

# Reversible ultraviolet-induced photoluminescence degradation and enhancement in GaN films

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UV-induced modifications in undoped metalorganic chemical vapor deposition grown GaN on sapphire are observed from 9 to 160 K. The photoluminescence intensities of bound excitons (3.476, 3.482 eV), the yellow band (2.2 eV) and the blue band (2.9 eV) change with time when a fresh sample is irradiated by 325 nm (He–Cd laser). The free exciton peak at 3.488 eV is unchanged by laser irradiation. Initially the blue and donor-bound exciton emission degrade rapidly and the yellow luminescence increases, each at the same rate. Later, the yellow luminescence degrades and the donor-bound exciton emission increases very slowly, at the same rate. Mechanisms are proposed that may explain the luminescence pathways and defects involved. © 1999 American Institute of Physics. [S0021-8979(99)06116-2]

## I. INTRODUCTION

GaN and GaN-related materials are wide band gap semiconductors with band gaps in the ultraviolet, blue and green, which are attracting great attention for their potential use in optoelectronic and high-temperature microelectronic devices.<sup>1</sup> There are still many unanswered questions about the mechanism of optical emission in these materials that are particularly significant since many such materials emit at energies below the band gap and band-edge excitons. Of notable interest are the roles of impurities and defects, and how they relate to the origin of the 2.2 eV “yellow” and 3.0 eV “blue” bands, and the general nature of the presumed role of donor-acceptor-pair (DAP) emission in subband gap emission.

Earlier work by us<sup>2,3</sup> and Xu *et al.*<sup>4</sup> has shown that the photoluminescence (PL) efficiencies of the yellow and blue bands, respectively, increased and decreased during ultraviolet laser irradiation of selected samples of undoped GaN thin films grown on sapphire. This work shows that the photoinduced modifications are more complex than these earlier reports suggested.

## II. EXPERIMENTAL PROCEDURE

One of the samples examined in this study exhibited strong photoinduced luminescence changes; it was grown using metalorganic chemical vapor deposition (MOCVD) on a sapphire substrate. This 3- $\mu\text{m}$ -thick film was grown without the addition of intentional dopants and was highly resistive. PL from this sample was measured using the 325 nm line of a He–Cd laser focused to a diameter of about 50  $\mu\text{m}$ . Spectra were taken at a given spot using low power, as in the PL

spectrum in Fig. 1 for which 50  $\mu\text{W}$  was used - corresponding to an intensity of about 2.5  $\text{W}/\text{cm}^2$ , to minimize the fast photoinduced changes seen at higher power. Higher powers were used to induce photoinduced modification with PL being monitored in a narrow spectral region in a band. New spots were examined in every run, except when sample recovery was investigated. The sample was examined at temperatures down to 9 K. Other GaN films were also examined briefly, including one other grown in the same way as the above sample (no apparent difference), and one each grown: undoped by hydride vapor phase epitaxy (HVPE) on sapphire, undoped on SiC, Si doped (*n* type) on SiC, and Mg doped (*p* type) on sapphire; they showed no sign of laser-induced modification.

## III. RESULTS

Figure 1 shows the PL spectra taken with low power (50  $\mu\text{W}$ , 2.5  $\text{W}/\text{cm}^2$ ) at 9 K at the beginning of (a) and end of (b) 20 min of irradiation. Both spectra show exciton emission (3.476–3.488 eV), blue-band luminescence (peak at 430 nm, 2.88 eV), and yellow-band luminescence (peak at 570 nm, 2.18 eV). Even at this low intensity, changes occurred in the PL during the 20 min exposure, with some exciton peaks decreasing slightly, the blue luminescence decreasing, and the yellow luminescence increasing. After 20 min the PL visually changed from blue to yellow. To lessen photoinduced changes during the spectral scan, both spectra in Fig. 1 were acquired in two 150 s long scan segments, from 345 to 495 nm and then from 495 to 645 nm, at different spots on the sample which were separated by at least 100  $\mu\text{m}$ . The uniformity of this 5 mm $\times$ 5 mm sample was confirmed by many measurements across it.

