

Time-resolved photoluminescence studies of an ionized donor-bound exciton in GaN

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Time-resolved photoluminescence (PL) spectroscopy has been used to study the radiative recombination of excitons bound to ionized donors in GaN doped with both Mg and Si at concentrations of $5 \times 10^{18}/\text{cm}^3$ and $1.5 \times 10^{17}/\text{cm}^3$, respectively. Low temperature ($T \sim 10\text{K}$) time-resolved, as well as integrated PL spectra, identify an ionized donor-bound (Si) exciton peak (D^+X) approximately 11.5 meV below and a neutral acceptor-bound exciton (A^0X) 20.5 meV below the free exciton peak. Rapid decay of the free exciton emission (≤ 20 ps) implies that excitons are quickly captured by acceptors and ionized donors. We find the (A^0X) emission lifetime is consistent with previous measurements for GaN:Mg epilayers, while the (D^+X) lifetime of 160 ps is longer than that of the well studied neutral donor-bound exciton (D^0X). The measured (D^+X) lifetime, in comparison with (D^0X) and (A^0X), suggests that the state is stable at low temperature.

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GaN and its related alloys are recognized as technologically important materials and have accordingly been extensively studied in recent times. Photoluminescence (PL) spectroscopy is one commonly employed method of semiconductor characterization. At low temperature, this technique may yield several discrete radiative recombination lines associated with the free carriers, impurities, and defects within the semiconductor. In the case of GaN, radiative recombination of excitons, both free and bound to neutral acceptors (A^0X) and donors (D^0X), have been extensively studied.¹⁻⁹ However, other expected transitions such as the ionized donor-bound exciton (D^+X) have only recently been identified.^{10,11} Consequently, the dynamics of this transition are still not well known.

Many GaN based devices incorporate p - n junctions or other bipolar structures in which ionized donors may be prevalent. Thus, the optical properties and dynamics of the (D^+X) state may play an important role in device performance. In this letter, we report the results of a time-resolved PL spectroscopy study of the (D^+X) transition in a GaN epilayer doped with both Si donors and Mg acceptors. The $1.7 \mu\text{m}$ GaN epilayer was grown by metalorganic chemical vapor deposition (MOCVD) on a (0001) sapphire substrate after low temperature (550°C) deposition of a thin GaN buffer layer. Si and Mg were incorporated during epilayer growth using SiH_4 and Cp_2Mg sources, respectively. Post-growth annealing in a Nitrogen ambient (30 min, 800°C) was performed to activate the Mg acceptors.¹² Secondary ion mass spectroscopy analysis verified an average Mg concentration of $5 \times 10^{18}/\text{cm}^3$ and Si concentration of $1.5 \times 10^{17}/\text{cm}^3$. The proportionately larger Mg concentration is expected to result in full compensation of the Si donors within the GaN. Consequently, even at low temperature, the donor states are expected to be completely ionized. Undoped epilayers produced by our MOCVD system exhibit free ex-

citon PL emission at low temperature, room temperature Hall mobility of $450 \text{ cm}^2/\text{Vs}$, and excess electron concentration of $n \sim 2 \times 10^{17}/\text{cm}^3$.

The sample was cooled to 10 K with a closed cycle helium refrigerator and optically pumped with a laser system which produces 10 ps pulses at 290 nm. PL emission was analyzed with a 1.3 m monochromator and detected with either a microchannel-plate photomultiplier tube for time-integrated spectra or a synchroscan streak camera (Hamamatsu C5680) for time-resolved spectra. The streak camera is capable of 2 ps time resolution. However, due to the combined effects of laser pulse width and temporal spread within the monochromator, the time resolution is estimated to be approximately 20 ps. The laser and PL collection systems have been described in more detail elsewhere.¹³

Figure 1 shows time-integrated PL spectra obtained under various excitation intensities, I_{exc} , spanning nearly 3 orders of magnitude. PL spectra representing different I_{exc} are shifted vertically for clear presentation. In Fig. 1, there are two predominant emission peaks seen near band edge and their relative intensities change with I_{exc} . We also find that the total band edge PL intensity (I_{PL}) varies superlinearly with I_{exc} , approximately as $I_{\text{PL}} \propto I_{\text{exc}}^2$, as shown in the inset of Fig. 1. Superlinear PL yield has previously been observed for exciton related emission⁶ and generally reflects the intrinsic nature (dependence on both photoexcited electrons and holes) of the transition.

