

## Photoluminescence and cathodoluminescence analyses of GaN powder doped with Eu

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A high yield process to produce gallium nitride (GaN) powder doped with europium (Eu) is presented. Eu is *in situ* incorporated into GaN powder through the reaction between a molten alloy of Ga and Eu along with  $\text{NH}_3$  at 1000 °C using Bi as a wetting agent. This procedure provides a method to produce a GaN:Eu phosphor with high yield and low cost. Room temperature photoluminescence (PL) measurements are studied on GaN:Eu powders with different Eu concentrations. The maximum PL intensity is obtained at a Eu concentration of 1.25 at. %. Cathodoluminescence spectra at room temperature exhibit many detailed transitions in the 530–630 nm range. © 2006 American Institute of Physics. [DOI: 10.1063/1.2162667]

Group III nitrides have wide applications in optoelectronic devices, such as light-emitting diodes, ultraviolet or blue lasers, and full color displays.<sup>1–3</sup> The band gaps of III nitrides range from the ultraviolet to the near infrared. Furthermore, these semiconductor materials show very promising applications as electroluminescent devices when they are doped with rare earth ions.<sup>4</sup> Wide band gap semiconductors, like gallium nitride (GaN), doped with rare earth (RE) elements are especially interesting because of the decreased quenching effects of the luminescence at room temperature, as reported by Favennec *et al.*<sup>5</sup> RE ions have higher luminescence efficiency as compared to other semiconductors such as Si or GaAs.<sup>6</sup> Er, Eu, Tm and other RE elements have been doped into GaN by several research groups.<sup>4</sup> In most of cases, GaN is in the form of an epilayer on top of different substrates (sapphire, Si, or SiC). The layer can be prepared by metalorganic chemical vapor deposition (MOCVD),<sup>7</sup> molecular beam epitaxy (MBE),<sup>8</sup> sputtering<sup>9</sup> or other techniques. The RE elements can be incorporated into the GaN film either *in situ* or they can be implanted after the growth of the film. There are, however, few reports that focus on RE doped GaN in the form of a powder.

GaN:RE powder enables the possibility of hybrid integration with a variety of optically inactive materials because of the flexible powder form. Hirata *et al.*<sup>10</sup> used a combustion system to make GaN:Eu and  $\text{Ga}_2\text{O}_3$ :Eu powder. In their process,  $\text{Eu}(\text{NO}_3)_3 \cdot \text{XH}_2\text{O}$ ,  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{N}_2\text{H}_4$  were used as the precursors and ammonium hexafluoro-metal method was applied for nitridation. GaN powder doped with Eu also has been prepared by El-Himri *et al.*<sup>11</sup> using ammonolysis of the freeze-dried precursors.  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{GaCl}_3$ ,  $\text{EuCl}_3$ ,  $\text{GaF}_3$  + Hf and  $\text{EuF}_3$  are employed as their starting materials. Recently, we have developed a high yield synthetic procedure to prepare high purity GaN powder using Bi as a wetting agent.<sup>12</sup> In addition, Er has been incorporated into GaN powder,<sup>13</sup> and the emission of green light was reported when the powder was optically excited below the GaN band gap. In this letter, we report a procedure for producing GaN:Eu powder.

Strong red light emission was observed from this powder when it was optically excited by either above or below the GaN band gap, or by an electron beam.

The precursors used for making the GaN:Eu powder are 99.9999% gallium, 99.999% bismuth shot, 99.9% europium ingot and 99.9999% ammonia.  $\text{Eu}_2\text{O}_3$  can be formed if the Eu is exposed to air because Eu is very reactive to oxygen at room temperature. In our process, Eu initially forms an alloy with Ga and Bi in a glovebox; 25 g of Ga are mixed with 0.5–3 mol % of Eu and 3 mol % Bi in a glovebox. The mixture is sealed into a quartz tube under vacuum, then heated up to 830 °C for several hours to form alloys. As the temperature is reduced, we expect that Eu and Ga form the intermetallic compound  $\text{EuGa}_4$ , while Bi either reacts with Eu to form EuBi or a GaBi alloy according to the published phase diagrams.<sup>14</sup> When the tube has cooled down to room temperature, the product is transferred to the reaction quartz tube, which is then loaded into a vertical furnace, pumped down and back filled with Ar, and heated under flowing Ar. When the melt temperature reaches the appropriate reaction temperature of 1000 °C, the gas is switched from Ar to  $\text{NH}_3$ .

