

Red light emission by photoluminescence and electroluminescence from Eu-doped GaN

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Visible light emission has been obtained at room temperature by photoluminescence (PL) and electroluminescence (EL) from Eu-doped GaN thin films. The GaN was grown by molecular beam epitaxy on Si substrates using solid sources (for Ga and Eu) and a plasma source for N₂. X-ray diffraction shows the GaN:Eu to be a wurtzitic single crystal film. Above GaN band gap photoexcitation with a He–Cd laser at 325 nm resulted in strong red emission. Observed Eu³⁺ PL transitions consist of a dominant narrow red line at 621 nm and several weaker emission lines were found within the green through red (543 to 663 nm) range. Below band gap PL by Ar laser pumping at 488 nm also resulted in red emission, but with an order of magnitude lower intensity. EL was obtained through use of transparent indium–tin–oxide contacts to the GaN:Eu film. Intense red emission is observed in EL operation, with a spectrum similar to that seen in PL. The dominant red line observed in PL and EL has been identified as the Eu³⁺ 4*f* shell transition from the ⁵D₀ to the ⁷F₂ state. © 1999 American Institute of Physics. [S0003-6951(99)00735-4]

The evolution of modern full color displays such as the cathode ray tube has been marked by several major breakthroughs in material research. One such breakthrough, proposed in 1955, required a red emitting phosphor with narrow emission around 610 nm.¹ This challenge was met, 10 years after its proposal, by Levine and Palilla with their report² of highly efficient cathodoluminescence of the YVO₄:Eu³⁺ phosphor with a principal red line emission at 619 nm. Due to the spectral sensitivity of the human eye, the 619 nm emission is still red in color and appears brighter than a deeper red emission (i.e., at longer wavelength). In recent years display and lighting technology is pushing for more rugged, and for power and space efficient systems. It is believed that these needs will be met best through use of individually colored light emitting devices (LEDs). However, mixing of red, green, and blue LEDs in a single system brings forth difficulties in integration of individual LED material and electrical requirements.³ In addition to the rare earth (RE) element Eu³⁺, several of the trivalent REs emit red (Pr, Sm), blue (Tm, Ce), or green (Er, Tb) light. The host requirements for optical activity are similar in most REs due to the luminescing properties of an incompletely filled 4*f* shell, which is electrically shielded from the surrounding host material. Therefore, proper selection of red (Eu), green, and blue emitting REs as dopants in a common host material system could simplify some critical integration problems in the next generation of display and lighting technology. RE luminescence has been demonstrated in a variety of hosts such as fluoride glasses,^{4–6} LiNbO₃,⁷ ZnO,^{8,9} and ZrO₂¹⁰ and SnO₂,¹⁰ and Al₂O₃ and CaF₂¹¹ lanthanide OBr-based powder phosphors,¹² RE complexes in sol-gels¹³ and wide band gap semiconductors including GaP,¹⁴ SiC,¹⁵ and III–V^{16–18} compounds.

The III–V compound GaN is an advantageous host for

RE-based LEDs since it can provide carrier generation to excite the RE, it is transparent to visible RE emission, and it is thermally and chemically rugged. We have recently shown that *in situ* doped GaN:RE LEDs can produce green^{19,20} light based on Er³⁺ doping and red²¹ light through Pr³⁺ doping. GaN implanted with REs resulting in photoluminescence^{22,23} and cathodoluminescence²⁴ has also been reported. For these GaN:RE LEDs the fabrication process is much simpler than that of traditional junction-based LEDs. In this letter we report a red LED based on the Eu-doped GaN material system. Emission is dominated by a narrow peak at 623 nm which appears as an intense red emission to the naked eye. A photograph of this red EL emission is shown in Fig. 1 for a ring structure GaN:Eu LED with an area 7.65×10^{−4} cm² and ring width of 75 μm.

Eu-doped GaN films were grown in a Riber MBE-32 system on 2 in. *p*-Si(111) substrates. Solid sources were



FIG. 1. Photograph of red emission from a ring structure ITO/GaN:Eu LED of area 7.65×10^{−4} cm² and ring width of 75 μm, operating with 50 V and 0.6 mA. The dark notch in the upper part of the ring is caused by the probe tip obscuring the emission.