The temporal character of the PL features observed in Fig. 1 was recorded with the streak camera. Figure 2 shows time-resolved PL spectra recorded at three representative delay times relative to the incident laser pulse. The spectra recorded at times $t = 0, 50,$ and 1250 ps are arbitrarily scaled for presentation. The very short lived peak at 3.4845 eV is identified as the free exciton associated with the A valence band (FX_A).^{6,10} The FX_A position implies a binding energy of 20.5 meV for the 3.464 eV peak, which identifies it as (A^0X).^{10,14} The remaining peak at 3.473 eV has a binding energy of 11.5 meV which is in very good agreement with

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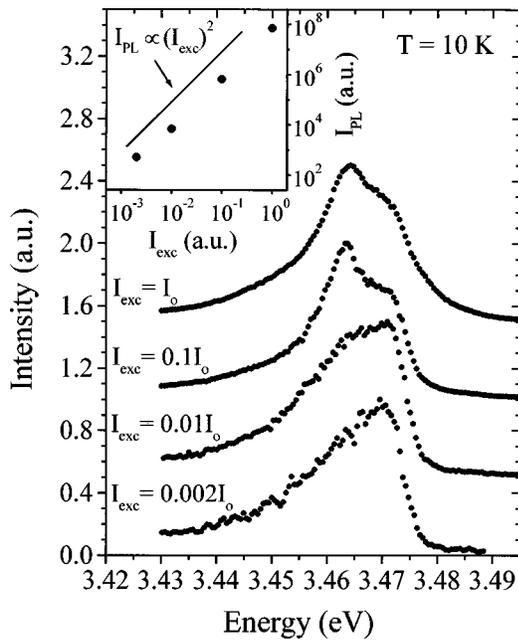


FIG. 1. Time-integrated PL spectra acquired at 10 K for different excitation intensities (I_{exc}). The inset shows the variation of the integrated PL intensity with I_{exc} .

the recently reported (D^+X) binding energy as determined from continuous wave PL spectroscopy measurements.^{10,11} The (D^+X) assignment is further supported by the expectation that the Si donors in the sample are fully compensated by the higher concentration of Mg acceptors.

The FX_A emission lifetime in this sample is very short (≤ 20 ps), which implies that excitons are either rapidly captured by ionized donors or neutral acceptors or quenched by other nonradiative processes. Furthermore, the time resolved data reveal that the FX_A emission decays before the onset of PL decay at the (D^+X) or (A^0X) emission energies.

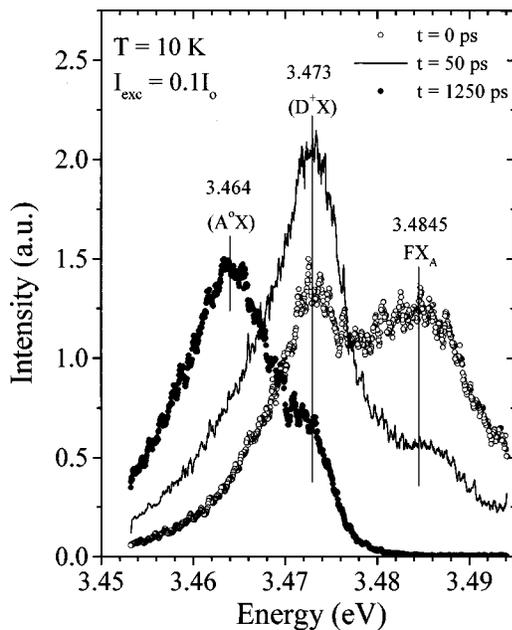


FIG. 2. Time-resolved PL spectra obtained at three different delay times relative to the incident laser pulse. From right to left, the spectra were measured at the point of laser excitation ($t=0$ ps), the onset of PL decay ($t=50$ ps), and a time 1.25 ns after the laser pulse.