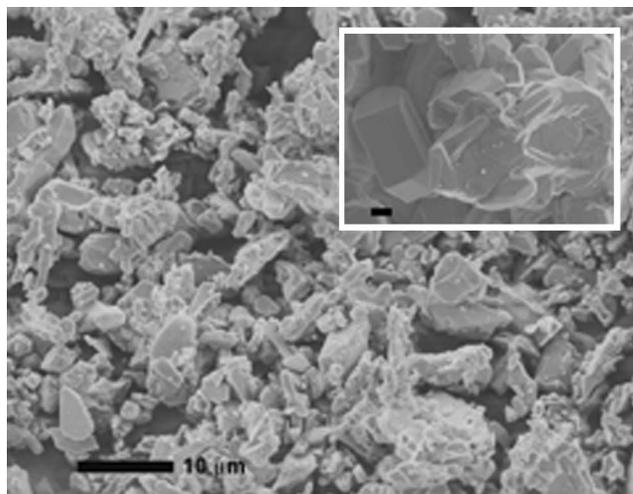


FIG. 1. Scanning electron microscopy (SEM) image of GaN powder doped with 2% Eu. The inset is the SEM image of close view of particles. The scale bar in the inset is 300 nm.

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At this temperature the entire charge should be molten, again according to the published phase diagrams. It takes about 5 h to convert the alloy completely into the desired final material.

After the reaction is completed, the tube is allowed to cool down to room temperature under flowing  $\text{NH}_3$ . The final product obtained from this process consists of a few chunks of material without any visible metal left. No further etching steps are needed to remove unreacted metals. The powder chunks are then removed easily from the quartz tube and ground into fine powder by mortar and pestle. To remove any residual Bi, the powder is annealed at  $1030^\circ\text{C}$  for a few hours to evaporate the Bi under flowing  $\text{NH}_3$ , which prevented the powder from decomposing. At this temperature, the Bi equilibrium vapor pressure is about  $10^3$  and  $10^6$  times higher than that of pure Ga and Eu, respectively, and much higher than the metal vapor pressures above their nitrides. The detailed synthetic procedure and mechanism have been discussed in other works.<sup>12,13</sup>

X-ray diffraction (XRD) analysis was performed on the powder. No elemental Eu, Ga, Bi, or EuN were detected in any of the samples with the various Eu concentration. All of the peaks in the measured XRD pattern matched the GaN peaks reported in the American Society for Testing and Materials x-ray powder data file very well. Figure 1 is a scanning electron microscopy (SEM) image which shows the morphology of the GaN:Eu particles. The SEM image exhibits its particle sizes distributed from 1 to  $5\ \mu\text{m}$ , with a majority around  $3\ \mu\text{m}$ . In this image, several particle morphologies can be observed, such as flake, polyhedra and needles where flake was the dominant one. The inset in Fig. 1 is a SEM image with a close view of particles. The particles are highly faceted and hexagonal structure is clearly observed. Many layers in the particle on the right side can be observed which indicates that the particle is grown layer by layer. Flake morphology indicated the lateral growth rate was much higher than the *c*-direction growth rate. It was apparent that the GaN:Eu powder synthesized here has very high crystalline quality from XRD and SEM.

Photoluminescence (PL) characterizations are carried out with a 1-mm-diam laser beam. Below band gap excitation was performed using an Ar laser (457.9 nm), and above band gap excitation was performed using a HeCd laser (325 nm). All PL measurements are performed at room temperature. The PL setups involve the excitation of the samples with the Ar (HeCd) laser at 16 mW, the collimation of the emission from the sample with a lens and the filtering of the excitation from the collimated, nonfocused beam using a Corning 3-70 sharp cut yellow filter (0-52 infrared transmitting filter), which has approximately 0.02% ( $\sim 0\%$ ) transmittance at 457.9 nm ( $< 340\ \text{nm}$ ), and the measuring of the signal using a 0.64 m ISA Instruments Spectrometer with input and output slits set at  $500\ \mu\text{m}$  and equipped with a Hamamatsu R928 photomultiplier tube. The efficient removal of the excitations from the signal is apparent from Fig. 2, in particular where the HeCd excitation would have appeared as a second order diffraction from the diffraction grating of the monochromator (at  $2 \times 325\ \text{nm} = 650\ \text{nm}$ ). Strong red light is emitted from the powder when it is pumped with either the above or below band gap laser. The red color is mainly due to the 621 nm peak which is the strongest of the Eu emissions. Figure 2 includes the spectra obtained from both excitations. The full widths at half maximum (FWHM)

