

Luminescent properties of GaN thin films prepared by pulsed laser deposition

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Abstract

The luminescent properties of GaN thin films grown by pulsed laser deposition have been studied to understand the nature of the luminescent centres and the recombination dynamics. The films were grown on heated sapphire substrates using KrF excimer laser ablation of GaN in a reactive atmosphere of nitrogen. At low temperature the continuous wave (CW) blue luminescence of the samples grown shows two sharp lines attributed to excitonic recombination localized at extended defects. An analysis of the temperature dependence of photoluminescence (PL) lifetimes assesses the relative contributions of radiative and non-radiative recombination in the centres responsible for these emissions. The measurement of room temperature nanosecond radiative lifetimes for these lines supports the excitonic attribution of the luminescence. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The group-III nitrides (InN, GaN, AlN) have attracted great interest in relation to their unique properties in the last few years. These nitrides and their alloys have a wide-band gap [1] and are particularly well suited to electronic devices at high temperature and in hostile environments. Amongst these materials, gallium nitride and its alloy InGaN are the most promising for optoelectronic applications such as light emitting diodes (LEDs) [1] and laser emitting from blue to ultraviolet [2,3]. At present, the most widely used method to grow GaN is metal-organic chemical vapor deposition [3] (MOCVD) and molecular beam epitaxy [4–6] (MBE). However, good quality GaN films were recently grown by pulsed laser deposition (PLD) [7–11]. All of these techniques yield defect rich samples which limit the lifetime of GaN based laser devices [12]. To improve the sample quality, it would be useful to understand the origin of the recombination processes. With this aim, we used picosecond time resolved spectroscopy to study

the lifetime of photoexcited carriers in GaN films grown via PLD on sapphire. Although these films are known to suffer from strains and structural defects due to a large lattice mismatch ($\sim 14\%$) with the substrate, the photoluminescence (PL) emission efficiency is high.

2. Sample and experimental details

Samples were grown under different conditions. The most representative one in this work was a 43 nm thick GaN layer grown on (11 $\bar{2}$ 0) sapphire substrate by laser ablation of a sintered GaN target. The 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; this was carried out to yield a mechanically robust target. Laser ablation was performed with the 248 nm wavelength of a KrF excimer laser, operated at 10 Hz and focused to a fluence of 2.8 J cm⁻² on the target. The substrate was placed 3.5 cm from the target and maintained at 720°C during the growth. The chamber was filled with nitrogen at a pressure of 0.13 mbar in order to obtain stoichiometric growth. The structural characterization

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of similar samples has been presented elsewhere [14]. For continuous wave PL measurements (CW-PL), we used the 325 nm line of an He–Cd laser with a power of 0.1 W cm^{-2} . The luminescence was recorded with 0.1 nm spectral resolution. The time resolved PL (TR-PL) measurements were carried out using a frequency doubled mode-locked Ti:sapphire laser operating at 356 nm , with a repetition rate tunable from 82 MHz to single shot and with a pulse duration of 1.5 ps . The time-averaged excitation power was $90 \mu\text{W}$ at 82 MHz , which resulted in a peak power of $\sim 10 \text{ W}$. The luminescence was dispersed by a 0.25 m grating monochromator (CHROMEX) and detected by a streak-camera operating in photon counting mode. The temporal resolution was less than 15 ps . The CW-PL and TR-PL measurements were performed at room temperature (RT) and at lower temperatures in the range $12\text{--}300 \text{ K}$ using helium cryostats. For the absorption measurements at room temperature and in the visible range, a double-beam spectrophotometer (Cary, Mod. 14) with a tungsten lamp was employed.

3. Experimental results

An absorption spectrum was taken in order to determine the band gap energy of the GaN film (at 300 K). Fig. 1 plots the square of the absorbance (α^2) versus energy. We found that the film is transparent in the visible spectrum, and the absorption edge is at 3.4 eV . Fig. 2 shows the 12 K PL spectrum of the GaN sample in the energy range below the band gap situated at 3.5 eV [13,14]. The spectrum is dominated by two narrow lines at 3.360 and 3.306 eV , labelled I3 and I4, respectively [15]. The spectrum also displays a smaller peak at 3.23 eV .

