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Surface and bulk exciton recombination dynamics in GaN freestanding films via one- and two-photon excitations

Yongchun Zhong · Kam Sing Wong · Weili Zhang · D. C. Look

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Abstract We have measured the photoluminescence (PL) lifetime of a freestanding GaN film using one- and two-photon excitations to demonstrate the dramatic difference in exciton recombination dynamics at the surface and in the bulk. An ultra-long exciton PL lifetime of 17.2 ns at 295 K is observed from a GaN freestanding film using two-photon excitation, whereas less than 100 ps lifetime is observed for one-photon excitation, suggesting that nonradiative processes from surface defects account for the short PL lifetime measured. The room temperature exciton lifetime of 17.2 ns is the longest ever reported for GaN film. A monotonic increase in two-photon excited PL lifetime with increasing temperature and the linear dependence of the exciton lifetime with emission wavelength show good agreement with the theoretical predictions, indicating that radiative recombination dominates for bulk excited state relaxation processes.

Y. Zhong (✉) · K. S. Wong
Department of Physics, Hong Kong University of Science and Technology, Kowloon, Hong Kong, P.R. China
e-mail: vzhong@ust.hk

K. S. Wong
e-mail: phkswong@ust.hk

W. Zhang
School of Electrical and Computer Engineering, Oklahoma State University, Oklahoma, OK 74078, USA
e-mail: w_wzhang@yahoo.com

D. C. Look
Semiconductor Research Center, Wright State University, Dayton, OH 45435, USA

D. C. Look
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH 45433, USA

1 Introduction

GaN is an emerging candidate material for fabrication of a variety of optical and electrical semiconductor devices having good high-frequency and high-temperature operational characteristics [1]. GaN films of good optical quality grown by molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE) have been reported in recent years [2–5]. The significant progress in growth techniques generates considerable interest in the photoluminescence (PL) excitonic lifetime as a probe to study sample quality [6–13].

It is well known that surface defects can act as nonradiative recombination centers, and thus can affect the lifetimes of photogenerated carriers as well as the performances of certain electronic devices [14]. All the time-resolved experiments performed so far show a bandedge PL lifetime of a few tens to a few hundreds of picoseconds, indicating strong nonradiative recombination processes [6–13]. The longest room-temperature PL lifetime ever reported is about 2 ns for a GaN film grown on a TiN porus network template, but even in this case it has a large fast decay component with a decay time constant of about 400 ps [13]. These PL experiments were done using above-bandgap excitation, and because of the very short absorption depth in this case (~a few hundred nanometers) the surface defects will strongly quench the excited carriers and excitons and consequently will produce a very short PL decay. One way to avoid this nonradiative process at the surface and study directly the intrinsic radiative

recombination is by using two-photon excitation to generate carriers within the bulk in a thick GaN film. In this paper, we report on the optical characterization and time-resolved studies of a freestanding GaN film. A room temperature exciton PL decay time of 17.2 ns using two-photon excitation is the longest ever reported for a GaN film. Furthermore, an observed monotonic increase of the PL lifetime versus temperature indicates that radiative recombination dominates from 8 to 295 K.

2 Experimental details

The experiments were carried out on a 250-μm-thick freestanding GaN film grown on a (0001) sapphire substrate by HVPE and then separated from the sapphire by laser liftoff [15]. Low-temperature PL measurements were carried out using a liquid-helium cryostat. A femtosecond titanium–sapphire oscillator and a regenerative amplifier were used as the excitation sources. A wavelength of 710 nm was typically used for the two-photon pumping and its second harmonic at 355 nm, as well the third-harmonic of the amplifier output at 267 nm, were used for one-photon experiments. Time-integrated photoluminescence (TIPL) experiments use a Spex 500 monochromator and time-resolved photoluminescence (TRPL) measurements were made with a Hamamatsu model C4334 streak camera coupled to a spectrometer.