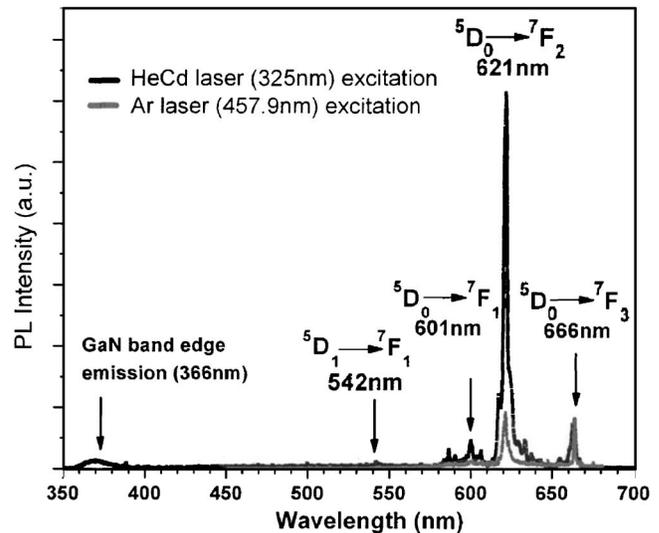


FIG. 2. Room temperature PL spectra of GaN powder doped with 1 mol % Eu.

are 2.2 and 8.1 nm for above band gap and below band gap excitations, respectively. The peak intensity for the below band gap excitation is much lower than above band gap excitation. This indicates an efficient electro-optical energy transfer process, in which the excitation energy is absorbed by the host material and is very quickly transferred to the  $\text{Eu}^{3+}$  ions.<sup>15</sup> The main  $\text{Eu}^{3+}$  emission at 621 nm corresponds to the  $^5D_0$ - $^7F_2$  transition within the  $4f$  shell which has been reported in other hosts like glasses<sup>16</sup> and ZnO.<sup>17</sup> The GaN band edge emission is very weak and broad compared to the emissions of  $\text{Eu}^{3+}$  ions. Other obvious peaks at 542, 601, and 663 nm can be attributed to  $^5D_1$ - $^7F_1$ ,  $^5D_0$ - $^7F_1$ , and  $^5D_0$ - $^7F_3$  transitions. The spectrum obtained from the powder is in agreement with the majority of the referenced literature.<sup>4,7-9</sup>

Figure 3 shows a series of PL spectra under HeCd laser excitation from GaN powders with different Eu concentration including a pure GaN powder sample without any Eu. The energy transfer from GaN host material to the  $\text{Eu}^{3+}$  ions is evident here. In Fig. 3, the 366 nm peak corresponding to the GaN band edge emission decreases dramatically when Eu is introduced into the powder. The emission peaks of the  $\text{Eu}^{3+}$  ions intensify with increasing Eu concentration up to

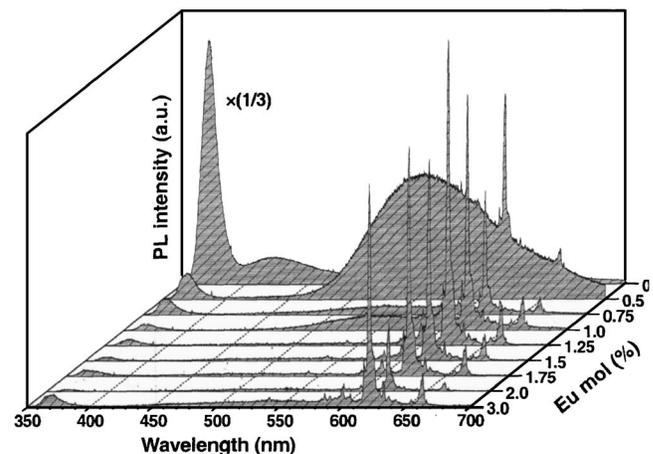


FIG. 3. Room temperature PL spectra of GaN powder doped with different Eu concentrations. The spectrum for the undoped GaN (0% Eu) has been scaled for ease of comparison.

