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Red emission from Eu-doped GaN luminescent films grown by metalorganic chemical vapor deposition

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Bright red emission has been obtained at room temperature from Eu-doped GaN films pumped by 325 nm HeCd laser. The luminescent films were grown by metalorganic chemical vapor deposition on GaN/Al$_2$O$_3$ substrates. Trimethylgallium (TMGa), ammonia (NH$_3$), and europium 2,2,4,4-tetramethyl-3,5-heptanedionate were used as sources for Ga, N, and Eu dopant, respectively. The influence of the V/III ratio during growth on the photoluminescence (PL) intensity has been studied using a fixed TMGa flow rate of 92 μmol/min and varying the NH$_3$ flow rate. The film growth rate (~2 μm/h) is nearly constant with V/III ratio over the range from ~30 to ~1000. The Eu incorporation in GaN films was found to decrease with increasing V/III ratio. The Eu PL intensity (normalized to the Eu concentration) exhibited a maximum at a V/III ratio of ~100. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1590738]

Narrow-band visible emission from rare-earth (RE) doped GaN electroluminescent devices[1–3] has generated the promise of bright, true color flat panel displays, which are also very rugged and can be operated under extreme conditions (of temperature, humidity, radiation, etc.). Most of the results reported to date have used molecular beam epitaxy (MBE) for the growth of *in situ* doped GaN:RE films. An alternate thin film technique (widely used in industry) for the growth of III–V compound semiconductor films is metalorganic chemical vapor deposition (MOCVD). *In situ* rare-earth doping of III–V compounds during MOCVD growth has been reported for GaAs:Er,[4–6] InP:Er,[7] GaP:Nd.[8] Hara *et al.* have reported[9] MOCVD-grown GaN:Tb films. They observed the characteristic green Tb emission at low temperature (24 K), with greatly reduced intensity at room temperature. In this letter, we report on the growth of GaN:Eu films by MOCVD and on very strong red Eu emission at room temperature.

Eu-doped GaN films were grown in an AIXTRON MOCVD system (AIX200), modified for growing RE-doped GaN. Commercially available GaN substrates on sapphire were used for Eu-doped GaN film growth. Trimethylgallium (TMGa) and ammonia (NH$_3$) were employed for the gallium and nitrogen sources, respectively. *In situ* europium doping was performed utilizing a europium beta-diketonate, europium 2,2,4,4-tetramethyl-3,5-heptanedionate, abbreviated as Eu(thd)$_3$. The growth procedure consists of three steps totaling 20 min: first an undoped GaN layer is grown for 1 min, next the Eu-doped GaN layer is grown for 18 min, and finally an undoped GaN cap layer is grown for 1 min. The growth temperature was 1025 °C for all GaN layers. The growth pressure was controlled at 50 mbar. The Eu(thd)$_3$ bath temperature was set at 135 °C, while keeping the dopant line temperature at around 140 °C to prevent vapor condensation during transport. The TMGa flow rate was fixed at 92 μmol/min, while the NH$_3$ flow rate was varied from 2.68 $\times 10^{-3}$ mol/min to 0.1 mol/min, resulting in a V/III flow rate ratio ranging from 29 to 1093. The growth rate was nearly constant at ~2 μm/h for all V/III ratios.

Figure 1 shows room temperature photoluminescence (PL) spectra of the undoped GaN/Al$_2$O$_3$ substrate and an Eu-doped GaN film grown by MOCVD. The PL was obtained with above-GaN-band gap excitation from a HeCd laser at a wavelength of 325 nm. The undoped GaN film shows intrinsic (band edge) luminescence at 363 nm. The Eu-doped GaN film exhibits very strong red emission at 621 nm, corresponding to the energy level transition from $^5D_0$ (2.14 eV) to $^7F_2$ (0.14 eV). The minor PL peaks at 543, 600, and 663 nm are associated with Eu transitions $^5D_1$ (2.35 eV) to $^7F_1$ (0.07 eV), $^5D_0$ (2.14 eV) to $^7F_1$ (0.07 eV), and $^5D_0$ (2.14 eV) to $^7F_3$ (0.27 eV), respectively. These lines are nearly identical to those observed[10] in GaN:Eu grown by MBE. The peak at 633 nm is probably due to the energy level transition from $^5D_1$ (2.35 eV) to $^7F_4$ (0.39 eV), which