3 Results and discussion

Fig. 1 shows the one- and two-photon excitation PL spectra of the sample at different temperatures. With increasing temperature, both the one-photon and two-photon PL spectra are red-shifted due to a decrease in the GaN bandgap with temperature. The dotted line shows the TIPL spectrum excited with the 355 nm laser (one-photon excitation). At a temperature of 8 K, the PL spectrum is dominated by the bound-exciton emission peak at 3.4727 eV, denoted by D^0X. There is a weak free A-exciton emission at 3.4798 eV, denoted by $E_X{}^A$. The spectrum also includes two weak luminescence lines attributable to a bound-exciton longitudinal-optical (LO) phonon replica at 3.3807 eV, and a free-exciton-LO phonon replica at 3.3882 eV, denoted by E_D-LO and E_X-LO, respectively. At higher temperatures, the excitonic and exciton-LO phonon replica lines broaden and are red shifted. Furthermore, free exciton emissions (i.e., $E_X{}^A$, E_X-LO) are greatly enhanced and the bound exciton emissions (i.e., D^0X, E_D-LO) strongly suppressed due to ionization of the neutral donors at higher temperature. The observed temperature dependence of the E_D-LO and E_X-LO peaks are consistent with

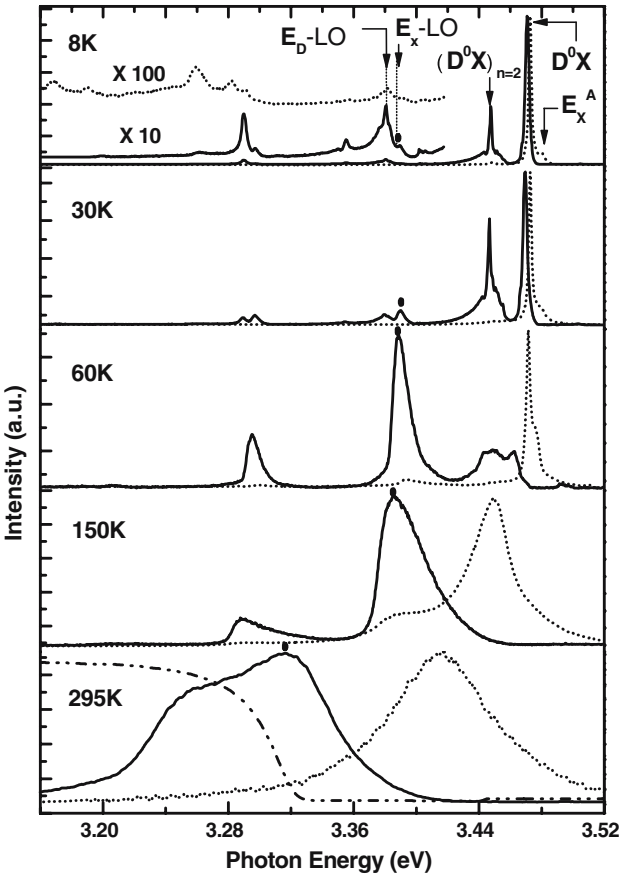

Fig. 1 The one- and two-photon-excited PL spectra at different temperatures. The dotted lines represent the one-photon excitation case and the solid lines, the two-photon-excitation case. The peaks marked with filled circles show the evolution of the exciton-LO-phonon emission peak. The dot-dash line is the transmission of the GaN film showing that the two-photon-excited PL peak is at the transmission edge of the sample

those reported for heteroepitaxial GaN films [16]. The peak at 3.4476 eV is in the region of two-electron $(D^0X)_{n=2}$ transitions; however, its intensity appears to be too large for a two-electron transition. The low energy peaks at 3.2594, 3.2898 and 3.2974 eV are likely due to donor–acceptor-pair (DAP) emission and two-phonon assisted exciton emissions (i.e., E_D-2LO and E_X-2LO) respectively [16]. A detailed spectroscopic assignment of the PL peaks at low temperatures for strain-relaxed GaN films can be found in ref. [17].

The solid lines show the TIPL spectrum excited with the 710 nm laser light, and the two-photon excitation process is confirmed by the PL intensity depending on the square of the excitation intensity. The excitonic emission bands of the two-photon-induced PL are all red shifted compared to those resulting from one-photon excitation. This red shift is due to self-absorption in the two-photon case, because the PL has to propagate a long distance (i.e., 100–200 μm) from the center of the sample before it can escape to the

surface [18]. This self-absorption also suppressed the bandedge emission and makes the low-energy emission peaks (i.e., the LO-phonon-assisted PL peaks) appear to be stronger. For the two-photon-excited emission at temperatures of 100 K or above, the band-edge exciton emission is completely self-absorbed and the dominant emission peak is in fact the exciton-LO-phonon emission as shown in Fig. 1. The strong self-absorption at the bandedge at higher temperatures can be explained by the broadening and extension of the Urbach band-tail to lower energies with increasing temperature [19].

