could be due to a broadening of the donor bound exciton line, or to a change of the main luminescence path (to free electron–neutral donor transition for instance).[22] The temperature dependent PL study we have performed on such samples have shown that the quenching of the PL intensity is the same as that of the I_2 line reported in Figs. 3–5. We therefore conclude from these experiments that the low temperature PL of slightly Si-doped GaN ($n\leqslant10^{18}\,\mathrm{cm}^{-3}$) is still dominated by neutral donor bound exciton recombination.

IV. *p*-DOPED (Mg-DOPED) GaN

We shall begin this discussion by the study of slightly *p*-type GaN. Figure 6 shows the PL spectra as a function of excitation intensity and temperature of MBE-grown Mg-doped GaN, with a room temperature free hole concentration below $10^{17}\,\mathrm{cm}^{-3}$. At low temperature, the spectra is composed of a near edge excitonic peak and a broad, phonon replicated band near 3.27 eV. The energy of the excitonic peak is lower than that typical for donor bound excitons in our MBE-grown samples and similar to that of excitons labeled I_1 that we observe in very weakly Mg doped, *n*-type GaN grown either by MBE or MOVPE.[22] We assign this transition to acceptor bound excitons. Note that in other works, this line is rather assigned to ionized donor bound excitons.[16] We prefer its assignment to neutral acceptor bound excitons because of its strong phonon replication strength,[22] and of its predominance in the band edge PL in *p*-doped GaN, as shown in Fig. 6. Figure 6 also shows that the 3.27 eV band blue shifts with an increase of the excitation intensity, which is typical of neutral donor–acceptor pairs (D^0A^0) recombination. Also, as the temperature increases above 50 K, the D^0A^0 band is progressively replaced by free electron–neutral acceptors (eA^0) recombinations at higher energy, due to the thermal ionization of the donor. The energy position of the eA^0 band as a function of temperature is well given, as expected, by $E_g-E_A+kT/2$ assuming an optical acceptor depth E_A of 224 meV. Note that within the precision of the experiment, this is the same value as for the residual acceptor observed in undoped GaN[10,13,18,22] (see Figs. 1 and 5). This means that, either the residual acceptor in GaN is Mg, or that Mg and the residual acceptor have the same depth (and same phonon coupling strength), or that, if the Mg doping is too slight, the acceptor related PL is still dominated by the unknown residual acceptor (C for instance[13,22]). Figure 7 gives the temperature dependence of the intensities of the PL bands reported in Fig. 6. The intensity of the I_1 line is well described by using Eq. (3), giving an activation energy of 11 meV. This is precisely the binding energy of the I_1 line relative to the free exciton A.[22] So, as for the case of donor bound excitons discussed previously, we ascribe the quenching of the I_1 line to thermal detrapping of the bound excitons. As also shown in Fig. 7, the intensity of the integrated D^0A^0, eA^0 bands and their first phonon replica also follows Eq. (3), with an activation energy of 190 meV. This result is very similar to the one reported above in Fig. 5, and we already mentioned that the 170–190 meV energy corresponds to the thermal depth of Mg acceptors. However, the expressions used in the preceding section were relative to acceptor occupation in an *n*-type sample. In *p*-type GaN, even at room temperature, only a few

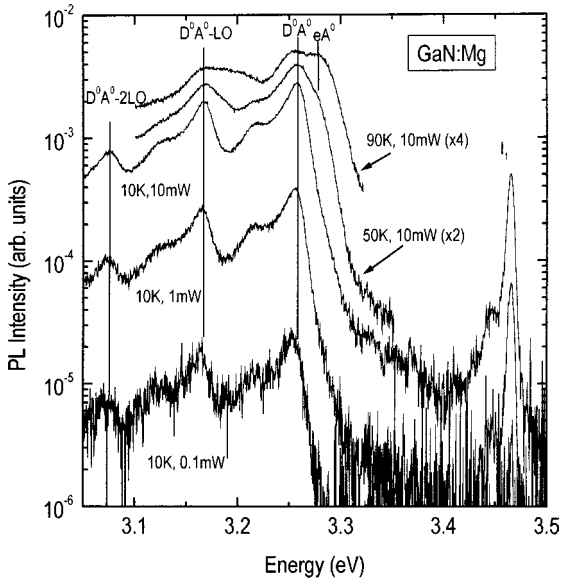

FIG. 6. Temperature and excitation intensity dependent luminescence spectra of an Mg-doped, slighty *p*-type GaN sample grown by MBE. Note the rapid quenching of the I_1 line and the progressive replacement of D^0A^0 transitions by eA^0 ones (see the text).