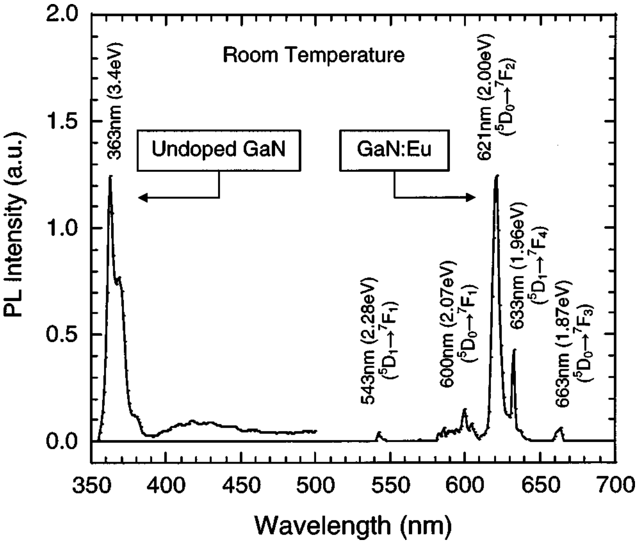

FIG. 1. Room temperature PL spectra of undoped and Eu-doped GaN films obtained with a HeCd laser (325 nm).

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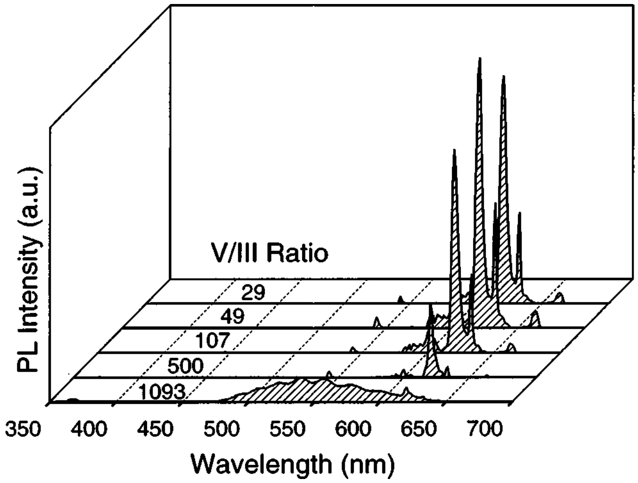

FIG. 2. PL spectra of GaN:Eu films grown with different V/III ratios.

is consistent with the result reported[11] by Monteiro and coauthors. Since these two spectra were measured under identical conditions, it is apparent that the PL intensity of the Eu emission in the doped GaN film is comparable to the intrinsic emission from high quality commercial GaN substrates. Interestingly, only very weak band edge PL and yellow band emission appear in the GaN:Eu spectrum.

The relative flow rate of group V (N) and group III (Ga) gas precursors has a significant influence on the photoluminescence intensity of the GaN:Eu films. Figure 2 shows PL spectra of the Eu-doped GaN films grown with different V/III ratio values. The intensity of main Eu emission peaks at 621 and 633 nm increase significantly with decreasing V/III ratio. The effect of V/III ratio on the Eu 621 nm peak and on the GaN band edge emission of 363 nm is shown in Fig. 3. The Eu PL intensity increases with decreasing V/III ratio while the opposite trend is observed for the GaN band edge emission. After growth of the Eu-doped layer, the GaN band edge emission was significantly reduced. In this case we used different measurement conditions for the Eu red emission and the GaN band edge emission in order to have the appropriate sensitivity for each measurement. Therefore, no quantitative comparison should be made between the two emissions in Fig. 3. However, the trends for the two emissions are accurate and can be compared. It is interesting to note that conventional GaN growth is performed at V/III ratios ranging from ~1000 to ~9000.

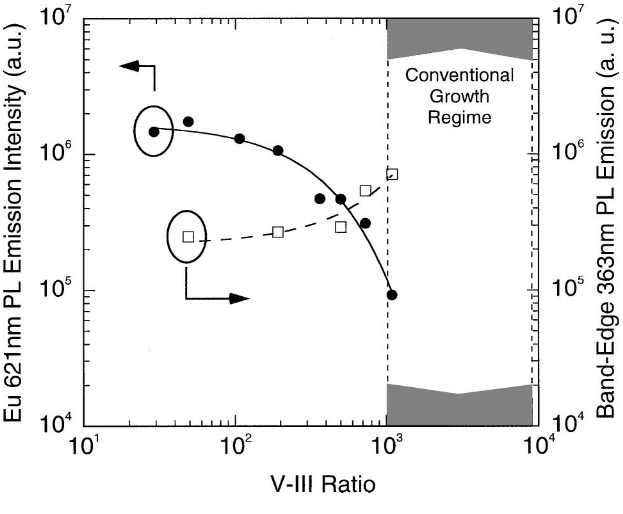

FIG. 3. Influence of V/III ratio on red emission from Eu dopant (621 nm) and GaN band edge (363 nm) emission.