Figure 2 shows the PL spectrum excited by 707.8 nm laser at 30 K. There is a small peak at 353.84 nm, which is corresponding to the second harmonic generation (SHG) of the laser. The PL spectra do not change with changing the excitation laser wavelength, while the small SHG peak changes with the excited wavelength. This is shown in the figure inset. In the figure inset, the small peak at 356.24 nm is the free exciton emission peak at 30 K. Because of the strong self-absorption of the sample, these two peaks are very weak corresponding to the other PL peaks.

Furthermore, at temperature 30 K and excited by the 710 nm laser, the intensity of the bound exciton emission (D_0X) is linear depended on the square of excited power. It is shown in Fig. 3. It clearly indicates that the excited process using 710 nm laser is a two-photon process.

Figure 4 (a) and (b) show the PL decay at various temperatures for one-photon-excited and two-photon-excited exciton emission peaks, respectively. A drastic difference in decay times is seen for the two cases. For the one-photon-excited PL, the emission lifetime decreases with increasing temperature and exhibits a multi-component exponential decay, with decay time constants ranging from a few tens to a few hundreds of picoseconds. This behavior suggests rapid capture and nonradiative recom-

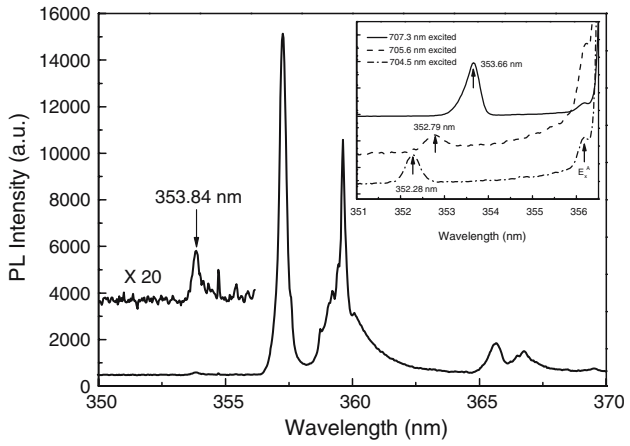

Fig. 2 SHG and the PL spectrum excited by 707.8 nm laser at 30 K. Inset figure shows the free exciton emission peak and the SHG excited by laser with different wavelength at 30 K

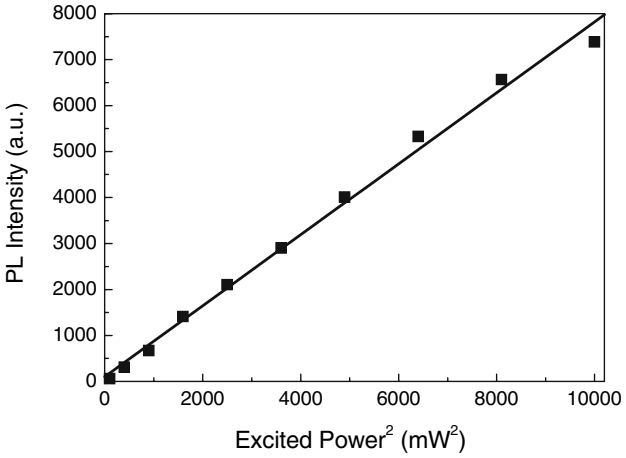

Fig. 3 At temperature 30 K and excited by the 710 nm laser, The bound exciton emission (D_0X) intensity as a function of the square of excited power