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used to supply the Ga (7N purity) and Eu (3N) fluxes, while an SVTA radio frequency (rf)-plasma source was used to generate atomic nitrogen. Extra precaution in placement and use of the raw Eu material in the MBE system was taken since Eu is by far the most reactive rare earth.²⁵ For the nitrogen plasma an rf power of 400 W and an N₂ flow rate of 1.5 sccm were used, yielding a chamber pressure of mid-10⁻⁵ Torr. The Ga cell temperature ranged from 870 to 890 °C. A GaN buffer layer was first deposited for 10 min at a substrate temperature of 600 °C. For the main growth the substrate temperature was ramped to 800 °C, an initialization layer of undoped GaN was grown for 10 min and then a GaN:Eu film was grown for 2 h. The Eu cell temperature was varied from 350 to 450 °C for the growth of various films, resulting in an estimated Eu concentration of 10¹⁸–10²¹/cm³ based on previous work with GaN:Er. The resulting thickness of the GaN:Eu layer averaged ~2.4 μm. For LED fabrication, an indium–tin–oxide (ITO) film (90% In₂O₃ and 10% SnO₂) was rf sputtered onto the GaN:Eu to form optically transparent film contacts. Standard liftoff procedures were used in LED patterning. The ITO film was sputtered in a 133 W, 5 mTorr Ar plasma with a plasma induced dc bias of -183 V. After sputter deposition for 1 h and a 2 min anneal at 450 °C in an N₂ ambient, the main ITO film characteristics were: ~4200 Å thickness, ~5.5 Ω/square sheet resistance and greater than 85% transmission throughout most of the visible spectrum. PL characterization was performed with a He–Cd laser at 325 nm (~5 mW) and Ar laser at 488 nm (~25 mW) which provide above band gap and below band gap excitation, respectively. The emission spectra were analyzed by an Acton Research spectrometer equipped with a photomultiplier sensitive in the ultraviolet (UV)-visible spectrum. High-pass filters and dichroic mirrors were utilized to block the laser pump light. The spectrometer resolution for PL and EL measurements was ~0.16 and ~2.4 nm, respectively. Both electroluminescence (EL) and photoluminescence (PL) measurements were performed at 300 K. The crystallinity of the GaN:Eu thin film was investigated using x-ray diffraction. The x-ray spectrum of a Eu-GaN film is nearly identical to that reported for Er-GaN.¹⁸

Above band gap excitation with a He–Cd laser resulted in strong red emission due to a dominating peak at 621 nm. An example of a PL spectrum covering the UV-visible range is shown in Fig. 2. The GaN near band edge emission at 368 nm with a full width that half maximum (FWHM) of ~12 nm (~55 meV) and the green/yellow-band emission are observed. The main Eu³⁺ emission at 621 nm corresponds to the ⁵D₀→⁷F₂ transition of the 4f shell, which is a known laser transition²⁶ for Eu³⁺. The FWHM of the 621 nm line is ~6 nm, corresponding to an energy linewidth of ~20 meV. Strong emission from the ⁵D₀→⁷F₂ transition has been reported under photostimulation in several other Eu³⁺-doped hosts such as glasses,^{4,5,6} ZnO,⁸ lanthanide OBr-based phosphors,¹² and sol-gels.¹³ A FWHM of ~11 nm (~35 meV) has been reported for PL of the ⁵D₀→⁷F₂ transition observed in a fluoride glass⁴ host. The excited levels ⁵D₁ and ⁵D₀ most frequently luminesce^{26,27} with emission from ⁵D₀ more prevalent than emission from any other ⁵D_J level. Therefore, the minor peaks in the spectrum of Fig. 2 are believed to be transitions from ⁵D₁ and ⁵D₀ to the ⁷F_J lev-