Figure 2(a) shows the emission spectra at 9 K from the three band-edge exciton recombination peaks at 3.476,

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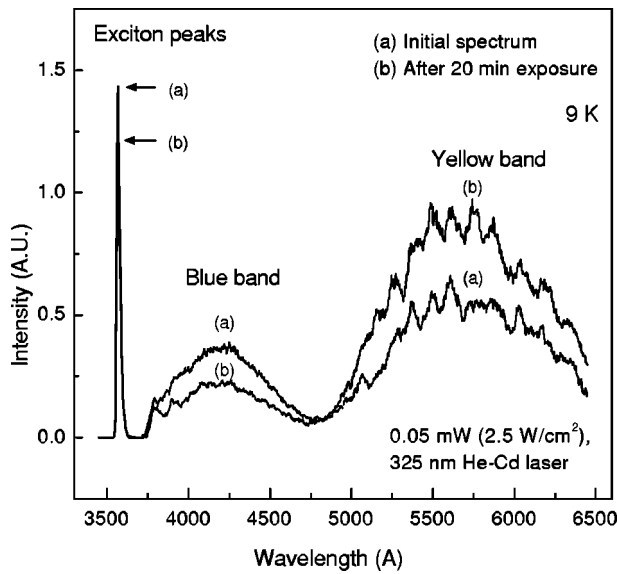


FIG. 1. Low power UV-induced photoluminescence spectra of a GaN film taken: (a) initially and (b) after 20 min irradiation.

3.482, and 3.488 eV ( $\pm 0.5$  meV) at different times during irradiation. The intensities of the two exciton peaks at 3.476 and 3.482 eV increased during this irradiation (1.9 mW), with no change in peak energy, while the exciton peak at 3.488 eV did not change at all. The PL spectrum from the recombination of these excitons is plotted at several temperatures in Fig. 2(b). Above 29 K, the 3.488 eV peak becomes dominant. Several HVPE samples had this same three-peak excitonic PL spectrum. The spectra in Fig. 2 were acquired in 100 s long scans with an integration time of 1 sec.

Figure 3(a) plots the PL intensity (10 K) at three wavelengths during irradiation with 1.9 mW ( $97 \text{ W/cm}^2$ ), specifically at 356.1 nm (3.482 eV, excitonic emission), 430 nm (2.88 eV, blue band), and 570 nm (2.18 eV, yellow band). Each wavelength was monitored with the laser impinging at a fresh spot, with the initial PL intensity normalized to unity. Generally, the 3.482 eV exciton peak decreased to 75%–85% of the initial intensity during the first 2 min, then slowly increased to 1.5–3 $\times$  the initial intensity, changing little after about 1.5 h. The 3.476 eV exciton peak behaved the same way. The blue band decreased rapidly to about 10% of its initial intensity. The yellow band intensity increased to 3–4 $\times$  its initial value during the first 2 min and then slowly decreased to 1.5 $\times$  the initial value after 4–5 h of irradiation. Figure 3(b) shows the initial yellow band enhancement and blue-band degradation, at different wavelength and lower intensity than in Fig. 3(a); the integration time was 0.1 sec.

For the run plotted in Fig. 3(a), the initial fast excitonic decay, blue-band decay, and initial yellow-band rise are each characterized by the same exponential rate  $\gamma_1 = (30 \text{ s})^{-1}$ . The slow exciton rise and yellow band decay are both characterized by the rate  $\gamma_2 = (28 \text{ min})^{-1}$ . Both rates increased monotonically, although sublinearly, as laser power was increased from 0.64, 1.9 to 8.0 mW (33–407  $\text{W/cm}^2$ ), with  $\gamma_1$  increasing from 1.3 to 8.3  $\text{min}^{-1}$  and  $\gamma_2$  increasing from 0.022 to 0.11  $\text{min}^{-1}$ . The rates of photoinduced modification were essentially the same for both the 3.476 and 3.482 eV