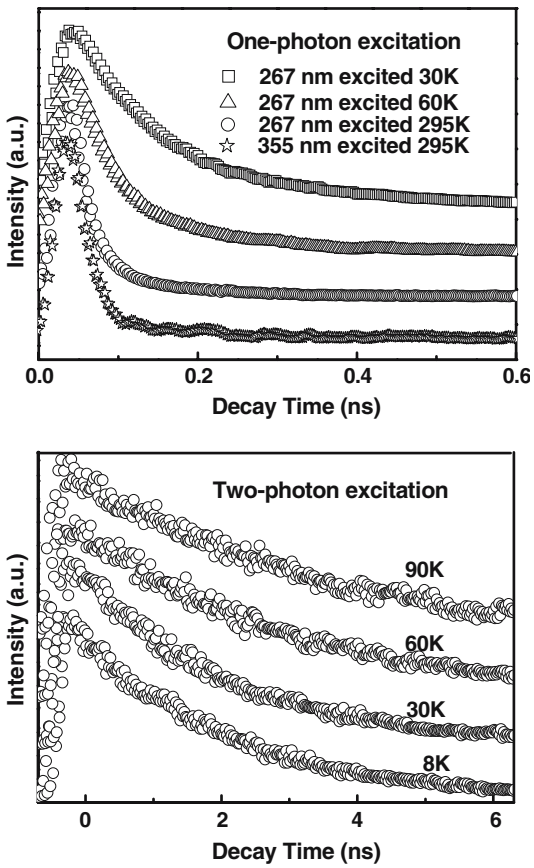

Fig. 4 (**a**) The PL decay of the one-photon-excited exciton emission peak at various temperatures. The room temperature PL decay times for both the 267- and 355-nm excitations are about the same. The 355-nm excitation intensity is more than three orders of magnitude lower than that using 267-nm excitation. This indicates that the fast PL decay is not a result of a nonlinear recombination process (such as Auger) due to the higher excitation intensity at 267 nm. (**b**) The two-photon-excited exciton emission decay at various temperatures

bination resulting from surface defects. On the other hand, the two-photon-excited PL lifetime increases with increasing temperature, opposite to the one-photon case. It indicates that the two-photon exciton emission is dominated by radiative recombination. The PL lifetime has a single exponential decay in the nanosecond time scale at all temperatures. It is well known that self-absorption or photon recycling may influence the true PL lifetime [20–22]. However, the contribution from photon recycling should be small for the range of excitation intensities ($\Delta n < 10^{16}$ cm^{-3}) used here [21]. Furthermore, for recombination processes with significant photon recycling, a sharp nonlinear decay in the PL is expected immediately after the laser pulse [22]. The fact that we observe a single exponential decay with nanosecond decay time can rule out photon recycling as a contribution to PL lifetime.

Figure 5 shows the two-photon-excited emission lifetime τ of the impurity-bound/free exciton and exciton-LO phonon replica as a function of temperature. A monotonic increase in τ with increasing temperature is seen. The inset shows the emission decay at 8, 120, and 295 K. A single exponential decay can be fitted to the time-resolved PL data for all temperatures. At room temperature (295 K), an ultra-long exciton PL lifetime of 17.2 ns is observed.

Several models of radiative recombination processes for excitons in quantum wells and bulk semiconductor films have been developed by various authors [23–25]. Assuming that relaxation processes are much faster than the recombination processes and that excitons always have a thermal distribution while decaying radiatively, the radiative lifetime is given by an average over the thermal distribution. Assuming a Boltzmann distribution in kinetic energy space, the fraction, r, of excitons with a kinetic energy smaller than ΔE is given by [24]:

$$r(T) = \frac{2}{\sqrt{\pi}} \int_0^{\Delta E/k_B T} \sqrt{\varepsilon \cdot e^{-\varepsilon}} d\varepsilon \quad (1)$$

The temperature-dependent radiative lifetime is then:

$$\tau(T) = \tau_0 / r(T) \quad (2)$$

where τ_0 is the radiative lifetime at temperature 0 K. Equations (1) and (2) are fitted to the exciton-LO phonon lifetime with τ_0 and ΔE as fitting parameters. The solid curve in Fig. 5 shows good agreement with the experimental data for $\tau_0 = 2.18$ ns and $\Delta E = 8.4$ meV. The parameter ΔE is related to the emission lifetime and it is about twice that of the low-temperature exciton linewidth (5.3 meV, Fig. 1) deduced from Gaussian fitting. The theoretical curve shows good agreement with both the exciton and exciton-LO-phonon emissions.

The radiative lifetime τ of the exciton state is given by [24]

$$\tau = 2\pi\varepsilon_o m_o c^3 / n e^2 \omega^2 f = \left(\pi \varepsilon_o m_o c^2 \hbar V / n e^2 E_p a_x^3 \right) \lambda \quad (3)$$

where $f = E_p / \pi \hbar \omega \left(V / a_x^3 \right)$ is the oscillator strength of the optical transition, E_p is the interband momentum matrix element, V is the volume of the unit cell, a_x is the exciton radius, n is the refractive index, and the other symbols have their usual meaning. Equation (3) shows that the radiative lifetime τ is proportional to the emission wavelength λ. Fig. 6 shows the measured τ as a function of λ and a clear linear dependence is observed as predicted by the theory.

