Temperature-varied photoluminescence and magnetospectroscopy study of near-band-edge emissions in GaN

D. G. Chtchekine
Physics Department, Emory University, Atlanta, Georgia 30322

Z. C. Feng* and S. J. Chua
Institute of Material Research and Engineering, 3 Research Link, 117602 Singapore

G. D. Gilliland
Physics Department, Emory University, Atlanta, Georgia 30322

(Received 20 June 2000; revised manuscript received 13 December 2000; published 13 March 2001)

Near-band-edge emissions from wurtzite GaN films grown on sapphire by metalorganic chemical vapor deposition have been studied by temperature-varied photoluminescence and magnetospectroscopy. Free-exciton emissions of the *A* band (FE_A) and *B* band (FE_B) as well as the neutral donor-bound exciton (D^0,X) emission were identified. An extensive temperature-varied study of the donor-bound exciton emission shows that at low temperatures ($T \leqslant 25$ K) the main channel of thermal dissociation of the (D^0,X) complex is through the release of a free exciton with thermal activation energy very close to the exciton binding energy. A temperature-varied study of the strong bound-exciton emission at 11.7 meV below the FE_A line indicates that this complex dissociates through the release of a free exciton. We present arguments that due to the character of its temperature decay, this emission cannot originate from an ionized donor-bound exciton (D^+,X). An exciton bound to a shallow acceptor (A^0,X) is a likely candidate for this emission. A magnetospectroscopy study with magnetic field varied up to 9 T allows us to identify the first excited state ($2S$ state) of the *A*-band free exciton at 3.5035 eV [$(E_{FE}^{2S})_A-(E_{FE}^{1S})_A=18.3\pm0.4$ meV]. Using the Aldrich-Bajaj potential to account for electron-phonon interaction in GaN, we performed a variational calculation of the binding energies for an *A*-band free-exciton ground ($E_{bind}^{1S}=24.81\pm0.52$ meV) and first excited ($E_{bind}^{2S}=6.51\pm0.12$ meV) state. By matching the calculated values with experimentally determined energy separation between these states, we obtain the *A*-band hole nonpolaron mass $m_h^*=0.52\pm0.04$.

DOI: 10.1103/PhysRevB.63.125211 PACS number(s): 78.55.Cr, 81.05.Ea, 81.15.Gh, 81.40.Tv

I. INTRODUCTION

GaN and related materials and structures have been intensively studied with remarkable breakthroughs in the growth of these materials and device applications in recent years.[1–5] Photoluminescence (PL) and other optical spectroscopy techniques have been employed as important methods to investigate these materials for quality control, impurity identification, native structural defects characterization, ternary composition determination, and so on. Because of the limits in the material quality produced so far, PL emission linewidths in GaN are usually not sufficiently narrow to detect effects such as j-j coupling and Zeeman splitting, which would help in a positive identification of the new lines. In some cases, broad linewidths prevent the observation of relatively weak emissions altogether. Residual compressive strain of thin (a few μm) GaN films results in an energy shift of optical transitions and thus renders useless classification of transitions just by their energy positions. However, recent improvements in the quality of epitaxial GaN films have facilitated the detection of new near-band-edge emissions and fine structures.[6–15]

To identify the origin of some optical transitions in GaN, we conducted a detailed temperature, magnetospectroscopy, and excitation power PL study on a number of doped and undoped GaN films in this paper. Usually, with increasing temperature, excitons bound to shallow impurities are expected to dissociate thermally, while free-exciton emission should persist due to the large binding energy (~25 meV) of free excitons in GaN. Neutral donor-bound exciton (D^0,X) emission is one of the dominant emissions in GaN at low temperatures. The dissociation of the (D^0,X) center can proceed via the release of a free exciton, a free electron, or Auger nonradiative recombination,[16] depending on the ratio of exciton binding energy (E_{bind}^X) and exciton localization energy (E_{loc}^X). Since the GaN is a strong emitter due to the direct band gap and strong binding between electron and hole, the nonradiative Auger process is expected to compete poorly with the strong radiative recombination only. From the temperature dependence of the (D^0,X) PL intensity, it was found[17] that the decay of a shallow donor-bound exciton is a two-channel process with activation energies 4.5 ± 1 and 32 ± 2 meV corresponding to exciton localization energy and shallow donor binding energy, respectively. Exciton localization energy determined from the temperature study is thus ~40% lower than the corresponding localization energy determined from PL data. Recently, there have been reports on the emission from excitons bound to ionized donors[7,8] (D^+,X) in GaN. The ability of an ionized center to bind an exciton depends on the ratio of the electron and hole masses σ. (D^+,X) complex is stable for materials with values of σ less than some critical value $\sigma_{critical}$. If the mass ratio is higher than the critical value, the complex is not stable due

to the small hole binding energy. Variational calculations of Skettrup, Suffczynski, and Gorzkowski[18] and Rotenberg and Stein[19] predict σ_{critical} to be 0.426 and 0.45, respectively. The electron effective mass is relatively well established in GaN, whereas for the hole effective mass there is a rather big spread in reported values. Recent publications reported 0.22 (Ref. 20) $<m_e<0.236$ (Ref. 21) and 0.4 (Ref. 22) $<m_h<0.75$.[23] Thus the currently available estimate of electron-hole mass ratio $0.29<\sigma<0.59$ is not conclusive with respect to the σ_{critical} criterion. For comparison, we should note that in direct wurtzite materials where the ionized donor-bound exciton complex has been identified [CdS,[24] CdSe,[25] and ZnO (Ref. 26)] the σ ratio is below 0.24.