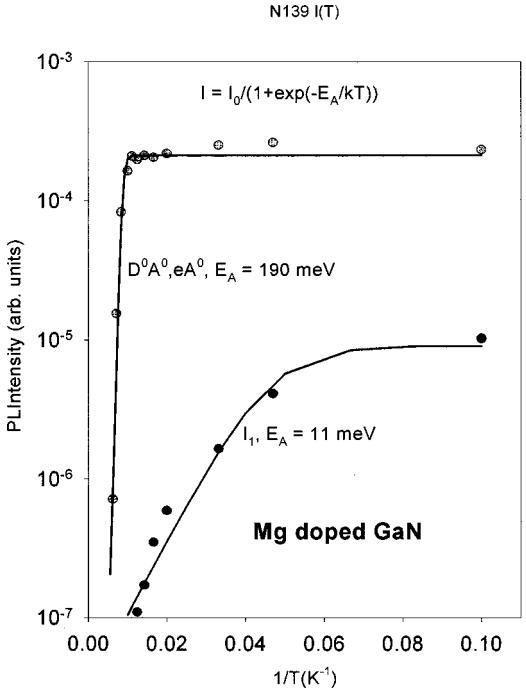

FIG. 7. Temperature dependence of the intensities of the luminescence transitions for the sample shown in Fig. 6.

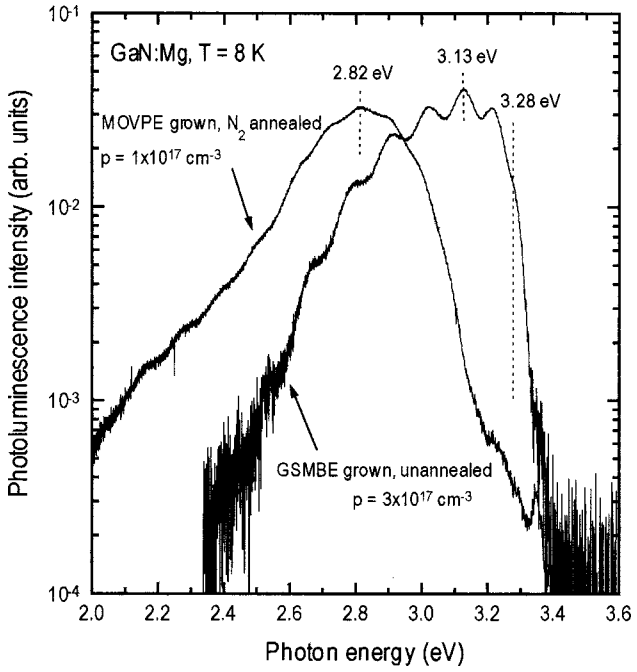

FIG. 8. Comparison between typical low temperature luminescence spectra of highly Mg-doped GaN samples grown either by MOVPE or MBE.

percent Mg acceptors are thermally ionized.[19,35] The decay over orders of magnitude of acceptor related PL cannot be related to the slight decay of neutral acceptor density. We also note in Fig. 6 that the replacement of the D^0A^0 band by eA^0 band, i.e., the release of free electrons, is not related to a strong decay of the overall acceptor PL intensity. All these remarks seem to indicate that in slightly Mg doped GaN, the decay of PL intensity is due to free hole release, i.e., the same cause as in undoped GaN.