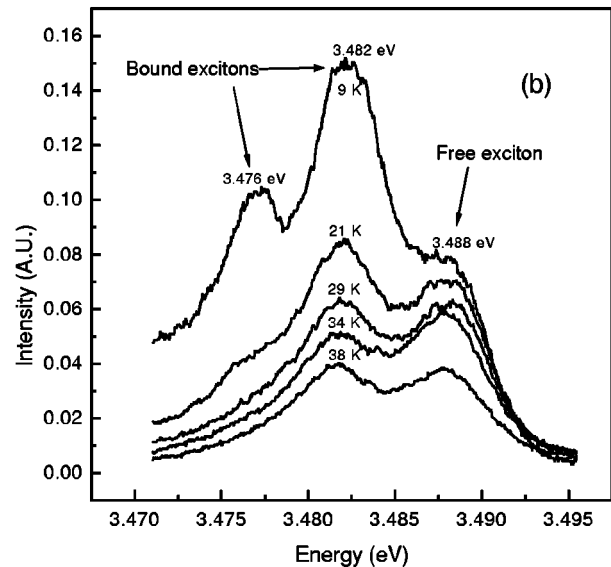
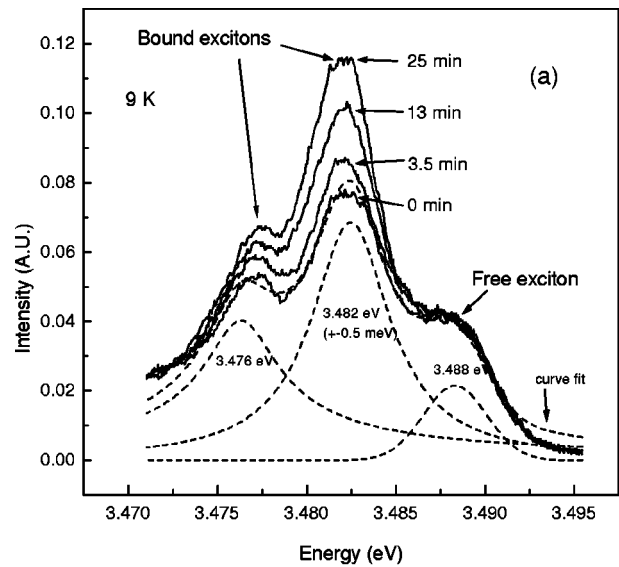


FIG. 2. GaN excitonic emission: (a) at selected times during irradiation at one spot at 9 K and (b) at different temperatures, with each spectrum taken at a different spot.

exciton lines and were unchanged across both the blue and yellow bands, as confirmed by observations at different wavelengths in each band [Fig. 3(a) and 3(b)]. They were also the same across the sample.

After UV modification was induced at 9 K, samples were warmed to room temperature and then cooled again to 9 K, and reexamined by PL at the same spot. With one exception, the PL signal at each monitored wavelength after this temperature cycling was the same as that before initial irradiation, i.e., there was full “recovery.” The initial intensity of the (bound) exciton peak at 3.476 eV decreased every cycle, and could not be seen after  $\sim 50$  cycles. The possibility of recovery was also examined at 9 K. After irradiation for 9 min (0.64 mW), the laser was blocked for 5 min, and it was then unblocked. The blue emission (410 nm) intensity (normalized to 1.0 at the start) decreased to 0.19 after the 9 min irradiation, increased by  $\sim 30\%$  to 0.25 after the 5 min