A temperature-dependent PL study can give a valuable insight into the stability of the (D^+,X) center. There are two most likely channels of thermal dissociation of the (D^+,X) complex: through the release of a free exciton and through the release of a hole. If the dissociation proceeds through the release of a free exciton, the activation energy of this process should be equal to the exciton localization energy on the D^+ center, which can be precisely determined from the PL spectrum. In materials where the binding energy of the hole to the neutral donor is sufficiently weak, a break off of the hole may be energetically more favorable than a break off of a free exciton. The prevailing mechanism would depend on the donor ionization energy, exciton binding energy, and ionized donor localization energy. Knowing these parameters, one can make a reasonably accurate prediction for the dissociation channel and its thermal activation energy, and compare this prediction with activation energy determined from the PL intensity temperature study of the (D^+,X) line.

In our GaN films, free-exciton (FE) and bound-exciton (BE) emissions are well resolved and exciton localization energies can be precisely determined. Determination of the free-exciton binding energy is less straightforward and usually requires knowledge of the band gap from reflectance measurements. An alternative way to measure the binding energy is to identify the first excited state ($2S$ state) of the free exciton. The first excited state of FE_A has been recently predicated by Shan *et al.*[27] in a photoreflectance (PR) study and by Volm *et al.*[23] in PL spectra. Transition energy was used as a primary criterion in identifying the $2S$ state. These authors calculated the FE_A binding energy using the Coulomb potential approximation and obtained 21 ± 1 meV (Ref. 27) and 26.7 ± 0.5 meV.[23] This is a rather large discrepancy considering that in both studies the GaN epilayer was grown on sapphire by metalorganic chemical vapor deposition to the thickness of a few μm, so that both epilayers can be considered equally strained. Therefore, this discrepancy might come from the incorrect identification of the $2S$ state.

In this paper, we employed magnetospectroscopy to identify the first excited state of FE_A. Since the excited excitonic states have much larger diamagnetic shifts than the ground state, one can positively identify the $2S$ state directly from magneto-PL spectra. Using experimental data for the energy separation between the ground and the first excited states, we perform a variational calculation on the free-exciton binding energy in the approximation of the Aldrich-Bajaj[28] potential (which models the electron-hole interaction) and obtain the value of the heavy-hole mass.

TABLE I. Sample information—GaN epitaxial layer characteristics.

Sample no.	Thickness (μm)	Doping	Carrier concentration (300 K) n (cm^{-3})
1	3.3 μm	Si	$<10^{15}$ [a]
2	2.0 μm	undoped	$<10^{15}$ [a]
3	1.8 μm	Si	2.53×10^{18}
4	2.0 μm	Si	6.27×10^{16}
5	1.9 μm	undoped	3.8×10^{15}

[a]Samples no. 1 and no. 2 are highly resistive. An upper range was estimated according to the Hall instrumental measurement limitation.

II. EXPERIMENT

The experimental GaN samples were grown on (0001) sapphire, coated with a thin (~200 Å) GaN buffer, by metalorganic chemical vapor deposition (MOCVD) technology. All the GaN films with thickness ranging from 1.8 to 3 μm, undoped or Si-doped, are transparent and have mirrorlike surface. Sample information, including epilayer thickness, doping type, and carrier concentration are listed in Table I. Carrier concentrations were determined by Hall–Vander Pauw measurements at room temperature. The Si-doped films generally resulted in n-type characteristics with carrier concentrations of $n\sim10^{16}-10^{18}\,\text{cm}^{-3}$. Undoped GaN samples showed a lower n-type carrier concentration of $n\sim10^{15}-10^{16}\,\text{cm}^{-3}$. But some epitaxial layers were highly resistive and the carrier concentrations in these samples were not measured. Because these samples are of a high purity, we believe that high resistivity is due to the low concentration of impurities rather than a high level of compensation.

Photoluminescence (PL) spectra were obtained using the 325-nm line of a cw He-Cd laser with ~500-μW excitation power focused to ~300 μm resulting in ~0.5-W/cm^2 excitation power density. Samples were cooled to liquid-helium temperatures in a variable temperature (1.5–300 K) liquid-helium cryostat with optical access. The PL signal was dispersed by a 0.85-m double spectrometer, and detected by a cooled S-20 photomultiplier tube operating in the photon-counting mode.

Magnetospectroscopy measurements were carried out in a superconducting magnet cryostat in Faraday geometry with magnetic field varying from 0 to 9 T and samples cooled to liquid-helium temperatures.

III. EXPERIMENTAL RESULTS

A. Si-doped GaN epilayer and I_X emission

Figure 1 shows the low-temperature (LT) photoluminescence of a Si-doped GaN film (sample no. 1), measured at 10 and 27.5 K, respectively. The PL spectrum is dominated by three narrow linewidth peaks in the near-band-edge region.

