

TEMPERATURE DEPENDENCE OF BOUND EXCITON EMISSIONS IN GaN

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ABSTRACT

The dissociation channels of two prominent bound exciton complexes in wurtzite GaN thin films are determined via an extensive temperature dependent photoluminescence study. The shallow donor bound exciton dissociation at low temperatures ($T \leq 50$ K) is found to be dominated by the release of a free exciton with thermal activation energy consistent with the exciton localization energy. At higher temperatures a second dissociation channel with activation energy $E_A = 28 \pm 2$ meV is observed. The dissociation of a bound exciton complex with exciton localization energy $E_{loc}^X = 11.7$ meV is also dominated by the release of a free exciton. In contrast to previous studies evidence is presented against the hypothesis of this emission being due to the exciton bound to an ionized donor. We find that it originates most likely from an exciton bound to a neutral acceptor.

INTRODUCTION

Recent progress in the epitaxial growth of high quality GaN materials has permitted the observation of new photoluminescence (PL) emissions. Although some of these new transitions have been positively identified,^{1,2} broad PL linewidths preclude the definitive identification of other emissions. A bound exciton emission located ~ 12 meV below the free exciton is an example of such emission. This emission has been identified as a neutral acceptor-bound exciton (A^0, X)^{3,4} or a neutral donor-bound exciton (D^0, X)⁵ and more recently was assigned to an ionized donor-bound exciton (D^+, X).^{6,7} The identification of the various emissions in GaN is essential to understanding and improving device performance via better dopants and more efficient luminescence.

The temperature dependence of the PL intensity of a bound exciton complex can be used to identify the kinetics of its thermal dissociation, and thus to provide a valuable insight into the origin of this complex. The main channel of thermal decay is the one with the least activation energy, E_A . In the case of a neutral donor-bound exciton complex in GaN the exciton delocalization from the neutral donor ($E_{loc}^X \sim 6$ meV) is likely to be the minimum-

energy dissociation channel of that complex. Temperature dependent photoluminescence studies have been employed previously to investigate neutral donor-bound exciton emissions in GaN and other materials.⁸⁻¹⁰ However, there exists some discrepancy in the reported values for the delocalization energy of the exciton bound to a neutral donor. The PL temperature study can be also used to clarify the origin of the bound exciton emission with $E_{\text{loc}}^{\text{X}} = 11.7$ meV, which we call I_{X} emission. If this emission is due to the ionized donor-bound exciton complex the minimum-energy dissociation is expected to proceed through the break-off of a loosely bound hole, and thus the thermal activation energy equals the binding energy of the hole. On the other hand, if the I_{X} emission originates from a neutral-impurity-center, the exciton delocalization is expected to be the lowest energy channel for thermal dissociation.

EXPERIMENT

We report on two lightly Si-doped GaN samples, each grown on (0001) sapphire with ~20 nm -thick GaN buffer by metalorganic chemical vapor deposition (MOCVD). Sample A has a GaN layer thickness of 3.3 μm and was highly resistive. Sample B has an epilayer thickness of 2 μm and a room temperature (RT) carrier concentration of $n \cong 6.3 \times 10^{16} \text{ cm}^{-3}$, as determined by Hall measurements.

PL spectra were obtained using the 325 nm line (3.815 eV) of a cw He-Cd laser focused to ~300 μm diameter 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 optical cryostat. The PL signal was dispersed by a 0.85-m double spectrometer providing accuracy of 0.01 nm, and detected by a cooled S-20 photomultiplier tube operating in photon-counting mode.

RESULTS AND DISCUSSION

Figure 1 shows the low temperature PL emissions from both samples. Free exciton (FE,X) emissions are identified by their PL intensity being insensitive to the temperature compared to the bound exciton emissions (D^0, X) and I_{X} (see Figure 2). (D^0, X) emission is identified by its well known spectral position ~6 meV below the A-band free exciton ($\text{FE}_{\text{A}, X}$).