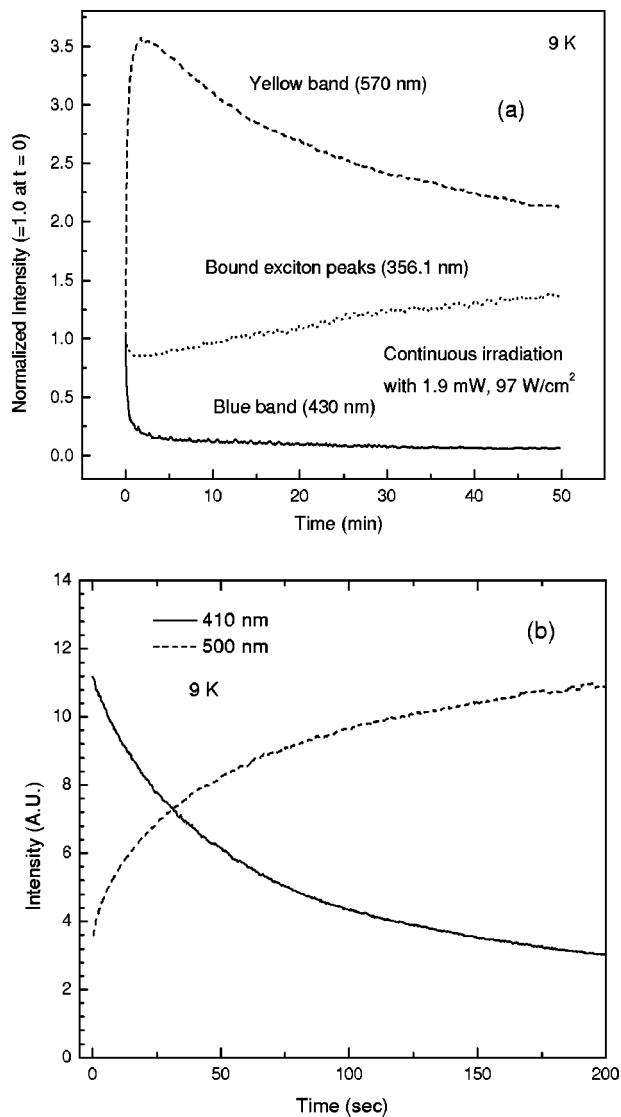


FIG. 3. Time dependence of the photoinduced changes of GaN: (a) excitonic, blue- and yellow-band PL, and (b) blue- and yellow-band PL initially—at different wavelengths than in (a). Note the similar time dependences and the symmetry in (b).

blocking period and then began to decay again with continued irradiation. The 3.482 eV exciton line and the yellow band showed no recovery at 9 K.

Qualitatively similar photoenhancement and subsequent photodegradation were observed up to  $\sim 120$  K for the yellow band, and photodegradation was observed up to  $\sim 160$  K for the blue band, with time dependences that were qualitatively similar to those at 9 K. UV modification of the 3.482 eV exciton line was observed only up to  $\sim 30$  K. Exciton emission, in general, decreased greatly above  $\sim 40$  K.

#### IV. DISCUSSION

The intensity of the exciton peak at 3.488 eV did not change during laser irradiation [Fig. 2(a)], and consequently it is thought to be due to free excitons.<sup>5</sup> Since the intensity of the two exciton peaks at 3.476 and 3.482 eV varied during irradiation, they are probably due to bound excitons, likely bound to neutral donors.<sup>6</sup> The relative PL intensities from the

three excitons [Fig. 2(b)] varied with increasing temperature in a way that is very different from that seen during UV irradiation, so the observed effects during irradiation cannot be attributed to laser heating.

The blue band is thought to be a free-to-bound transition,<sup>7</sup> possibly associated with Mg impurities<sup>8</sup>, and the yellow band is generally attributed to a DAP process.<sup>9,10</sup> It is hypothesized that the bound excitons are bound to donors that are responsible for the yellow band, because the behavior of bound excitonic PL qualitatively inversely follows the yellow PL and yellow-band DAP recombination decreases the concentration of neutral donors.

UV-induced PL degradation and enhancement were observed in selected undoped samples grown by MOCVD on sapphire (and not in all such grown films), and not in films that were grown by HVPE, those that were doped, or those grown on SiC. It is not clear how the undoped, high-resistivity films differ. Glaser and co-workers<sup>11,12</sup> have found that the (Zeeman)  $g$ -values of the optically detected magnetic resonance (ODMR) detected in the blue and yellow bands from the MOCVD sample reported here are very similar to those found in these same bands from other high-resistivity GaN layers that did not exhibit the UV-induced transformation. While this suggests that the same states may be involved in the blue- and yellow- band emission in each of these samples, it also suggests that the differences in these samples may be in differing concentrations of, or types of, defects such as grain boundaries or dislocations. The yellow band has, in fact, been attributed to dislocations.<sup>13</sup> Moreover, while the changes in donor-bound exciton and yellow- and blue- band PL occur at the same rates, Fig. 3(a) shows that the changes are not perfectly correlated.

The temporal dependence is obviously complex. A model for the short-time behavior is expected to involve the initial presence of carriers of one type (e.g., electrons) on “blue” metastable centers, which have a barrier for capturing further electrons. As holes are initially generated by excitation, the blue band is observed. Then, as the number of electrons on blue centers decreases as more holes are generated, there is an increase in the yellow PL and a decrease in excitonic PL, as the number of neutral donors is being reduced. It is tentatively assumed that blue-band emission is outside the dislocation associated with the yellow band, in the bulk region. For the longer-time behavior, it is suggested that space charge regions surrounding dislocations repel further carriers, leading to the decrease of the yellow band.<sup>14</sup> The lack of total recovery at room temperature for emission, particularly after many cycles, suggests that there are photochemical or recombination-enhanced defect reactions.

#### ACKNOWLEDGMENTS

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