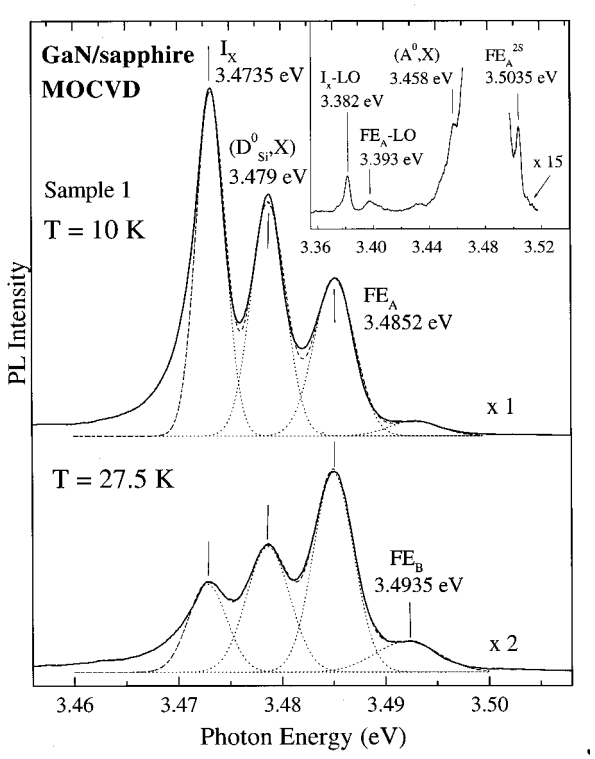

FIG. 1. Low-temperature PL spectra of a lightly Si-doped MOCVD-grown GaN sample no. 1. Bound-exciton emissions at 3.479 and 3.4735 eV markedly reduce their PL intensity as the temperature is raised from 10 to 27.5 K due to thermal dissociation. Dashed lines represent the fit with Gaussian line shapes (dotted lines). The inset shows a strong phonon replica of the I_X emission at 3.382 eV, and a transition at 3.5035 eV due to the first excited state of the free exciton (*A* band).

As the temperature is raised, two low-energy emissions (3.4735 and 3.4790 eV) decrease in their PL intensity significantly relative to two high-energy emissions (3.4852 and 3.4932 eV), but the peak energy positions of these four bands are almost unchanged. When the temperature exceeds 60 K, two low-energy emissions are quenched while two high-energy ones stay and vary following the band-gap variation with the temperature (data not shown here). We therefore assign high-energy lines at 3.4852 and 3.4935 eV to *A*-band and *B*-band free-exciton transitions, respectively, and low-energy lines to bound-exciton complexes, respectively. The energy separation between the *A* and *B* free exciton in our sample is 8 meV, consistent with other studies[27,29] of thin (several μm) GaN epilayers grown on sapphire. The line labeled FE_A^{2S} at 3.5035 eV, shown in the inset of the figure, is 200 times weaker than the FE_A line and can be observed at low temperatures and in very high-quality samples only. The origin of this line will be discussed later. The peak at 3.4790 eV is assigned to the shallow (D^0,X) transition. We measured the shallow donor localization energy in this sample to be 6.2 meV, in agreement with the values reported in the literature.[8,23] All near-band-edge lines can be reasonably well fitted with Gaussians, which indicates that each of these lines is an inhomogeneously broadened single transition. This allows an accurate study of the relationship of intensity versus temperature and excitation power in these samples.

The line labeled I_X is located 12 meV below the free-exciton line FE_A. It is very strong at low temperature and is observed only in some of our samples. A strong LO-phonon replica is also observed at 3.382 eV (I_X-LO in the inset of Fig. 1). The intensity ratio of the no-phonon line to phonon replica emission is $\sim$50 in all of our samples in which this emission is present. With increasing temperature, both the zero-phonon line and the phonon replica of the I_X emission reduce their intensity drastically and disappear completely beyond 60 K. Based upon the temperature dependence of the I_X line, its narrow linewidth ($\sim$4.0 meV), high oscillator strength, and energy position just below the *A*-band free exciton and (D^0,X) transitions, we conclude that this emission, I_X, originates from a bound-exciton complex. The nature of this PL line will be further discussed later. The line labeled (A^0,X) at 3.458 eV is located 27 meV below the free-exciton line FE_A. This line has been previously assigned to the excitons bound to a neutral Mg acceptor.[30] The line labeled FE_A-LO at $\sim$3.40 eV is a one-phonon assisted emission of the *A*-band free exciton. Its line shape is asymmetric with an extended high-energy shoulder and intensity maximum somewhat above the energy $E=E_{\mathrm{FE}_A}-E_{\mathrm{LO}}=3.393\,\mathrm{eV}$. This line shape reflects the Maxwellian energy distribution of free excitons with their kinetic energy measured relative to the exciton band minimum. The line shape of the FE_A-LO emission is contrasted to the line shape of the I_X-LO line, which is inhomogeneously broadened and has the same line shape as the no-phonon emission at 3.473 eV. This is consistent with the assignment of the I_X emission to the bound exciton complex since excitons bound to impurities do not have kinetic-energy homogeneous broadening.