Sample B shows a ($\text{FE}_{\text{A}, X}$) emission and a dominant (D^0, X) emission originating from neutral Si donors. Sample A also exhibits these two emissions. However their absolute position is blue-shifted by ~2.5 meV in comparison with Sample B. This is likely due to the difference in the degree of the residual stress. Sample A also exhibits two additional emissions: a B-band free exciton ($\text{FE}_{\text{B}, X}$) (very weak in Sample B) and a strong emission line labeled I_{X} at 3.4735 eV, which is located at 11.7 meV below the A-band free exciton line ($\text{FE}_{\text{A}, X}$). The I_{X} emission is marked by a strong LO-phonon replica at 3.382 eV, indicating a strong electron-phonon coupling. We determine an LO-phonon energy of $\hbar\omega_{\text{LO}} = 91.5$ meV, consistent with the literature.¹¹ In Sample A the first excited state (2S state) of the A-band exciton is observed at 3.5035 eV, as also shown on Figure 1. The positive identification of this emission was confirmed by a magneto-spectroscopy study which will be published elsewhere. From the energy separation between 1S and 2S states we can determine the free exciton binding energy in the Coulomb potential approximation: $E_{\text{b}}^{\text{X}} = 4/3 \times (E_{2\text{S}} - E_{1\text{S}}) = 24.4 \pm 0.5$ meV, consistent with other reports.²

To assess the temperature variation of the integrated intensity of the (D^0, X) and I_{X} emissions all strong near-bandedge lines have been fitted with Gaussian lineshapes (see Figure 1). The low-energy tails of the (D^0, X) and I_{X} emissions were disregarded during fitting;

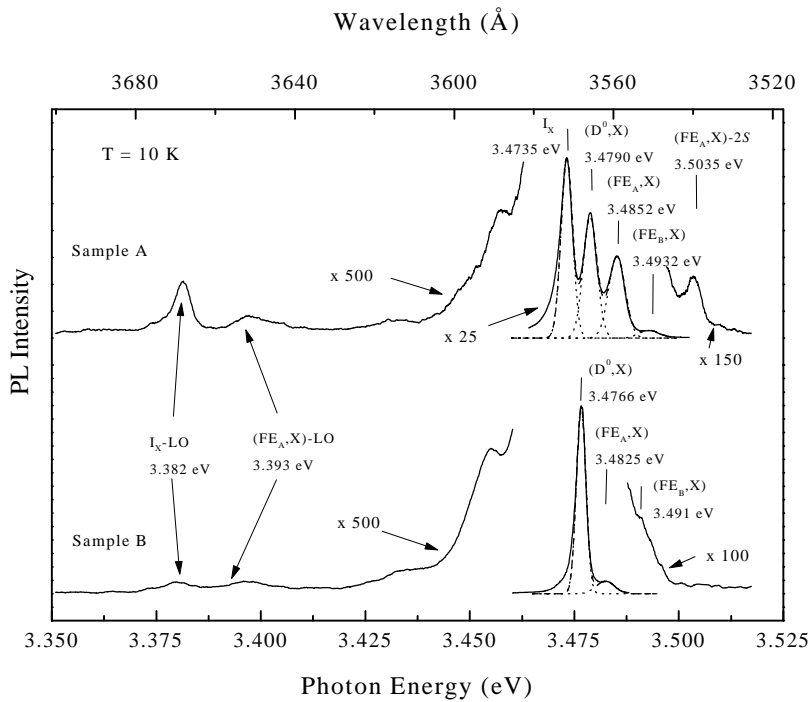


Figure 1. Low-temperature PL spectra of Samples A and B. Sample A is marked by a strong emission I_X at 3.473 eV. Dashed lines represent the fit with gaussian lineshapes (dotted lines). Strong LO-phonon replica of the I_X emission is observed at 3.382 eV. Transition at 3.5035 eV is due to the first excited state of the A-band free exciton.

importantly this does not change the character of their temperature dependence. A two-channel dissociation Arrhenius model was used to fit the temperature dependence of the PL integrated intensity of the (D^0,X) emission in Sample B:

$$\frac{I(T)}{I(0)} = \frac{1}{1 + C_1 \times \exp\left(-\frac{E_{1A}}{kT}\right) + C_2 \times \exp\left(-\frac{E_{2A}}{kT}\right)} \quad (1)$$

where $I(T)$ and $I(0)$ are the integrated intensities of the (D^0,X) emission at temperature T and 0 K, respectively, E_{1A} and E_{2A} are activation energies and C_1 , C_2 are constants.

