

Green emission from Er-doped GaN powder

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Green light emission has been directly obtained from Er-doped GaN powder. Er is incorporated into GaN powder through the reaction between molten (Ga+Er) and NH₃ at 950–1050 °C using Bi as a wetting agent. Photoexcitation with an Ar laser results in strong green emissions from two narrow lines at 537 and 558 nm, which are identified as Er transitions from the ²H_{11/2} and ⁴S_{3/2} levels to the ⁴I_{15/2} ground state. Microprobe analysis reveals that Er atoms are distributed across powder particles. © 2005 American Institute of Physics. [DOI: 10.1063/1.1923175]

The recent demonstration of visible (blue, green, red) and infrared (1.54 μm) electroluminescence from rare earth (RE)-doped GaN brings significant interest to this class of materials for possible applications in optical communications and full color displays.^{1,2} The growth of bulk GaN crystal presents opportunities for GaN related electronic and optical devices.³ The properties of Er-doped GaN and other III–V semiconductors have been reviewed by Zavada and Zhang⁴ and Steckl *et al.*⁵ The GaN-based semiconductor structures are of great interest because they appear to be optically robust, and chemically and thermally stable. Favennec *et al.*⁶ reported a strong dependence of the emission intensity of the Er³⁺ ions on the band gap of the host semiconductor and on the material temperature. The wide band gap of GaN leads to a reduced RE quenching of emission and thus to the observation of strong RE emission at room temperature.⁶ In these works, the incorporation of Er atoms into GaN is achieved by either *in situ* epitaxial growth with the GaN layer or ion implantation after the layer growth step. Er incorporation in GaN powder could enable hybrid integration with a variety of optically inactive materials. However, to date, RE doping in GaN powder has been rarely investigated. In this letter, we report direct observation of a strong green emission from Er-doped GaN powder. The Er is doped *in situ* into GaN during the powder synthesis process.

The starting materials are 99.9999% pure gallium, 99.999% bismuth shot, 99.9% erbium ingot, and 99.9999% ammonia. An ammonia purifier is used to remove residual water vapor and oxygen. Ga (25 g) is mixed with 1 mol % of Er in a quartz tube. Bi (1 mol %) is added as a wetting agent to help the conversion process. The quartz tube is then loaded into a vertical furnace. After purging the tube with Ar for 1 h, the sample is heated under flowing Ar. When the melt temperature reaches the appropriate reaction temperature (between 950 and 1050 °C), the gas is switched from Ar to NH₃. Then the furnace is kept at the same reaction temperature for 3–5 h.

After the reaction, the sample is cooled to room temperature under flowing NH₃. The yield of the powder synthesis is greater than 99% within 1 h. No residual Ga or Er metal can be observed visually. No etching step is necessary to remove

unreacted metals. The powder chunk can be moved easily from the quartz tube. Then the material is crushed and slightly ground with a mortar and pestle into fine powder. GaN:Er powders prepared under different reaction temperatures (950–1050 °C) show similar properties in terms of structure and luminescence analyses. Further characterization discussed in this letter is based on a GaN:Er sample prepared at 1000 °C.

The Bi wetting agent is mainly used to prevent GaN crust formation which impedes the reaction of the remaining Ga with NH₃. At temperatures higher than 262 °C, the low surface tension component, Bi, is present at the surface of the binary melt.⁷ The high density phase completely wets the exposed surface by intruding between the lower density phase and the gas phase. This Bi interface wetting helps the conversion of Ga into GaN without any crust formation. The detailed mechanism of Bi in this process has been discussed in another paper.⁸ If necessary, the removal of the Bi wetting agent from the GaN powder can be performed by heating the powder to 1030 °C under flowing NH₃ gas for several hours. At this temperature, the Bi equilibrium vapor pressure is about 1200 Pa, more than 1000 times greater than that of Ga and Er. No Bi–Ga phases are known,^{9,10} and BiN is unstable under the reaction conditions.^{11,12} Bi is easily removed by evaporation whereas the NH₃ prevents the GaN from decomposing. After the removal process, Bi cannot be detected by x-ray diffraction techniques. Glow discharge mass spectrometry analysis reveals that the remaining Bi is less than 50 ppm.