Other emissions present in this sample include shallow donor-acceptor-pair (DAP) recombination with a no-phonon line at 3.28 eV and deep-level yellow emission centered around 2.2 eV (not shown here). The intensity of deep-level and DAP emissions was stronger in high-resistivity samples no. 1 and 2 ($I_{\text{band edge}}/I_{\text{deep level}}\sim 10^2$) compared to *n*-type samples ($I_{\text{band edge}}/I_{\text{deep level}}\sim 10^4$). Weak PL intensity of the DAP and deep-level emissions compared to the near-band-edge emissions indicates the low concentration of deep-level impurities and a high sample quality.

B. Magnetophotoluminescence spectroscopy

To address the problem of exciton binding energy in GaN, we have conducted a magnetospectroscopy study of the near-band-edge emissions. Figure 2 shows the low-temperature PL spectrum of sample no. 2 (undoped GaN) in a semilogarithmic scale at different magnetic field in Faraday geometry (magnetic field is parallel to the laser excitation **K** vector). We do not observe Zeeman splitting in any of the near-band-edge emissions which is consistent with magnetospectroscopy studies done by other groups on (D^0,X) (Ref. 6) and FE (Ref. 31) emissions. There is also no observable diamagnetic shift in any excitonic emissions except for the emission labeled FE_A $(n=2)$. Indeed, the value of the diamagnetic

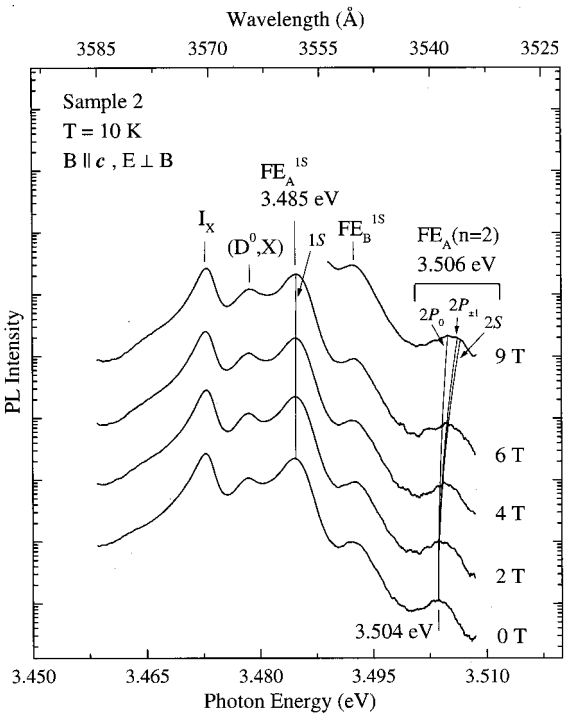

FIG. 2. PL spectra of sample no. 2 at different magnetic fields in the Faraday configuration. Only emission at 3.504 eV exhibits a diamagnetic shift and thus is identified as the $n=2$ state of FE_A. Calculated diamagnetic shifts are shown for the $1S$, $2S$, $2P_0$, and $2P_{\pm 1}$ states of the *A*-band exciton.

shift for the exciton ground state is expected to be small compared to the emission linewidths. However, the exciton in the first excited state is expected to be more strongly influenced by the magnetic field due to the larger exciton radius ~60 Å (compared to ~30 Å for the ground state). Indeed, we calculated the diamagnetic shift according to $e^2B^2\langle|\Psi|^2\rangle/(8\mu_{ex}c^2)$ for $1S$ and $2S$ and $2P$ states[32] of the *A*-band exciton. The results of our calculation are shown in Fig. 2. The emission energy of the line at 3.504 eV has shifted up ~2 meV, consistent with our calculation for the $n=2$ states. On the other hand, the FE_A line at 3.485 eV is unaffected by magnetic field, also consistent with our calculation. With increasing magnetic field, the $n=2$ state splits into *S* and *P* states. This splitting contributes to the broadening of the observed emission at higher fields. However, this splitting is too small to resolve in our samples. Thus, we identify this emission as the first excited state of the *A*-band exciton. To confirm our assignment of the $2S$ transition at 3.504 eV, we estimate the binding energy of the *A*-band free exciton in the Coulomb potential approximation to be $\frac{4}{3}[E_{FE}(1S)-E_{FE}(2S)]=24.4$ meV, consistent with the results obtained using other methods in recent literature.[23,27]

IV. THEORETICAL ANALYSIS AND DISCUSSION

A. Photoluminescence intensity analysis

The functional form of the temperature dependence of the PL emission intensity with one or more channels of nonradiative decay can be expressed in terms of the radiative transition rate W_R and temperature:[33]

$$\eta=\frac{I(T)}{I(0)}=\frac{1}{1+\sum_i \frac{\omega_i}{W_R}\times\exp\left(\frac{E_i}{kT}\right)}, \tag{1}$$

where η is the luminescence efficiency, ω_i is a temperature-independent constant, E_i is the activation energy of ith channel of nonradiative decay, and $I(0)$ and $I(T)$ are the integrated PL intensity at 0 K and $T>0$ K, respectively.

In this work, we consider one- and two-channel models of nonradiative decay for bound-exciton complexes. In the case of one channel of nonradiative decay, Eq. (1) becomes

$$\eta=\frac{1}{1+C_1\times\exp\left(\frac{E_1}{kT}\right)}. \tag{2}$$

For two channels of nonradiative decay, it is

$$\eta=\frac{1}{1+C_1\times\exp\left(\frac{E_1}{kT}\right)+C_2\times\exp\left(\frac{E_2}{kT}\right)}, \tag{3}$$

where $C_i=\omega_i/W_R$.