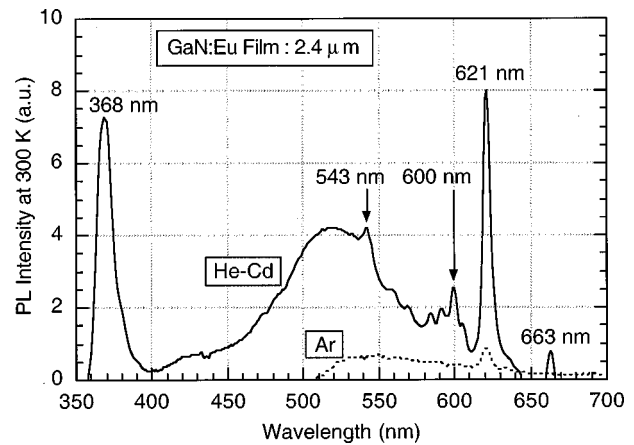


FIG. 2. UV and visible PL spectrum of Eu-doped GaN film grown on Si at 800 °C with Eu cell temperature of 400 °C. The PL is performed at room temperature with a He–Cd laser at 325 nm (solid line) and an Ar laser at 488 nm (dotted line).

els, in agreement with the majority of referenced literature. Peaks at 543, 600, and 663 nm are attributed to ⁵D₁→⁷F₁, ⁵D₀→⁷F₁, and ⁵D₀→⁷F₃ transitions. Eu–Eu energy transfer has been reported in fluoride glass⁴ at higher (>0.1 mol %) Eu concentrations. The energy transfer mechanism would reduce the emission from ⁵D_{J>0} states which was not witnessed in GaN:Eu. High emission probability from ⁵D₀ is likely due to nonradiative (phonon) relaxation from the closely spaced ⁵D_{J>0} states to the ⁵D₀ state. The energetic spacing from ⁵D₀ to the ⁷F_J states is considerably larger, therefore nonradiative relaxation from ⁵D₀ requires a multiphonon process, resulting in a higher probability of optical emission. Below band gap Eu³⁺ excitation by an Ar laser yielded only a 620 nm peak, with a magnitude much smaller than what was seen with He–Cd excitation. Although the above band gap He–Cd excitation method is primarily indirect for rare earths in the GaN host it is more efficient than below band gap Ar laser RE excitation, due to increased absorption above the GaN band gap and resultant carrier generation/recombination. Several other unidentified emissions are observed in the PL spectrum but are not labeled since it has not yet been determined whether they arise from ⁵D₀ to crystal-field-split ⁷F_J levels or transitions from the ⁵D₁ state. None of the observed PL emission lines is believed to be attributed to emission from the divalent Eu²⁺ ion, which exhibits fewer and broader bands of emission.^{28,29}

Shown in Fig. 3 is an energy band diagram of Eu-doped GaN which incorporates the observed PL results. Variations in host material system, processing conditions, and operating temperature play a role in determining the actual wavelengths of Eu emission. Several 4f levels of Eu³⁺ are easily determined based on relative positioning of multiple peaks. The energy levels were first quantified into the diagram from a thorough investigation of Eu-doped fluoride glass,⁴ then some of the observed levels were energetically aligned to reflect observed PL emission. The levels that were mapped energetically to the GaN:Eu spectra are ⁵D₀, ⁷F₃, ⁷F₂, and ⁷F₁. Their respective energies are listed in italics in Fig. 3. Also shown in Fig. 3 are the He–Cd and argon laser excitation photon energies and the lower edge of the GaN conduction band.