The temperature dependence of I_X emission was analyzed using a single-channel dissociation Arrhenius model:

$$\frac{I(T)}{I(0)} = \frac{1}{1 + C \times \exp\left(-\frac{E_A}{kT}\right)} \quad (2)$$

Figure 2 shows the temperature dependence of the integrated intensity of the (FE_A,X) , (D^0,X) and I_X emissions, together with the results of the fitting. As shown, the temperature dependence of the (D^0,X) emission in Sample B is well described with the two-channel dissociation model of Eq. (1). We obtain activation energies $E_{1A} = 5.9 \pm 0.2$ meV and $E_{2A} = 28$

± 2 meV. The activation energy E_{1A} is in excellent agreement with the energy of exciton localization on a shallow donor $E_{loc}^X = 6.2 \pm 0.4$ meV (see Figure 1). The temperature dependence of the (D^0, X) emission in Sample A (fitted with a single-channel dissociation model due to a limited temperature range) exhibits thermal activation energy $E_A = 5.6 \pm 0.3$ meV, which is also in a very good agreement with the exciton localization energy and the value of E_{1A} in Sample B. Therefore, we conclude that the dominant channel of thermal dissociation

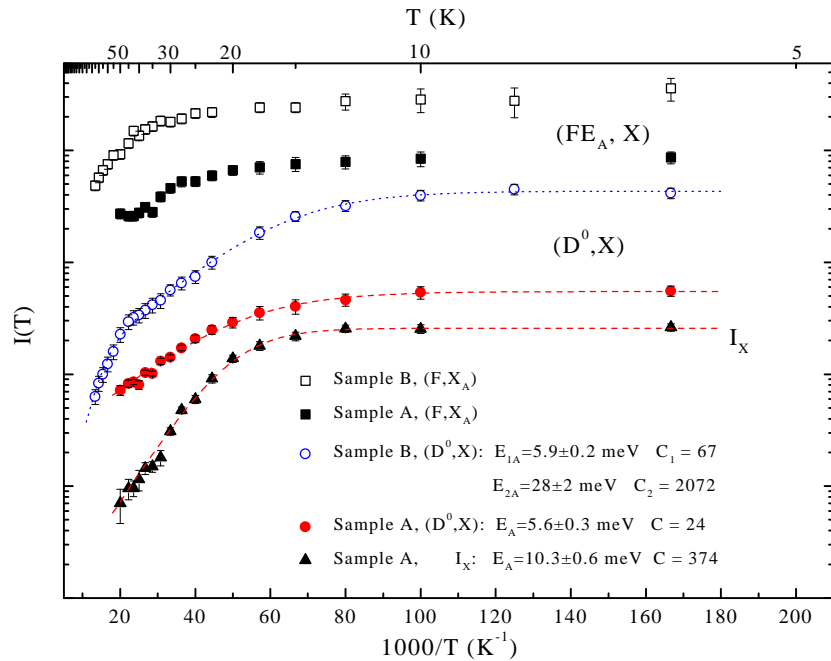


Figure 2. Temperature dependence of the integrated PL intensity of (FE_A, X) emission (Samples A and B), (D^0, X) emission (Samples A and B), and I_X emission (Sample A). The plots are vertically displaced for the convenience of viewing. Dotted and dashed lines represent fits with Eq. (1) and Eq (2), respectively.

for the (D^0, X) complex at low temperatures ($T \leq 50$ K) is the release of a free exciton.

At higher temperatures another thermal dissociation channel with activation energy $E_{2A} \cong 28$ meV is clearly observed (see Figure 2). The second dissociation channel may be due to the decay of the (D^0, X) complex via simultaneous exciton delocalization and exciton dissociation with activation energy $E_{2A} \cong E_b^X + E_{loc}^X \cong 30$ meV.¹² Alternatively, a neutral donor ionization process, with activation energy $E_{2A} = E_D \cong 29$ meV,¹³ may also affect the PL intensity of the (D^0, X) emission, since it reduces the number of the neutral-donor centers to which photo-excited excitons can bind to form the (D^0, X) complexes.⁸ A detailed study of 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 Eq. (2) in the experimental temperature range, resulting in $E_A = 10.7 \pm 0.6$ meV. This activation energy is very close to the exciton localization energy of the I_X complex: $E_{loc}^X = 11.7$ meV. This indicates that the I_X bound exciton complex dissociates by releasing a free exciton, similar to the (D^0, X) complex.

It has been suggested that the I_X emission is due to the exciton bound to the ionized

donor.^{6,7} The (D^+,X) complex is more stable in systems with a smaller ratio of the electron and hole effective mass $\sigma = m_e/m_h$.¹⁴ Maintaining the hole bound to the donor is the weak link in the stability of the (D^+,X) complex. A somewhat similar situation was reported in GaP¹⁵ where the thermal release of the hole was favored over the exciton delocalization for isoelectronic traps.