Figure 3 shows the temperature dependence of the integrated intensity for the (D^0,X) and I_X emission from four GaN films. As shown, the temperature dependence of the (D^0,X) emission in samples no. 3, no. 4, and no. 5 is well described with the two-channel dissociation model of Eq. (3). The thermal activation energy E_1 of the (D^0,X) emission from all samples is in excellent agreement (within 0.3 meV) with the energy of the exciton localization energy determined optically (see Table II). In GaN, the exciton localization energy (~6 meV) for the (D^0,X) complex is much smaller than the free-exciton binding energy (E^X_{bind} ~25 meV) and the shallow donor binding energy [29 meV (Ref. 34)]. Therefore, it is reasonable to conclude that the release of a free exciton is the dominant channel of thermal dissociation for the (D^0,X) complex at low temperatures ($T\leqslant 25$ K) in GaN.

At higher temperatures, a new thermal dissociation channel with activation energy $E_2\cong 28$ meV (see Table II) is clearly observed. This dissociation channel may be due to the decay of the (D^0,X) complex via simultaneous exciton delocalization and exciton dissociation[35] with activation energy $E_2=E^X_{bind}+E^X_{loc}\cong 30$ meV. Alternatively, a neutral donor ionization process, with activation energy $E_2=E_D\cong 29$ meV, may also affect the PL intensity of the (D^0,X) emission, since it reduces the number of the neutral-donor centers to which photoexcited excitons can bind from the (D^0,X) complex.[17] A detailed study of the exciton kinetics is required to determine which of these two channels governs the temperature dependence of the (D^0,X) emission at higher temperatures.

The temperature dependence of the I_X emission is well fit by the one-activation energy Arrhenius formula [Eq. (2)]. The thermal dissociation energy of the I_X emission is mea-

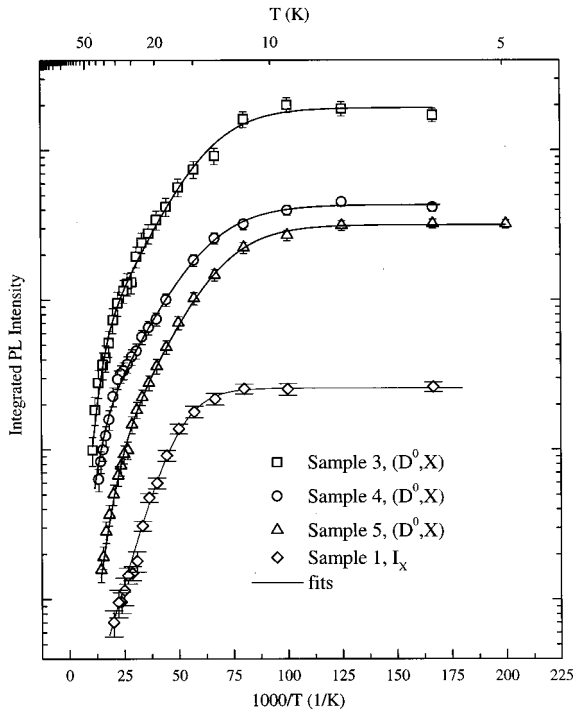

FIG. 3. Temperature dependence of integrated PL intensity of (D^0,X) emission (samples no. 3, no. 4, and no. 5) and I_X emission (sample no. 1). Fits with Eq. (2) (sample no. 1) and Eq. (3) (samples no. 3, no. 4, and no. 5) are shown with solid lines. In the experimental temperature range, the thermal dissociation of the (D^0,X) is well described by a two-channel process, whereas I_X complex disassociates through one channel. Plots are displaced vertically for easier viewing.

sured to be 10.3 meV, see Table II. This activation energy is consistent with the energy position of the I_X emission, which is 11.7 meV below the free-exciton emission FE_A at 3.485 eV. Thus the detailed temperature study confirms the assignment of the I_X emission as a bound-exciton complex and indicates that in the experimental temperature range (5–45 K), the main mechanism of thermal dissociation of this complex is the release of a free exciton.

B. Polaron effects

In polar materials, a charged particle interacts strongly with the lattice, therefore the polaron effect should be taken into account. The polaron radius for an electron and a hole in GaN can be estimated to be 14 and 9 Å, respectively. The exciton radius in GaN is 31 Å. Since the sum of polaron radii is comparable to the exciton radius, we expect that electron-phonon interaction has a significant effect on the exciton binding energy in GaN. It can be shown that the interaction between an electron and a hole via an exchange of longitudinal optical phonons results in an increase of the exciton binding energy. To calculate the exciton binding energy taking into account the electron-phonon interaction, we have performed a variational calculation with the electron-hole interaction described by the Aldrich-Bajaj[28] potential. The effects of band mixing are expected to be important in GaN since the separation between the first and second valence bands (~8 meV) is relatively small. Since the Aldrich-Bajaj potential uses the effective-mass approximation, we assume that these effects are included in the value of the hole effective mass. Thus the parameters that determine the exciton binding energy are the effective masses of the electron m_e^* and the hole m_h^* and the dielectric constant in the optical ε_∞ and static ε_0 limits. Since the dispersion and electron effective mass are rather well established for gallium nitride, we can determine the effective hole mass by varying it to fit our experimental data. We take the nonpolaron electron effective mass $m_e^*=0.2$, which corresponds to the electron polaron mass $m_e^p=0.22$ measured recently by cyclotron resonance.[20] Static and optical dielectric constants are taken as $\varepsilon_0=9.5$ and $\varepsilon_\infty=5.35$, respectively.[36] The variational calculation was carried out for both ground and first excited states. From the experimentally determined difference in the binding energy of $1S$ and $2S$ states, we have solved the following transcendental equation for the effective hole mass m_h^*:

$$E_{\text{bind}}^{1S}(m_h^*)-E_{\text{bind}}^{2S}(m_h^*)=18.3\pm0.4 \text{ meV}. \quad (4)$$

For the hole nonpolaron effective mass, we obtain $m_h^*=0.52\pm0.04$. The corresponding polaron hole mass is $m_n^p=0.59\pm0.045$. For the exciton binding energy, we obtain $E_{\text{bind}}^{1S}=24.81\pm0.52$ meV and $E_{\text{bind}}^{2S}=6.51\pm0.12$ meV for the ground and excited state, respectively. Binding energy of the exciton in a ground state calculated with the Coulomb potential for the determined hole polaron mass is 24.1 meV. Thus the electron-phonon interaction results in an increase of the binding energy by 0.7 meV, which is roughly 3% of the Coulomb potential value. The corresponding increase in the binding energy for the first excited state is 0.5 meV. The polaron effect is smaller for the $2S$ state due to the larger distance between the electron and hole for the exciton excited state and therefore the reduced interaction between the electron and hole through the exchange of phonons. Therefore, the Coulomb potential provides a rather accurate approximation for GaN when used with polaron masses of electrons and holes.

TABLE II. Theoretical fitting results for the integrated intensity versus temperature for I_X and (D^0,X) emissions with Eqs. (2) and (3), respectively. Exciton localization energy for each emission (determined optically) is given for comparison.

Sample no.	Emission	E_1 (meV)	E_2 (meV)	C_1	C_2	E_{loc} (meV)
1	I_X	10.3		374		11.7
3	(D^0,X)	6.2	33	91	7836	6.2
4	(D^0,X)	5.9	28	67	2072	6.2
5	(D^0,X)	6.2	24	136	8964	6.0

C. Origin of the I_X emission

Recently, there have been several reports of emission located at ~12 meV below the first free-exciton line. This emission was assigned to the neutral acceptor-bound exciton

(A^0,X) by Pakula *et al.*,[37] Kawakami *et al.*,[29] and Grandjean *et al.*[38] and to the ionized donor-bound exciton (D^+,X) by Reynolds *et al.*[7] and Santic *et al.*[8] In our sample no. 1 and sample no. 2, an emission labeled I_X is observed at 11.7 meV below FE_A. Because of their nearly identical spectral position relative to the FE_A line and the presence of the characteristic strong LO-phonon replica,[8,29] we believe that the emission I_X observed in our samples is identical to the emissions reported by the above groups.

Let us consider the stability of the ionized donor-bound exciton complex. As mentioned earlier, the (D^+,X) complex is more stable in materials with a smaller ratio of the electron and hole effective mass $\sigma=m_e/m_h$. This can be understood qualitatively by noting that in the (D^+,X) complex, the electron is tightly bound to the positively charged donor, which makes the hole effectively see a neutral center (D^+,e). Since holes with smaller mass have larger kinetic energy, they can overcome the weak attractive potential of the neutral donor more easily. Therefore, keeping the hole bound to the donor is a weak link in the stability of the (D^+,X) complex. In our study, we determined the ratio of electron and hole polaron masses $\sigma=m_e^p/m_h^p=0.22$ (Ref. 20) /0.589 $=0.374$. We can estimate the hole binding energy for (D^+,X) in GaN using the calculation of Skettrup, Suffczynski, and Gorzkowski[18] with the help of the plot in Fig. 1 in their report. To find an upper limit for the hole binding energy, we take an electron-hole mass ratio of $\sigma=0.3$, which is more favorable to the stability of the (D^+,X) complex. With shallow donor binding energy $E_d=29$ meV,[34] we obtain the hole binding energy $E_h\sim 0.3$ meV (in the Coulomb potential approximation used by Skettrup, Suffczynski, and Gorzkowski[18]). As was mentioned earlier, in polar semiconductors the electron-phonon interaction can increase the binding energy of an electron and a hole. However, in the case of the (D^+,X) complex, the hole is far removed from the donor, whereas the electron is tightly bound to it. Using the calculation by Skettrup, Suffczynski, and Gorzkowski,[18] we estimate the expectation value of the distance between the electron and the hole and between the hole and the donor to be $\sim$120 Å for $\sigma=0.3$. Since the sum of the polaron radii for electrons and holes is only $\sim$20 Å, the effect of the electron-phonon interaction on the (D^+,X) binding energy should be much less significant than that on the free-exciton binding energy. Using the result of our calculation for the correction of the free-exciton binding energy due to the electron-phonon interaction (0.7 meV for the $1S$ state), we obtain an upper limit of the hole binding energy in the (D^+,X) center to be 1 meV.