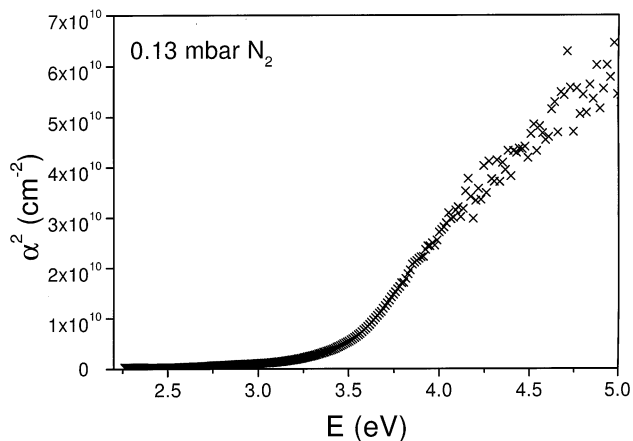


Fig. 1. Absorption spectra for a sample grown by PLD in 0.13 mbar of N_2 at a deposition temperature of 720°C using a laser fluence of 2.8 J cm^{-2} .

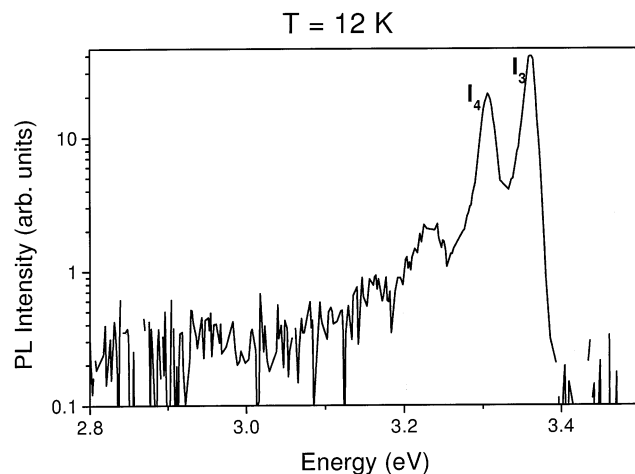


Fig. 2. CW-PL spectrum of the PLD GaN film at 12 K .

The widths of the peaks are 0.016 and 0.022 eV for the I3 and I4 lines, respectively. On the basis of these observations, I3 and I4 were attributed to the recombination of excitors bound to extended defects. Moreover, the PL behavior under hydrostatic pressure suggests that these excitors are strongly localized [18].

Fig. 3 displays the temperature dependence of the PL spectra of the GaN film in the range between 12 and 300 K with 325 nm excitation.

The spectra evolve from a single wide emission band (at room temperature) into at least two well resolved lines (from 200 to 10 K). We observe the simultaneous appearance from 200 K of a weak band at 3.23 eV and of four small peaks centered at lower energies. The doublet nature of the I3 peak is interesting in that it can be resolved in the temperature range between 125 and 75 K . This behavior needs more investigation in order to clarify its physical origin and will be the subject of a further study.

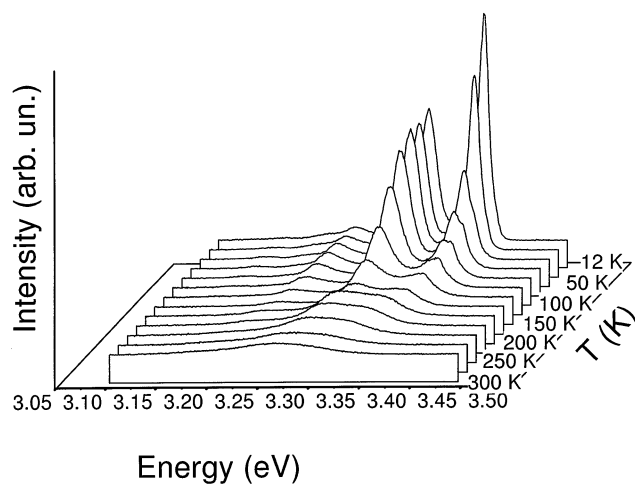


Fig. 3. CW-PL spectra of GaN films made by excitation as a function of temperature in the range between 12 and 300 K . The spectra have been left shifted for clarity.

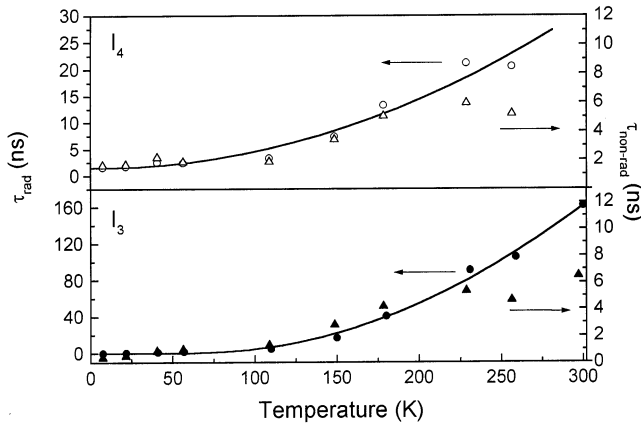


Fig. 4. Temperature dependence of the radiative (τ_{rad}) and non-radiative ($\tau_{\text{non-rad}}$) lifetimes of peaks I4 and I3 between 7.5 and 300 K.

