

Photoluminescence of localized excitons in pulsed-laser-deposited GaN

M. Cazzanelli,^{a)} D. Cole, J. F. Donegan, and J. G. Lunney
Department of Physics, Trinity College, Dublin 2, Ireland

P. G. Middleton and K. P. O'Donnell
Department of Physics and Applied Physics, University of Strathclyde, Glasgow, Great Britain

C. Vinegoni^{b)} and L. Pavesi
Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Trento, Povo (Trento), Italy

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Continuous-wave photoluminescence (PL) and time-resolved photoluminescence of gallium nitride layers grown by pulsed laser deposition are compared. The temperature dependence of the photoluminescence decay time and the PL-integrated intensity allows a determination of radiative and nonradiative time constants of GaN. We find that luminescence peaks centered at 3.360 and 3.305 eV at low temperature can be attributed to recombination of excitons localized at extended defects. The photoluminescence radiative lifetime at room temperature is on the order of tens of ns.

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There is a long history of interest in GaN as a material for the fabrication of blue and UV light emitters.¹⁻⁹ This interest was renewed after the recent demonstration of laser emission at room temperature from GaN.¹⁰ However, the physical mechanisms leading to efficient light emission from this material are not well understood. The energy gap (at 1.6 K) is 3.503 eV for bulk material and the principal emission peak in the luminescence spectrum at 1.6 K is observed at 3.477 eV.¹¹ There are also reports of strong luminescence lines well below the band gap, for thin-film samples grown on different substrates.^{1,7} At 6 K these lines are at 3.365 eV (I_3) and 3.309 eV (I_4). Previous studies attributed I_3 to a LO phonon replica of shallow bound excitons⁴ or to the neutral donor of the nitrogen vacancy.⁷ I_4 was previously attributed to a donor-acceptor pair transition.⁷ In the work of Wetzl *et al.*¹ the excitonic nature of these recombinations was proposed mainly on the basis of the relatively low activation energies (I_3 , 27 meV and I_4 , 14 meV) of these lines in contrast to the much higher values expected for donor-acceptor transitions. The behavior of those transitions under hydrostatic pressure also suggested that they were due to recombination of excitons localized at extended defects.¹ In this study we present continuous-wave (CW) and time-resolved (TR) photoluminescence (PL) studies of GaN grown on sapphire by pulsed laser deposition (PLD). The emission of PLD GaN is dominated by I_3 and I_4 emissions. Our interest was focused on the physical origin and luminescence dynamics of these lines.¹²

The main sample investigated was a 43 nm thick GaN layer grown on a (11 $\bar{2}$ 0) sapphire substrate by laser ablation of a sintered GaN target. Target pellets were prepared by pressing 99.99% pure gallium nitride powder at 7×10^8 Pa

for 5 min, followed by a sintering at 620 °C in N₂ atmosphere for 12 h in order to yield a mechanically robust target. The laser ablation was performed with a 248 nm, KrF excimer laser, operating at 10 Hz and focused to give a fluence of 2.8 J cm⁻² on the target. The substrate was placed at 3.5 cm from the target and maintained at 720 °C during growth. The chamber was filled with nitrogen at a pressure of 0.13 mbar to encourage stoichiometric growth. The dynamics of the expansion of the laser ablation plasma into the nitrogen atmosphere was monitored using a negatively biased ion probe operating in the time-of-flight mode.¹³ It was found that the best films were obtained when the gas pressure was chosen to give a doubly peaked ion signal. This kind of signal arises when the ion mean-free path is about equal to the target-substrate separation.¹⁴ The first peak is due to ions transmitted through the gas, and the second is due to a blast wave launched by ions colliding with the gas. The structural characterization of similar samples has been presented elsewhere.^{15,16} The CW-PL measurement used the 325 nm line of a He-Cd laser at an excitation density of 0.1 W cm⁻². The luminescence was recorded with 0.1 nm spectral resolution. The TR-PL measurement was done using a frequency-doubled mode-locked Ti:sapphire laser operating at 356 nm. The time-averaged excitation power was 90 μW at 82 MHz and the pulse width was 1.5 ps. A streak camera, with 10 ps time resolution was used in the photon-counting mode to record the spectra.

A comparison between the low-temperature (12 K) CW-PL spectra of the starting powder targets and the PLD epitaxial GaN film is presented in Fig. 1(a). The powder shows a broad luminescence band in the region 2.7–3.5 eV with weakly resolved features at 3.409, 3.265, and 3.185 eV. In contrast, the film shows two narrow lines at 3.360 and 3.306 eV, which we attribute to the I_3 and I_4 lines observed previously.^{1,7} Figure 1(b) shows an overview of the temperature-dependent behavior of the CW-PL of the PLD GaN film; the spectrum evolves from a single broad blue band in the temperature range 300–200 K to a spectrum showing three well-resolved lines below 200 K. In addition

^{a)}Author to whom correspondence should be addressed. Current address: University of Geneva, Group of Applied Physics, 20, Rue de l'École de Médecine, Geneva, Switzerland. Electronic mail: mcazzane@science.unin.tn.it

^{b)}Current address: Department of Physics and Astronomy, University of Pittsburgh, PA 15260.