The GaN powder doped with Er is examined by powder x-ray diffraction (XRD). Figure 1 shows the XRD pattern of GaN:Er powder after the removal of Bi. The Er doped GaN can be identified as the wurtzite structure based on the XRD pattern. All of the peaks in the pattern match well with those of hexagonal GaN reported in the ASTM x-ray powder data file. No free Ga, Er, and Bi phases are detected by XRD technique. It is clear that the (0002) peak is much stronger than the (10 $\bar{1}$ 1) peak although (10 $\bar{1}$ 1) should be the strongest peak according to the PDF card. This indicates significant preferred orientation in the XRD powder sample. This can be explained clearly with scanning electron microscopy (SEM) images as discussed next.

The SEM picture of the powder in Fig. 2 reveals the powder particle's surface morphology, which provides an ex-

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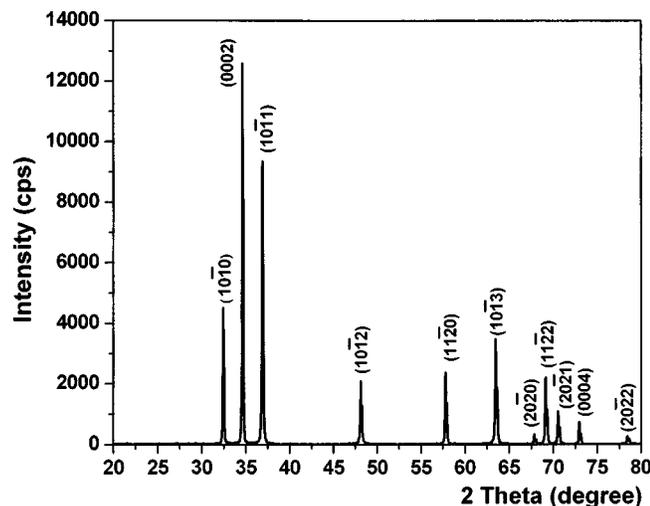


FIG. 1. Representative x-ray diffraction pattern of the GaN powder doped with 1 mol % Er after the removal of Bi. All peaks match with wurtzite GaN structure without any free Ga, Bi, or Er detected.

planation for the strong preferred orientation. The SEM image shows particle sizes distributed from 1 to 10 μm , with a majority around 5 μm . Although several particle morphologies can be observed (plates, polyhedra, and needles), the predominant shape is platelet. The aspect ratios of the plates range from 5 to 10. The strong (0002) orientation indicated in XRD is caused by the alignment of the plates during the XRD sample preparation.

Er has a high solubility in liquid Ga at high temperature. Shkol'nikova *et al.*¹³ noted that the Er solubility in Ga went up from 0.5% to 2.13% (mass fraction) with a temperature increase from 450 to 650 $^{\circ}\text{C}$. The solid solubility of Er in Ga at the reaction temperature (~ 1000 $^{\circ}\text{C}$) will be higher than this. Considering that the ionic radius of Er^{3+} is 1.75 \AA compared to 1.30 \AA for Ga^{3+} , it might be expected that the equilibrium concentration of Er that can be doped into GaN at 1000 $^{\circ}\text{C}$ is rather small. In our case, given the high yield of the powder synthesis and the platelet morphology, it is believed that the lateral growth rate of GaN in this process is very high. Under this high growth rate, Er may be incorporated at higher concentrations than the equilibrium concentration even though the synthesis is performed at relatively

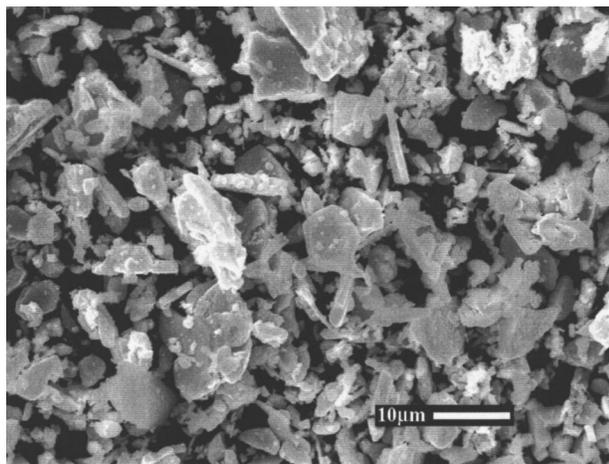


FIG. 2. Scanning electron microscopy image of the morphology of the synthesized GaN:Er powder; particles range from 1 to 5 μm and platelet particles are the majority.