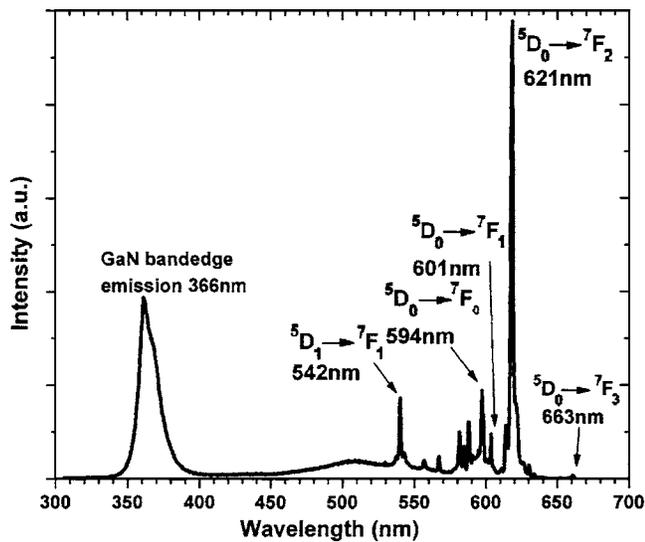


FIG. 4. CL of the GaN powder doped with 1% Eu at room temperature. Many detailed transitions can be observed in the 530–630 nm range.

1.25%, and weaken for higher doping concentrations. The decrease of the GaN band edge peak emission indicates increased energy transfer from the GaN to the  $\text{Eu}^{3+}$  ions. For the Eu emission, the decrease in emission for doping concentrations higher than 1.25% is probably due to cross relaxation between  $\text{Eu}^{3+}$ - $\text{Eu}^{3+}$  ions which are closer to each other and/or form clusters merely from the high concentration of the  $\text{Eu}^{3+}$  ions. In our experiments, 1.25 mol % of Eu is the best sample with regard to red light emission. Concentration quenching is a well documented phenomenon where, for example, the luminescence from Eu in GaN was increasingly quenched in samples with Eu concentrations with more than 2 at. %.<sup>18</sup> Note that the researchers were comparing samples with 0.1, 2, 5 and 16 at. % Eu in this reference.

The FWHM for 621 nm peaks is about 2.2 nm and shows relative constancy for various Eu concentrations in Fig. 3. Our data are consistent with energy transfer processes in RE doped GaN,<sup>4</sup> which has been confirmed by means of a variety of techniques such as photoluminescence excitation,<sup>19</sup> Fourier transform infrared spectroscopy,<sup>20</sup> and deep level transient spectroscopy.<sup>21</sup> Our PL measurements showing energy transfer are consistent with the results in these publications.

Cathodoluminescence (CL) is measured at room temperature. The excitation source is a 3 KeV electron beam focused down to a 5-mm-diam spot and the signal is measured using an Acton Research Corporation monochromator model VM504 with entrance and output slits set at 500  $\mu\text{m}$ , equipped with a Hamamatsu F2763 photomultiplier tube. Note that the excitation used in this case (3 keV) is much stronger than the PL excitation. Such a strong excitation results in deep excitations of the material. This is the reason why some of the emission lines from the RE ions in the CL spectra were not observed under lower power PL excitation.

Figure 4 is a CL spectrum for GaN powder with 1% Eu. Both GaN band edge emission and  $\text{Eu}^{3+}$  ions emission at 621 nm are detected. However, the Eu ions emission at 621 nm is much stronger and sharper compared to the GaN band edge emission at 366 nm. The FWHMs are 1.6 and 14.2 nm for the 621 and 366 nm peaks, respectively. It is interesting to

note that there are many sharp peaks from 530 to 620 nm in the spectrum. All of these peaks are repeatable in samples with different Eu concentrations. This indicates the high crystalline quality of the host particles. Some of these peaks can be attributed to the transitions reported in the literature and which have been marked in the graph. Other peaks in the spectrum are believed to be transitions from other  ${}^5D_j$  to the  ${}^7F_j$  levels. These peaks in the CL spectrum can provide us with much information in order to understand the energy transfer processes between the  $\text{Eu}^{3+}$  ions and the GaN host.

In summary, we have reported the structural and optical emission characteristics of Eu-doped GaN powder. Eu is doped *in situ* into the GaN powder during the synthetic process. Strong red emission has been observed from the powder when it is optically pumped both below and above the band gap of the host material, and by electron beam, at room temperature. This work follows previous successes with pure GaN powder and Er-doped GaN powder. Finally, opportunities for low cost electroluminescent devices or hybrid structures are possible due to the powder form of this material.

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