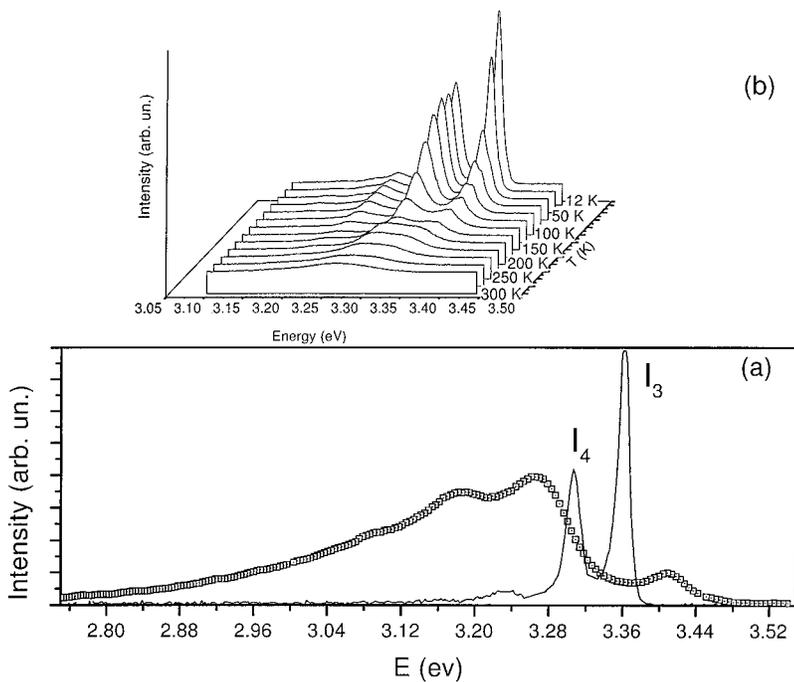


FIG. 1. (a) CW-PL spectra of the precursor powder (dot squares) and of the PLD-GaN film (full line) at 12 K. (b) CW PL as a function of temperature for PLD GaN.

to I_3 and I_4 , a third weaker peak centered at about 3.23 eV also appears below 200 K. Also noticeable is the doublet nature of I_3 in the temperature range from 125 to 75 K. Further investigations to clarify the physical origin of the doublet structure of I_3 are necessary.

Figure 2(a) shows the temperature variation of relative quantum efficiencies of I_3 and I_4 relative to the total low-temperature emission intensity integrated in the region 3.1–3.45 eV. This quantity is clearly an upper bound to the quantum efficiency of the sample, since: (i) even at low temperature there may be some nonradiative recombination, and (ii) there may be other emissions outside the integration region. It is clear that in the range 200–25 K, the quantum efficiency for I_3 is lower than for I_4 . TR-PL was also studied on this sample and the temperature-dependent luminescence lifetimes (τ_{lum}) of I_3 and I_4 are shown in Figs. 2(b) and 2(c). The lifetime increases with temperature, as was observed before for the decay time of the free exciton in GaN.¹⁷ From

the combination of the relative quantum efficiency [Fig. 2(a)] with the luminescence lifetimes [Figs. 2(b) and 2(c)] it is possible to make an estimate of the radiative (τ_{rad}) and non-radiative (τ_{nonrad}) lifetimes of the sample. The radiative (τ_{rad}) and nonradiative (τ_{nonrad}) lifetimes are related to the luminescence lifetime and quantum efficiency $\eta(T)$ by the equations

$$\tau_{rad}(T) = \frac{\tau_{lum}(T)}{\eta(T)} \tag{1}$$

and

$$\tau_{nonrad}(T) = \frac{\tau_{lum}(T)}{1 - \eta(T)}. \tag{2}$$

The extracted radiative and nonradiative lifetimes for I_3 and I_4 are shown in Fig. 3 in the temperature range 7–200 K. Both lifetimes increase with temperature; for the I_4 emission the qualitative behavior of luminescence lifetime, radiative, and nonradiative lifetimes is similar to that of the I_3 emission suggesting that the two lines have a similar physical origin. Both τ_{lum} and τ_{rad} are rather different for I_3 and I_4 , though the values of τ_{nonrad} are quite similar.