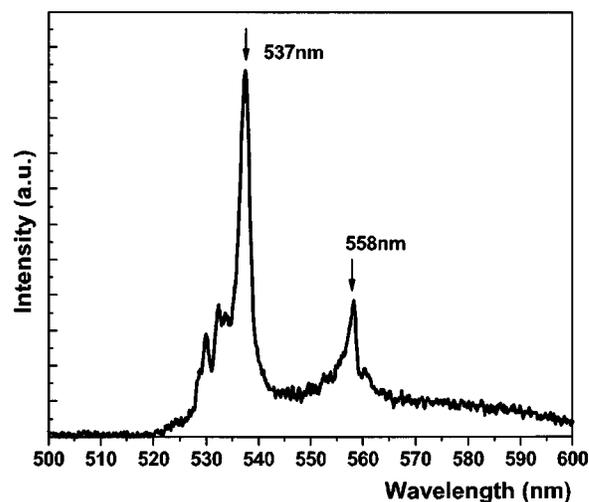


FIG. 3. Photoluminescence (PL) spectra of Er-doped GaN powder. The PL is performed at room temperature with the Ar laser line at 496.5 nm. Two narrow emissions at 537 and 558 nm are two characteristic $4f-4f$ inner shell transitions in Er^{3+} ions.

high temperature. Also, Citrin *et al.*¹⁴ and Steckl *et al.*⁵ have shown unusually high doping concentrations (up to $\sim 3-5$ at. %) of Er in GaN prepared by molecular beam epitaxy (MBE) at around 600 $^{\circ}\text{C}$,⁵ while preserving the optical activation of Er dopants. This is due to the strongly bonded GaN lattice and the substitutional incorporation of Er atoms in GaN lattice.^{5,14}

Photoluminescence (PL) characterization is performed at room temperature by exciting the sample with an argon laser at a wavelength of 496.5 nm (2.5 eV), corresponding to an energy smaller than the GaN band gap (3.4 eV). PL excitation results in green emission from the Er-doped GaN powder. The room temperature PL at visible wavelengths is shown in Fig. 3. Two major emissions are observed in the green region with the strongest lines at 537 and 558 nm. Green emission at 537 nm is one of the characteristic emissions due to the $4f-4f$ inner shell transition of Er^{3+} ions and is attributed to a transition from ${}^2H_{11/2}$ to the ground state ${}^4I_{15/2}$ whereas 558 nm corresponds to the transition from ${}^4S_{3/2}$ to ${}^4I_{15/2}$. The full-width at half-maximum of the 537 and 558 nm lines are 2.6 and 3.1 nm, respectively, which corresponds to an energy width of 11 and 13 meV. On the left-hand side of the 537 nm peak, there are some weaker peaks corresponding to other Er excited electron transitions. All the peak positions in this PL spectra of GaN:Er powder are very similar to the PL spectra obtained from metalorganic chemical vapor deposition grown GaN:Er layers¹⁵ or MBE grown GaN:Er layers.^{16,17}

Electron probe microanalysis (microprobe) is used to analyze the Er distribution in the GaN particles. Figure 4(a) shows a SEM image of several GaN particles each approximately 8–10 μm in width. These particles are selected for Er concentration distribution analysis using the microprobe technique. Figure 4(b) shows the microprobe mapping measurement results. In the picture, each color dot (blue, red, etc.) means that Er emission is detected from that spot. Different colors indicate the relative Er concentration in that GaN particle. The two bright spots mean that a very strong Er signal has been detected in those places. The origin of these brighter spots could be some second phase that contains a high concentration of Er. Given the low initial Er