We measured the exciton localization energy for the I_X to be 12 meV. Since the hole binding energy is so small compared to the exciton localization energy, the energy of the hole removal determines the thermal dissociation energy of the (D^+,X) complex. In other words, the lowest-energy thermal dissociation should proceed via the loss of a hole with activation energy $E_a\leqslant 1$ meV. On the contrary, our temperature-varied measurements show that the decay of the I_X emission is a single channel process with an activation energy $E_a=10.3$ meV. This indicates the release of an exciton and strongly argues against the ionized donor-bound exciton model for the I_X emission.

Let us further examine other possible candidates that may be responsible for the I_X emission, for example neutral acceptor, neutral donor, or an isoelectronic trap (ionized acceptor cannot bind an exciton in GaN). If I_X emission were related to a neutral donor, we would have been able to see it in samples with various carrier concentrations, just like (D^0,X) emission at 3.479 eV. On the contrary, we and other authors[8,29,38] observe strong I_X emission in samples with lower than average carrier concentrations. For our samples, it is unlikely that the I_X emission is related to a donor element that is present only in our high resistivity samples since these samples were grown in a particularly clean environment. It is also unlikely that I_X is due to an exciton bound to a deep donor, since strong lattice interaction favors nonradiative decay through lattice relaxation, whereas I_X emission is the strongest at low temperatures.

We note that the I_X emission is presented exclusively in high-resistivity or slightly *n*-type samples. This is consistent with the model of an exciton bound to a neutral shallow acceptor since in samples with high electron concentrations, holes are minority carriers and the shallow acceptor levels are predominantly ionized and therefore cannot bind an exciton. As was mentioned earlier, the I_X emission is marked by the strong LO-phonon replica, whereas the (D^0,X) emission at 3.479 eV does not have a strong phonon replica in our samples. This is also consistent with the acceptor model of the I_X line since acceptor levels are deeper than shallow donor levels and therefore have stronger coupling with the lattice. Table II shows that parameter C_i for the I_X emission is about three to six times larger than that for the (D^0,X) emission. This is likely to be primarily a result of the difference between radiative lifetimes of (A^0,X) and (D^0,X) complexes since $C_i=\omega_i/W_R$. Smith *et al.*[30] have measured the radiative lifetime of the neutral acceptor-bound exciton ($E_b=25$ meV) to be $\tau=450$ ps, which is 4.5 times longer than the lifetime of the (D^0,X) line.[39] Since the radiative lifetime of the bound exciton scales with its binding energy, we can estimate the lifetime of our I_X emission using a plot given by Smith *et al.*[30] of the radiative lifetime of the (A^0,X) emission versus transition energy. Thus we get $\tau_{\rm rad}\sim 300$ ps for the $I_X-(A^0,X)$ emission at 3.473 eV. The (D^0,X) radiative lifetime has been measured by Chen *et al.*[39] to be $\tau_{(D^0,X)}=130$ ps. Neglecting the difference in ω_i, we can obtain $\tau_{(A^0,X)}/\tau_{(D^0,X)}=300$ ps/130 ps$\sim$2.3. This is in qualitative agreement with the fitting results in Table II. Therefore, it is reasonable to believe that the neutral acceptor–bound-exciton model for I_X emission is the one most consistent with our data.

V. CONCLUSION

In summary, we have conducted a systematic study of near-band-edge emissions in high-quality GaN epitaxial films grown on sapphire. $FE_A(1S$ and $2S)$ and $FE_B(1S)$ emissions and several bound-exciton emissions are identified. Extensive temperature-varied study shows that at temperatures $T\leqslant 25$ K, the shallow neutral donor-bound exciton

complex dissociates through the release of a free exciton. At higher temperatures ($T \geqslant 25$ K), the second dissociation mechanism with activation energy $E_2 \cong 28$ meV becomes important. This process may include exciton breakup and/or donor ionization. A transition located at ~12 meV below the first free exciton is investigated. Thermal activation energy of this bound-exciton emission with $E_{\text{local}} = 11.7$ meV is found to be 10.3 meV, and it also indicates that the main channel of dissociation for this complex is the release of a free exciton. Our stability analysis of the (D^+, X) complex in GaN indicates that it should proceed with significantly smaller activation energy through the release of a free hole. Therefore, we resolve the uncertainty on the origin of this emission and conclude that this complex cannot originate from an ionized donor. It is suggested that this bound-exciton complex belongs to a shallow neutral acceptor. Magnetospectroscopy study allows us to reliably identify the emission due to the first excited state of the *A*-band free exciton. Using the Aldrich-Bajaj potential to model the electron-hole interaction in polar semiconductors, we performed a variational calculation of free-exciton binding energy in the ground and first excited states. Comparing the results of the calculation with our experimental data, we have determined the polaron and nonpolaron hole effective masses $m_h^p = 0.59 \pm 0.045$ and $m_h^* = 0.52 \pm 0.04$, respectively.

ACKNOWLEDGMENTS

We acknowledge Dr. K. K. Bajaj, Dr. D. J. Wolford, Dr. I. Ferguson, and I. N. Krivorotov for helpful discussions.

*Corresponding author. E-mail: zfeng@axcelphotonics.com. Present address: Axcel Photonics Inc., 45 Bartlett Street, Marlborough, MA 01752.