We shall now focus on highly Mg-doped GaN [$\approx 10^{19}$ at./cm^3], i.e., with room temperature free hole concentrations equal or higher to $10^{17}\,\mathrm{cm}^{-3}$. In the high Mg doping range, one has to make a distinction between MBE- and MOVPE-grown samples. Figure 8 shows typical PL spectra of MBE- and MOVPE-grown samples doped Mg in the $10^{17}\,\mathrm{cm}^{-3}$ range. Both spectra are deformed by Fabry–Perot interferences, since the luminescence is emitted in the transparency range of the samples. As can be seen, the PL of the MBE sample displays a band peaking near 3.1–3.2 eV, i.e., at an energy lower than that of the D^0A^0 pairs band observed in *n* type, or weakly Mg-doped samples (Figs. 1, 5, and 6). On the other hand, the spectrum of the MOVPE sample is dominated by a broad band in the blue range, near 2.8 eV. This blue band is typical of highly Mg-doped, MOVPE-grown GaN.[1,10,22,40–42] Its origin is not clear in the literature. Some authors assign it to recombinations involving the shallow acceptors and deep donor levels,[22,40,42] while others assign it to recombinations involving deep acceptor-like states.[15,41] We shall hereafter refer the 3.2 and the 2.8 eV bands as ''shallow acceptor'' and ''blue'' bands, respectively. Though in general for highly Mg-doped GaN, the 3.2 eV band is typical of MBE-grown samples, and the 2.8 eV one to MOVPE-grown ones, we mention that the blue band can also be recorded in MBE grown samples, particularly at room temperature,[43] and that in some MOVPE-grown samples, both the shallow acceptor and the blue band can be observed. An example is given in Fig. 9, displaying the temperature dependent PL spectra of a Mg-doped MOVPE-grown GaN sample. One can observe that with increasing temperature, the shallow acceptor band quenches first, fol-

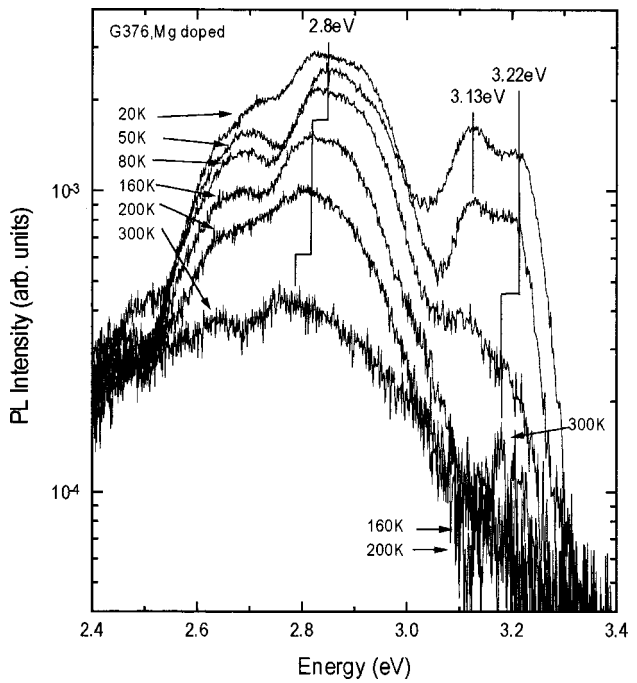

FIG. 9. Temperature dependent luminescence spectra of a highly Mg-doped MOVPE-grown GaN sample. Note the slight reappearance of the shallow acceptor band on the 300 K spectrum, when the blue band strongly quenches.

lowed by the quenching of the blue band. Interestingly, as underlined by the arrow in Fig. 9, the quenching of the blue band near 300 K is accompanied by a slight reappearance of the shallow acceptor band.