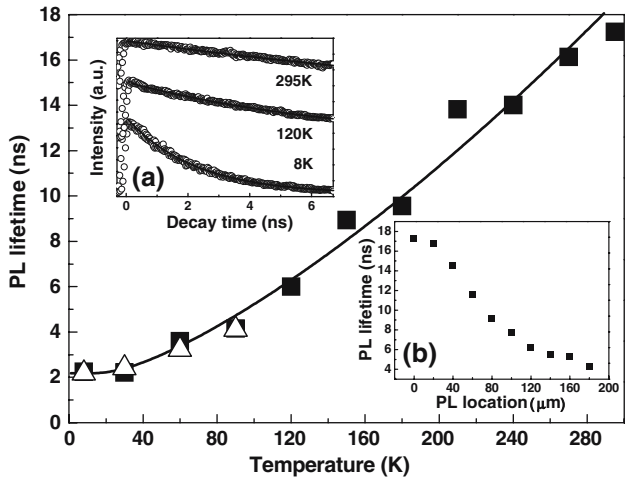

Fig. 5 The two-photon-excited exciton and exciton-LO-phonon emission lifetime as a function of temperature. The hollow triangles denote the experimental exciton emission, while the solid squares represent the experimental exciton-LO-phonon emission. As expected, the PL lifetimes of exciton and exciton-LO-phonon emission are about the same. The black curve is the theoretically fitted curve. Figure inset (**a**) shows the emission decay at different temperatures and the solid line is the single-exponential fit to the data; (**b**) shows the PL lifetime as a function of the location of the PL spot inside the sample

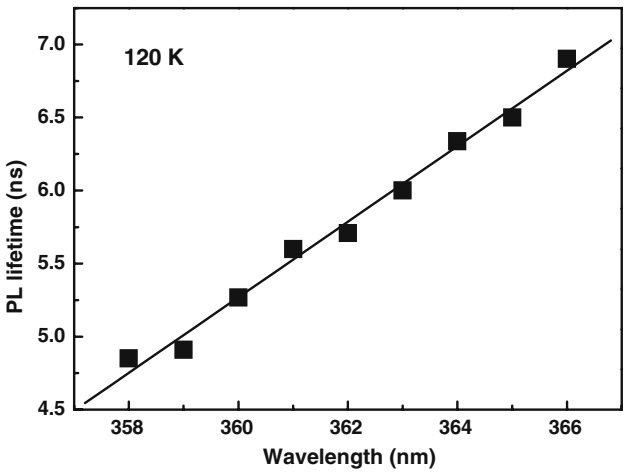

Fig. 6 The exciton lifetime as a function of emission wavelengths at 120 K

This is a further proof that the two-photon-excited exciton relaxation is dominated by intrinsic radiative recombination.

Inset (b) of Fig. 5 shows the two-photon-excited PL lifetime as a function of the location of a focused laser excitation beam moved along the cross section of the GaN film. The location ''0'' is near the center of the sample and increasing distance means the focused spot is moving toward the sample surface. Inset (b) shows the PL lifetime at the center location, which has the longest lifetime. The PL lifetime decreases as the spot moves away from the center of the sample and has the shortest lifetime (~4.5 ns) at the surface. This 4.5 ns PL lifetime is still considerably longer than the ~100 ps lifetime observed for the one-photon excitation case. However, one must note that the objective used for the two-photon excitation experiment had a numerical aperture of 0.1 and therefore the depth of field of the excitation spot was over 70 μm. Thus, there is substantial excitation volume within the sample even when the focusing is apparently at the surface. Still, this result clearly shows that the influence of the surface defects becomes stronger for excitation nearer to the sample surface. The conclusion is that the two-photon-excited emission is dominated by radiative recombination, and the one-photon-excited emission, by nonradiative recombination. In the one-photon-excited case, the PL spot is at the surface of the sample (absorption depth is only a few hundred nanometers for either 267 or 355 nm excitation wavelengths), and nonradiative recombination due to these surface defects becomes the dominant relaxation mechanism which causes the ultrafast PL decay. But in the two-photon case, the PL spot is deep inside the sample and far away from the surface, so that the influence of surface defects is very small and the free-exciton radiative recombination is the dominant mechanism.

4 Conclusion

In conclusion, exciton recombination dynamics in a free-standing GaN film grown by HVPE have been studied at various temperatures using one- and two-photon excitations. The studies show that in the one-photon-excitation case, the exciton emission is dominated by nonradiative recombination due to surface defects, whereas in the two-photon-excitation case, the nonradiative surface-recombination process is nearly absent and radiative recombination is the dominant mechanism from 8 to 295 K. At room temperature, the PL lifetime is up to 17.2 ns, which is the longest ever reported for GaN. The monotonic increase in PL lifetime with increasing temperature and the linear dependence of the exciton lifetime with emission wavelength are in excellent agreement with theoretical predictions for radiative recombination processes.

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