We can estimate the binding energy of the hole in the current system by evaluating the electron-hole mass ratio, σ . From the value of the free exciton binding energy the exciton reduced mass can be estimated to be $\mu^* = (m_e^p \cdot m_h^p)/(m_e^p + m_h^p) = 0.162$. Here all masses are taken to be polaron masses due to the strong electron-phonon interaction in GaN. Taking the electron polaron mass $m_e^p = 0.22$ ¹⁶, we find the hole polaron mass $m_h^p = 0.61$ and $\sigma^p = 0.36$. Since the value of σ^p is smaller than $\sigma_{crit.} = 0.43$,¹⁴ the (D^+,X) complex is theoretically allowed in GaN. The hole binding energy can be now estimated in the approximation of the Coulomb potential using the Figure 1 of Skettrup *et al.*¹⁴ To find an upper limit for the hole binding energy we take a value of the electron-hole mass ratio: $\sigma = 0.3$, which is more favorable for the existence of the (D^+,X) complex. Let's denote a neutral donor energy level E_D ($E_D = 29$ meV¹³) and ionized donor-bound exciton energy level $E_{(D^+,X)}$. Then from the Figure 1 of Skettrup we obtain $(E_{(D^+,X)} - E_D)/E_D \cong 1\%$ which yields a hole binding energy of $E_h = E_{(D^+,X)} - E_D \cong 0.3$ meV. Since the distance between hole and donor can be estimated¹⁴ at ~ 120 Å for $\sigma = 0.3$ and the sum of the polaron radii for electron and hole is ~ 20 Å in GaN, the electron-phonon interaction is not expected to affect the hole binding energy significantly. We may, therefore, conclude that the thermal dissociation of the (D^+,X) complex in GaN proceeds via the release of a free hole, with very small activation energy $E_A \leq 1$ meV, which should make the observation of this complex possible only at very low temperatures.

The results of Figure 2 for the I_X emission do not exhibit $E_A \cong 1$ meV; indeed we determine $E_A = 10.7$ meV. It is therefore very unlikely that I_X emission originates from a (D^+,X) complex. Since $E_A \cong E_{loc}^X = 11.7$ meV the main channel of dissociation for the I_X emission should be release of a free exciton, which is consistent with the neutral impurity-bound exciton model. Since the I_X emission indicates a strong coupling to LO-phonons, contrasting the (D^0,X) emission in our samples, we believe that it originates from a neutral acceptor-bound exciton. This hypothesis is also consistent with the fact that strong I_X emission is observed only in highly compensated samples. We can estimate the binding energy of this acceptor using Haynes' rule which has been shown to be valid for acceptors in GaN¹⁷: $E_b = E_{loc}^X/0.1 = 120$ meV. Therefore the free-to-bound (e, A^0) transition involving this shallow acceptor can be, in principle, observed around 3.390 eV. Unfortunately the observation of (e, A^0) emission is likely to be masked by the strong LO-phonon replica of the (FE_A,X) emission at 3.393 eV. The existence of such a shallow acceptor ($E_b = 120$ meV) in GaN would be significant since it would provide a more effective p -type dopant.

CONCLUSIONS

In summary, our temperature study of the shallow bound exciton emissions in GaN shows that the activation energy of thermal dissociation of the (D^0,X) complex at low temperatures ($T \leq 50$ K) is in good agreement with the exciton localization energy, thereby proving that at low temperatures the main dissociation channel of shallow bound exciton complexes in GaN is the release of a free exciton. At higher temperatures a second dissociation channel is clearly observed, which may be due to the process of simultaneous exciton delocalization and dissociation and/or neutral donor ionization. An analysis of the thermal

stability of the ionized donor-bound exciton leads to the conclusion that the least-energy thermal decay of this complex should proceed via the release of a free hole, with a very small activation energy $E_A \leq 1$ meV. This contradicts the results of our temperature study for the bound exciton emission with $E_{loc}^X = 11.7$ meV, for which we find the thermal activation energy $E_A = 10.7$ meV. Therefore, the assumption of this emission being due to the exciton bound to an ionized donor is not valid. Since the thermal activation energy and localization energy are in good agreement for this emission, similarly to the case of the (D^0, X) emission, we conclude that it originates from an exciton bound to a neutral impurity – most likely a neutral acceptor.

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