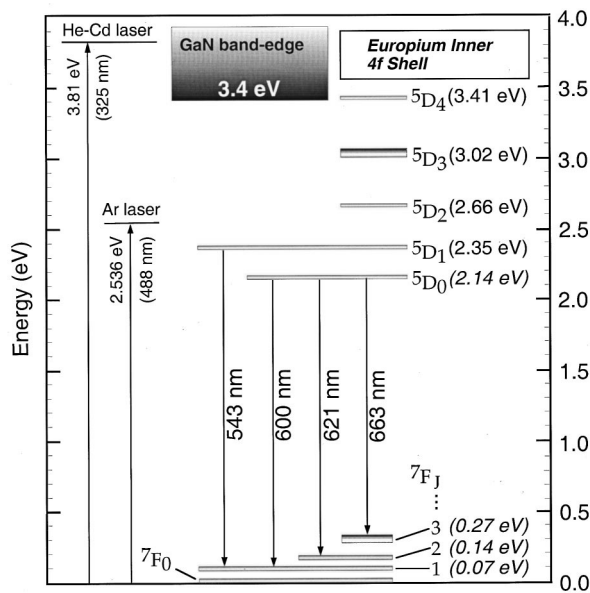


FIG. 3. Relevant energy levels in the PL of GaN:Eu films. Optically active level energies were adjusted to reflect observed values in GaN:Eu and are listed in italics. Laser excitation sources are represented along with the GaN band edge relative to Eu energy levels.

EL analysis was performed using the ITO/GaN:Eu LEDs for current injection resulting in excitation of Eu^{3+} luminescent centers in the GaN. The analysis was performed at nominally room temperature, without a heat sink. A typical EL spectrum is shown in Fig. 4. The data was obtained under a dc bias of 46 V and 12.5 mA. This represents a power input in excess of one half Watt, with heat likely causing a significant increase in operating temperature. As observed in the PL spectrum, the ${}^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition dominates the EL spectrum. Under EL the ${}^5D_0 \rightarrow {}^7F_2$ transition yields an emission line at 623 nm with a FWHM of ~ 7 nm (~ 22 meV). The EL spectrum is very similar to that of PL, with most peaks redshifted by 1–3 nm. This is not totally unexpected since the GaN:Eu growth for LED fabrication utilized lower Eu doping levels ($\sim 10^{18}$ – 10^{19} cm^{-3}) and the GaN crystallinity is degraded at very high Eu concentrations. The crystallinity of the host has been shown¹⁰ to produce a significant shift (~ 5 – 10 nm) in the peak wavelengths emitted from Eu-doped oxides. The EL emission from a contact area

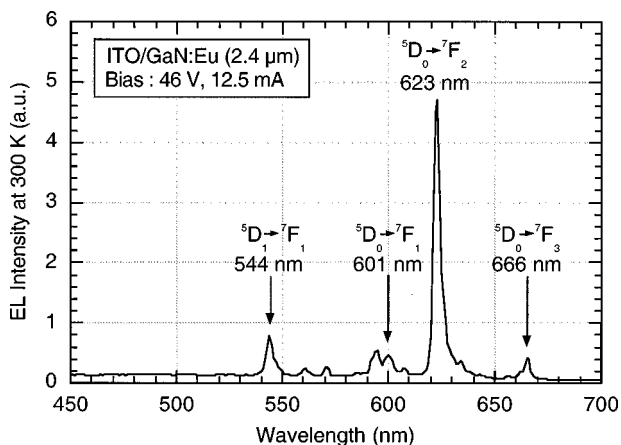


FIG. 4. Visible EL spectrum from ITO Schottky contact on GaN:Eu film. dc bias is applied at 46 V and 12.5 mA.

of $7.65 \times 10^{-4} \text{ cm}^2$ is easily visible to the naked eye in ambient lighting. No Eu^{2+} emission was observed in the EL spectrum. Peaks similar to that for GaN:Eu EL are reported in EL of ZnO:Eu⁹, cathodoluminescence¹⁰ of ZrO₂:Eu and SnO₂:Eu, and ion beam bombardment¹¹ of Al₂O₃:Eu and CaF₂:Eu.

In summary, we have reported the optical emission characteristics of Eu-doped GaN grown by solid source MBE on Si(111). We have observed a visible emission under both EL and PL from Eu^{3+} in GaN. This work follows previous successes with Er- and Pr-doped GaN, which yielded, respectively, green and red emission under EL and PL. This further supports our belief that GaN is a suitable environment for excitation of various RE dopants resulting in visible emission. The use of Si substrates for growth of the GaN:Eu thin films indicates the possibility of future integration with Si device technology.

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