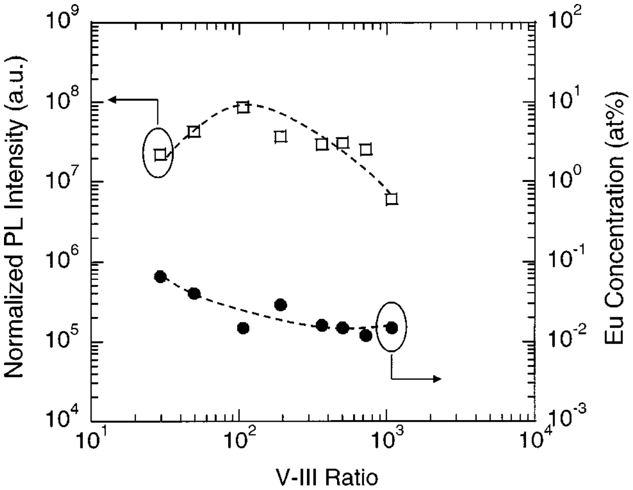

FIG. 4. Eu concentration and Eu-normalized PL emission (621 nm) vs V/III ratio.

Secondary ions mass spectroscopy measurements indicate that the Eu dopant concentration in GaN films is between ~0.01 to ~0.1 at. %. With the V/III ratio decreasing from 1093 to 29, the Eu concentration increases from 0.015 to 0.065 at. %, as shown in Fig. 4. This trend in Eu concentration partially explains the similar trend in Eu PL intensity versus V/III ratio. Normalizing the Eu 621 nm PL emission to the Eu concentration (also shown in Fig. 4) indicates that a maximum in PL efficiency occurs at a V/III ratio of ~100.

The decrease in Eu incorporation with increasing NH_3 flow rate was unexpected. It has been generally found[12] that trivalent RE^{3+} ions occupy substitutional sites on the Ga sublattice of GaN. In the case of GaN:Er this has been confirmed by both Rutherford backscattering (RBS) analysis[13] and extended x-ray absorption fine structure (EXAFS) analysis.[14] *In situ* Er doping of GaN films MBE-grown with increasing Ga flux (i.e., decreasing V/III ratio) resulted[15] in decreasing Er incorporation. This indicates a site competition between Er and Ga atoms and is consistent with the RBS and EXAFS conclusions. Eu incorporation into GaN appears more complicated. RBS results[11] for Eu-implanted GaN indicate that the Eu^{3+} lattice location is displaced from the normal Ga site. EXAFS results[16] on *in situ* doped GaN:Eu grown by MBE indicate two bond lengths between Eu and N.

The GaN:Eu films generally have a very smooth surface. An electron microphotograph of a film grown with a V/III ratio of 364 is shown in Fig. 5. The roughness of the film top surface is 2.1 nm as measured by atomic force microscopy. From the scanning electron microscopy (SEM) cross-section, no interface can be detected between the original (substrate) GaN layer and the MOCVD-grown GaN:Eu layer.

In summary, we have successfully grown strongly luminescent Eu-doped GaN films by MOCVD technique on GaN/Al_2O_3 substrates. The films have a very smooth surface morphology. Strong red emission from GaN:Eu films has been detected by pumping with 325 nm HeCd laser. The Eu

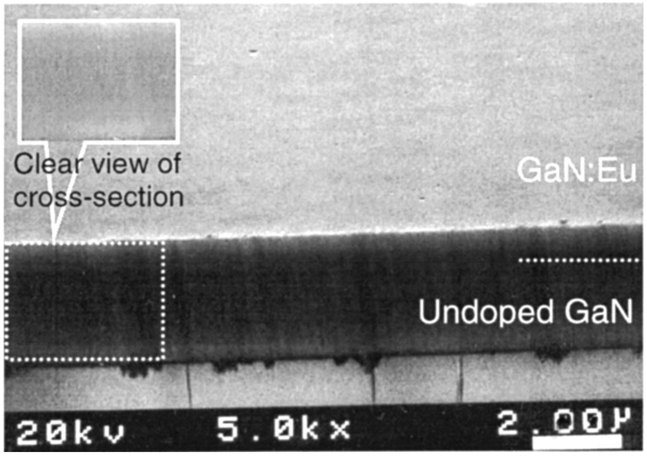

FIG. 5. SEM microphotograph of GaN:Eu film on GaN/Al_2O_3 substrate grown at 1025 °C and V/III ratio of 364.

concentration is in a range between 0.01 and 0.1 at. %. The V/III ratio during growth has a significant influence on Eu concentration and the red emission intensity.

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