The spectral position of the lines we observe are very close¹⁸ to those measured by Wetzel *et al.*,¹ and have been attributed to recombination of excitons bound to extended defects. The attribution is supported also by the weak dependence of the peak positions in temperature.¹⁹ As the temperature rises from 7 to 225 K the redshift of I_3 and I_4 is 27 and 17 meV, respectively, while the energy gap shifts by 72 meV.¹¹ The relatively long luminescence lifetimes also supports this interpretation.¹⁶ The behavior of the PL emission width versus temperature²⁰ shows that the lines are quite broad even at low temperature, and the linewidths depend only weakly on temperature. The increase of luminescence

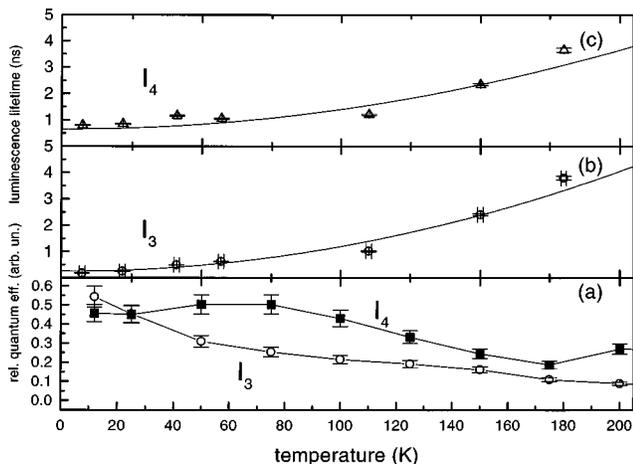


FIG. 2. Temperature dependence of (a) the relative quantum efficiency of I_3 (open circles) and I_4 (full squares). (b) I_3 luminescence lifetime and (c) I_4 luminescence lifetime. The full line is a guide for the eye.

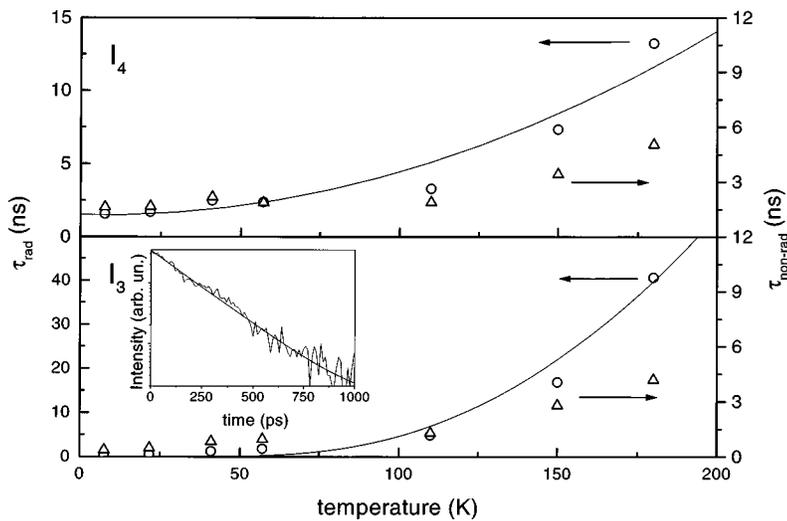


FIG. 3. Temperature dependence of radiative (τ_{rad}) and nonradiative (τ_{nonrad}) lifetimes of PLD GaN. The full line is a guide for the eye. Lower inset report is typical luminescence decay where the full line is an exponential fit.

lifetime with increasing temperature could be related to the thermal delocalization of excitons from extended defects. With increasing temperature, excitons that at low temperature are strongly localized to dislocations, start to delocalize and the radiative lifetime value increases to a value of a few nanoseconds. Further evidence of localization/delocalization of excitons in PLD GaN might be obtained by studying the absorption spectrum of thicker films. The radiative and nonradiative lifetimes plotted in Fig. 3 show that at high temperature the principal recombination channel is nonradiative, and that the radiative lifetime increases monotonically with increasing temperature. Formulas (1) and (2) were only applied in the temperature range 7–200 K, because at higher temperatures the lines evolve into a single broadband, and the individual contribution of the I_3 and I_4 lines to the $\tau_{\text{rad}}(T)$ and $\tau_{\text{nonrad}}(T)$ cannot easily be resolved. The radiative and nonradiative lifetimes were measured at a fixed average incident intensity of $\approx 1 \text{ W cm}^{-2}$; by increasing the incident intensity it should be possible to saturate the nonradiative trapping centers and to give a more precise estimation of the radiative and nonradiative recombination rates. We plan to perform this kind of investigation in the near future.

In summary, PLD gallium nitride shows a number of strong luminescence peaks from 6 K to room temperature. These peaks are well below the band gap of GaN and from comparison of CW-PL and TR-PL measurements we attribute them to recombination of excitons localized at extended defects. Additional measurements and theoretical modeling of the recombination dynamics is required in order to quantitatively understand the $\tau_{\text{rad}}(T)$ and $\tau_{\text{nonrad}}(T)$ behavior. No direct band-gap (free-exciton) emission is observed in this very thin sample, suggesting that it has a relatively high concentration of extended defects as compared to good quality bulk material. However, the tens of nanosecond lifetimes for the localized exciton emissions is promising for electroluminescent device applications.

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