[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997).
[2] *GaN and Related Materials*, edited by S. J. Pearton (Gordon & Breach, Amsterdam, 1997).
[3] *Gallium Nitride (GaN) I*, edited by J. I. Pankove and T. D. Moustakas, Semiconductors and Semimetals Vol. 50 (Academic, San Diego, 1998).
[4] *Group III Nitride Semiconductor Compounds—Physics and Applications*, edited by B. Gil (Clarendon, Oxford, 1998).
[5] H. Morkoç, *Nitride Semiconductors and Devices* (Springer, Berlin, 1999).
[6] D. Volm, T. Streibl, B. K. Meyer, T. Detchprohm, H. Amano, and I. Akasaki, Solid State Commun. **96**, 53 (1995).
[7] D. C. Reynolds, D. C. Look, B. Jogai, V. M. Phanse, and R. P. Vaudo, Solid State Commun. **103**, 533 (1997).
[8] B. Santic, C. Merz, U. Kaufmann, R. Niebuhr, H. Obloh, and K. Bachem, Appl. Phys. Lett. **71**, 1837 (1997).
[9] J. Jayapalan, B. J. Skromme, R. P. Vaudo, and V. M. Phanse, Appl. Phys. Lett. **73**, 1188 (1998).
[10] K. C. Zeng, J. Y. Lin, H. X. Jiang, and W. Yang, Appl. Phys. Lett. **74**, 3821 (1999).
[11] K. Kornitzer, T. Ebner, K. Thonke, R. Sauer, C. Kirchner, V. Schwegler, M. Kamp, M. Leszczynski, I. Grzegory, and S. Porowski, Phys. Rev. B **60**, 1471 (1999).
[12] B. J. Skromme, MRS Internet J. Nitride Semicond. Res. **4**, 15 (1999).
[13] D. G. Chtchekine, Z. C. Feng, G. D. Gilliland, S. J. Chua, and D. J. Wolford, Phys. Rev. B **60**, 15 980 (1999).
[14] L. K. Li, B. Turk, W. I. Wang, S. Syed, D. Simonian, and H. L. Stormer, Appl. Phys. Lett. **76**, 742 (2000).
[15] B. K. Meyer, D. M. Hofmann, and H. Alves, Mater. Sci. Eng., B **71**, 69 (2000).
[16] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Lett. **17**, 1262 (1966).
[17] B. K. Meyer, in *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, Mater. Res. Soc. Symp. Proc. No. **449** (Materials Research Society, Pittsburgh, 1997), p. 497.
[18] T. Skettrup, M. Suffczynski, and W. Gorzkowski, Phys. Rev. B **4**, 512 (1971).
[19] M. Rotenberg and J. Stein, Phys. Rev. **182**, 1 (1969).
[20] H. C. Alt, B. K. Meyer, D. Volm, A. Graber, M. Drechsler, D. M. Hofmann, T. Detchprohm, A. Amano, and I. Akasaki, Mater. Sci. Forum **196**, 17 (1995).
[21] B. K. Meyer, D. Volm, A. Graber, H. C. Alt, T. Detchprohm, A. Amano, and I. Akasaki, Solid State Commun. **95**, 597 (1995).
[22] J. W. Orton, Semicond. Sci. Technol. **10**, 101 (1995).
[23] D. Volm, K. Oettinger, T. Streibl, D. Kovalev, M. Ben-Chorin, J. Diener, B. K. Meyer, J. Majewski, L. Eckey, A. Hoffmann, H. Amano, I. Akasaki, K. Hiramatsu, and T. Detchprohm, Phys. Rev. B **53**, 16 543 (1996).
[24] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).
[25] C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. B **5**, 458 (1972).
[26] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **140**, A1726 (1965).
[27] W. Shan, B. D. Little, A. J. Fischer, J. J. Song, B. Goldenberg, W. G. Perry, M. D. Bremser, and R. F. Davis, Phys. Rev. B **54**, 16 369 (1996).
[28] C. Aldrich and K. K. Bajaj, Solid State Commun. **22**, 157 (1977).
[29] Y. Kawakami, Z. G. Peng, Y. Narukawa, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **69**, 1414 (1996).
[30] M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 3295 (1995).
[31] J. Campo, M. Julier, D. Coquillat, J. P. Lascaray, D. Scalbert, and O. Briot, Phys. Rev. B **56**, R7108 (1997).
[32] R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962).
[33] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).
[34] Y. J. Wang, R. Kaplan, H. K. Ng, K. Doverspike, D. K. Gaskill, T. Ikedo, I. Akasaki, and H. Amano, J. Appl. Phys. **79**, 8007 (1996).
[35] P. J. Dean, Phys. Rev. **157**, 655 (1967).
[36] A. S. Barker, Jr. and M. Ilegems, Phys. Rev. B **7**, 743 (1973).
[37] K. Pakula, A. Wysmolek, K. P. Korona, J. M. Baranowski, R. Stepniewski, I. Grzegory, M. Bockowski, J. Jun, S. Krukowski, M. Wroblewski, and S. Porowski, Solid State Commun. **97**, 919 (1996).
[38] N. Grandjean, J. Massies, M. Leroux, and P. Lorenzini, Appl. Phys. Lett. **72**, 82 (1997).
[39] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 1653 (1995).