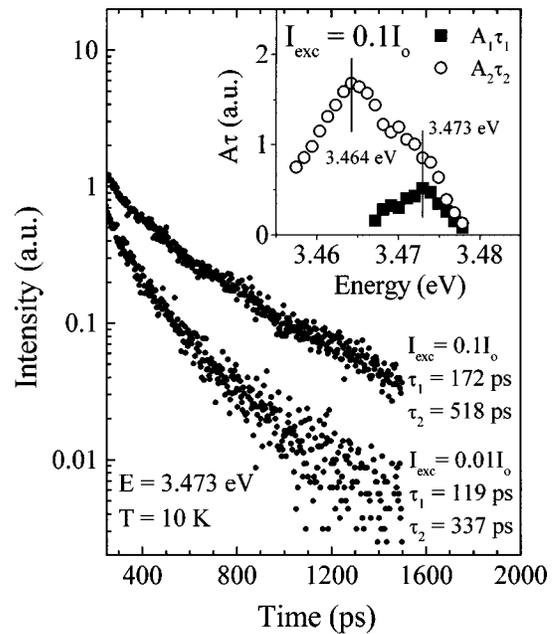


FIG. 3. Temporal decay of PL intensity at $E=3.473$ eV for two representative I_{exc} . The decays are described well by a two exponential function, which reflects the contributions of two distinct (overlapping) transitions as evidenced in Fig. 2. The inset shows time integrated intensities ($A\tau$) from a series of fit results of the form $I(t)=A_1 \exp(-t/\tau_1)+A_2 \exp(-t/\tau_2)$.

These facts support a model for (D^+X) formation, whereby ionized donors capture free excitons. It may also be possible that (D^+X) states form in a two step process involving free electrons and holes [$D^+ + e^- \rightarrow D^0$ followed by $D^0 + h^+ \rightarrow (D^+X)$]. Such a formation process is not precluded by any of our experimental observations. However, because the (A^0X) state most likely involves the capture of a free exciton, we believe that sufficient exciton formation must occur in this sample so that a two step capture process need not be invoked for (D^+X) formation.

Figure 3 shows the PL decay at the (D^+X) peak energy of 3.473 eV for two excitation intensities. Emission lifetimes were determined by least squares fits of one or two exponential decay form. The decays shown in Fig. 3 are not single exponential because they represent PL contributions at 3.473 eV from two distinct but overlapping transitions as shown in Figs. 1 and 2. The long lifetime component of $\tau_2=518$ ps ($I_{exc}=0.1I_0$) is comparable with a previously reported measurement of the (A^0X) emission lifetime for a GaN:Mg epilayer.⁴ The short lifetime component, $\tau_1=172$ ps, is related to (D^+X) emission. The two exponential fit has the form $I(t)=A_1 \exp(-t/\tau_1)+A_2 \exp(-t/\tau_2)$. In this way, the products $A_1\tau_1$ and $A_2\tau_2$ represent the time integrated intensities for each of two distinct emissions. The inset of Fig. 3 shows the emission energy dependence of the two decay components ($A_1\tau_1$, $A_2\tau_2$) extracted from a series of decay curves. The resulting profiles resemble very closely the time-resolved emission peaks shown in Fig. 2 and clearly demonstrate that the decay components τ_1 and τ_2 represent the recombination lifetimes of the (D^+X) and (A^0X) emission, respectively.

The expected lifetime for the (D^+X) emission may be estimated by using a theoretical relationship between the bound (F) and free exciton (F_{ex}) oscillator strengths of¹⁵

TABLE I. Comparison of experimentally measured parameters for low temperature (~ 10 K) PL emissions associated with bound exciton states in hexagonal GaN. Listed quantities include exciton binding energy (E_B), emission lifetime (τ_L), and thermal dissociation energy.