The temperature dependence of the PL intensities of the MOVPE-grown samples of Figs. 8 and 9 is displayed in Fig. 10. Both the shallow acceptor band and the blue band quenching are well fitted using Eq. (3), and the activation energies found range between 70 and 90 meV. Regarding the MBE-grown sample of Fig. 8, the quenching of the broad PL band, which includes unresolved shallow acceptors and blue bands, leads to an activation energy for quenching of 60 meV. These values are significantly lower than those found for the acceptor related PL bands in slightly Mg doped (Fig. 6) or *n*-type (Fig. 5) samples. We may think of different reasons for this. The 70–80 meV activation energy found for the blue band could be related to the ionization of a deep donor involved in the transition. This would be in agreement with the observation that the shallow acceptor band intensity increases when the blue band quenches (Fig. 9). However, assuming an optical depth in the 220–290 meV range for the Mg acceptors, this would place the zero phonon line of the blue band in the 3.12–3.2 eV range, a value which is rather high, though not unrealistic in the light of the width of the blue band. Unfortunately, this large width, and the unavoidable presence of Fabry–Perot interference fringes on the blue band makes a detailed lineshape analysis difficult. On the other hand, even if such an explanation based on deep donor ionization may apply to the blue band, it cannot apply to the shallow acceptor band, for which activation energies in the 60–90 meV have also been deduced. One may think of another reason for these low values of activation energies in highly Mg-doped GaN relative to slightly doped. It is that since large doping reduces compensation, hole release could be governed by half the thermal energy of the acceptor.[28] Indeed, the activation energies found in highly doped GaN are roughly half those found in slightly doped, or *n*-type samples, as shown above. However, this would be in contradiction with numerous Hall studies that have shown that in Mg-doped GaN, the hole release has an activation energy in the 160–180 meV range.[35,44] We then have no definite explanation for the relatively low activation energies found for the quenching of either the blue band or the shallow acceptor band in our highly Mg-doped GaN samples.

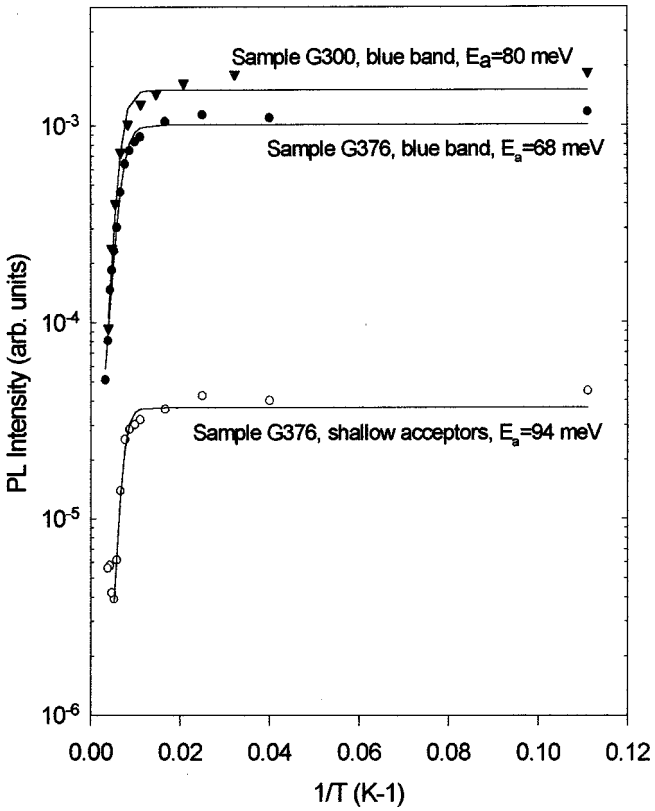

FIG. 10. Temperature dependence of the intensities of the luminescence bands recorded in the highly Mg-doped GaN samples grown by MOVPE corresponding to Figs. 8 and 9.

V. CONCLUSIONS

A series of undoped and *n*- and *p*-doped GaN samples grown using various techniques have been studied by photoluminescence as a function of temperature, in order to study the mechanisms for thermal quenching of the different transitions observed. The donor bound exciton line, dominant at low temperature, first quenches by thermalization towards the *A* free exciton band. At higher *T*, further quenching is related to the decay of the *A* exciton population which appears to be the source for both donor bound excitons and free *B* excitons. The activation energy for *A* exciton luminescence extinction is always of the order of the *A* exciton Rydberg, suggesting that in *n*-type samples, the *A* luminescence quenching is related to free hole release. Our data are consistent with a significant role of dislocations in these nonradiative recombinations. In slightly Mg-doped samples, the decay of the dominant neutral acceptor related PL bands is governed by an activation energy equal to the thermal depth of the acceptor. This again seems to point to free hole release as a step for nonradiative recombination. A significantly lower activation energy for PL quenching is measured in highly Mg-doped GaN, the origin of which is unclear at the moment.

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