TR-PL of the principal lines (I3 and I4) in the temperature interval between 7.5 and 300 K was studied. The I4 (I3) decay times (τ_{lum}) are ~ 65 ps (25 ps) at 7.5 K, increasing to 4 ns (6 ns) at RT. This increase in the lifetime with rising temperature has been found previously for free-excitons in GaN [19].

Combining the information obtained on the relative quantum efficiency obtained following the procedure critically discussed in [19,20] with the luminescence lifetime, it is possible to estimate the radiative (τ_{rad}) and non-radiative ($\tau_{\text{non-rad}}$) lifetimes. These are related to the measured τ_{lum} and to the relative quantum efficiency η (estimated in [19,20]; this quantity is clearly an upper bound to the absolute quantum efficiency of the sample, since even at low temperature there may be some non-radiative recombination and there may be other emissions outside the integration region) by the following equations:

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

$$\tau_{\text{non-rad}}(T) = \frac{\tau_{\text{lum}}(T)}{1 - \eta(T)}. \quad (2)$$

The temperature dependencies of τ_{rad} and $\tau_{\text{non-rad}}$ for peaks I4 and I3 are shown in Fig. 4. Again, the increase in temperature supports the usual attribution of the two emission bands. Although the radiative lifetimes are clearly very different for the two peaks, the non-radiative lifetimes are quite similar.

The T dependence of the integrated emission intensity of peaks I3 and I4 is shown in Fig. 5. For $T > 65$ K, there is a strong decrease in the intensity of I3 peak, while for the peak I4, the decrease in intensity starts at ~ 125 K.

In order to obtain an estimate of the thermal activation energy of peaks I3 and I4, we fitted the temperature dependence of the PL intensity to the simple model of Ashkinadze et al. [17]:

$$I_T = \frac{I_0}{1 + C(T)e^{-\frac{E}{k_B T}}} \quad (3)$$

where I_T is the PL intensity, I_0 the PL intensity at $T = 0$ K and E is the activation energy, $C(T)$ for high enough temperature [18] is given by:

$$C(T) = \frac{\tau_{\text{rad}}(T)}{\tau_{\text{non-rad}}(T)} \quad (4)$$

An estimate of the C temperature-dependent parameter for each excitonic peak was extracted from the data and is shown in Fig. 4. A fit of the experimental data for peaks I3 and I4 peaks is shown in Fig. 5. A good fit is obtained ($\chi^2 < 0.1$) which yields activation energies of 27 meV for peak I4 and 10 meV for peak I3.

These small activation energies and the energy shifts of I3 and I4 with the temperature, support the attribution of these lines to excitonic recombinations in agreement with Wetzel et al. [16]. The decrease in the energy of lines I3 and I4 with the increase in temperature is shown in the inset of Fig. 5. With rising temperature, phonon broadening causes the two lines to overlap such that at RT, a single band centered at 3.26 eV, is observed [11,14].

4. Conclusion

In summary, we have performed a study of the CW and TR PL of PLD-GaN over a wide temperature range. The analysis of the behavior of the luminescence intensity and the radiative lifetimes versus T allows us to attribute the dominant emission lines to excitors localized on extended defects. The order of magnitude of luminescence lifetime is very promising for the development of PLD-GaN based LEDs.

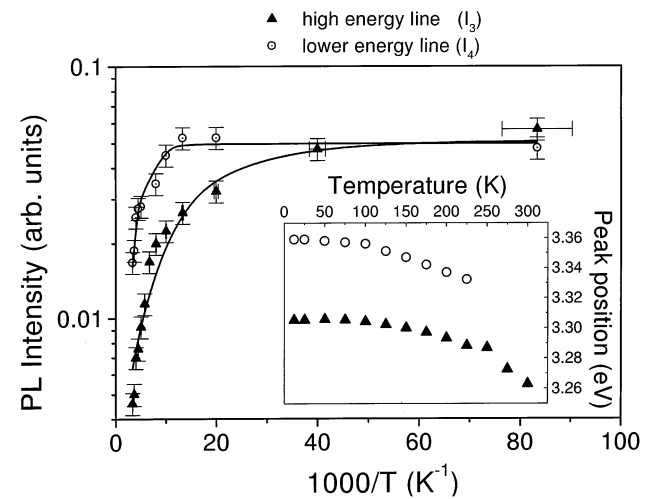


Fig. 5. Arrhenius plot of the integrated intensity of peaks I3 and I4. The lines are least square fits with a thermal activated quenching mechanism (see text). In the inset, the positions of peaks I3 and I4 as a function of temperature are shown.

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