Bound state	E_B (meV)	τ_L (ps)	Thermal dissociation (meV)	Relevant material/structure
(A^0X)	20–21.5	370–660	No data	p -type
(D^0X)	6–7	35–100	6	n -type, intentional and unintentional
(A^-X)	Existence is precluded
(D^+X)	11.2–11.5	160	No data	Bipolar structures, intentional and unintentional codoping

$$F = (E_0/E_b)^{3/2} F_{\text{ex}}. \quad (1)$$

Here, E_b is the binding energy of the exciton, $E_0 = (2\hbar^2/m)(\pi/\Omega_0)^{2/3}$, m is the effective mass of the free exciton, and Ω_0 is unit cell volume. From Eq. (1), the ratio of radiative lifetimes for two distinct bound exciton transitions is expressed as

$$\tau_1/\tau_2 = F_2/F_1 = [(E_b)_1/(E_b)_2]^{3/2}. \quad (2)$$

The authors' laboratory previously reported a 100 ps lifetime for (D^0X) emission with a 7 meV binding energy.² These values, together with the measured (D^+X) binding energy of 11.5 meV, yield from Eq. (2) an expected lifetime of 210 ps for (D^+X) emission. Although the expected lifetime is somewhat longer than the measured (D^+X) emission lifetime of $\tau = 160$ ps, the trend of increased lifetime for increased binding energy is evident.

Decay lifetimes were measured as a function of PL emission energy (not shown) for the three representative excitation intensities. Both the (A^0X) and (D^+X) emissions exhibited a trend of decreasing lifetime with increasing emission energy. For example, at $I_{\text{exc}} = 0.1I_0$ the (D^+X) lifetime decreased monotonically from $\tau = 180$ ps at $E = 3.468$ eV to $\tau = 120$ ps at $E = 3.478$ eV. A similar dependence of emission lifetime on emission energy has been observed for excitons bound to neutral acceptors and donors in GaN.^{2,4} It may be understood as the result of a distribution of exciton binding energies due to local variations of the crystal quality at the impurity sites. Following Eq. (2), lower energy emission (larger binding energy) will exhibit a longer radiative lifetime than higher energy emission. The decay lifetimes were measured for three excitation intensities. The average (D^+X) lifetime increased slightly with increasing I_{exc} from approximately $\tau = 120$ ps at $I_{\text{exc}} = 0.01I_0$ to $\tau = 160$ ps at $I_{\text{exc}} = I_0$. The (A^0X) lifetime, on the other hand, was maximum for $I_{\text{exc}} = 0.1I_0$ ($\tau = 660$ ps).

Table I displays a summary of parameters for the four most fundamental bound exciton states in hexagonal GaN. The quantities listed include exciton binding energy (E_B), emission lifetime (τ_L), and thermal dissociation energy. No parameters are indicated for the ionized acceptor-bound exciton (A^-X) because, to our knowledge, it has not been observed. In fact, effective mass arguments preclude the existence of this state in hexagonal GaN.^{10,16} The values given in Table I represent this work and a survey of references.^{1–11} While this survey is not exhaustive, we believe it is representative of the majority of published data for the listed parameters.

In conclusion, the recombination dynamics of a (D^+X) transition in MOCVD grown GaN doped with both Si and Mg have been studied with time-resolved PL spectroscopy. The band edge PL at 10 K is found to consist of (D^+X) and (A^0X) transitions as determined from the observed binding energies. We find that the measured (D^+X) lifetime of $t = 160$ ps is longer than reported values of the (D^0X) emission lifetime, which is consistent with the relatively larger binding energy of (D^+X). The magnitude of the (D^+X) lifetime at $T = 10$ K, in comparison with (D^0X) and (A^0X), implies that the state is reasonably stable and not subject to rapid nonradiative decay. Because ionized donors are expected to be prevalent within bipolar or codoped structures, the optical properties and dynamics of the (D^+X) transition is of relevance to the characterization, modelling, and performance of many GaN based devices.

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