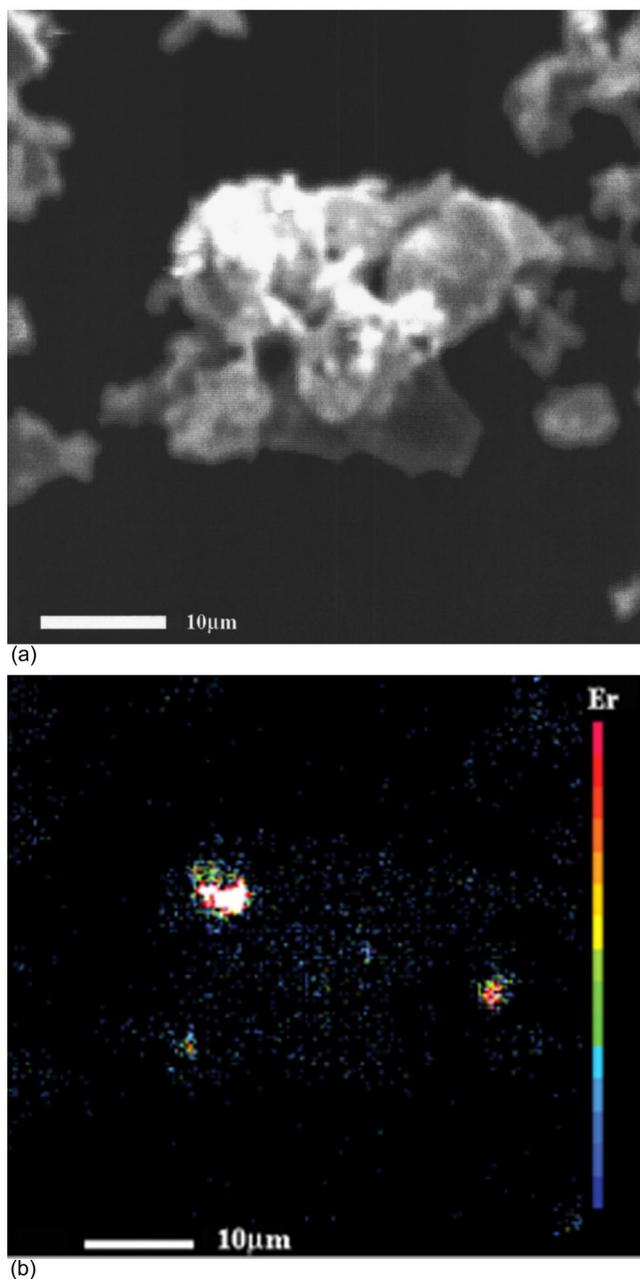


FIG. 4. (Color online) (a) Scanning electron microscopy image of particles of GaN doped with Er. (b) Microprobe mapping analysis on these particles. Different colors indicate the relative Er concentration in that GaN particle. Red is the highest concentration and blue is the lowest. The white bright spot indicate very high Er concentration and possible second phase is suspected.

content of 1%, it is not surprising that any second phase would not be visible in the x-ray diffraction patterns. We are continuing to investigate this possibility. The broadly distributed blue dots reveal that the remaining Er atoms are distributed across all the GaN particles.

An important goal for future studies on rare earth doping in GaN powder is the possibility of making full color displays in a cost-efficient manner. GaN powder doped with rare earth elements can be made into dispersion using appropriate polymer to disaggregate particles. Different coating techniques can be used to deposit a GaN:RE layer on various substrates. These layers can be further fabricated into electroluminescence devices. For light emitters on-chip, these coating layers of GaN:RE can withstand high temperatures (up to 1000 °C), opening the door to active structures compatible with CMOS technology.

In conclusion, we have reported the structural and optical characteristics of Er-doped GaN powder. Er is doped *in situ* into the GaN powder during the synthesis process. We have observed visible emission from the GaN:Er powder. Microprobe analysis suggested that a second phase containing high Er concentration may be present, but that the remaining Er was distributed fairly evenly in the GaN particles.

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- ¹A. J. Steckl and J. M. Zavada, Mater. Res. Bull. **24**, 33 (1999).
- ²A. J. Steckl, J. Heikenfeld, M. Garter, R. Birkhahn, and D. S. Lee, Compound Semicond. **6**, 48 (2000).
- ³G. Kamler, J. Zachara, S. Podsiadlo, L. Adamowicz, and W. Gebicki, J. Cryst. Growth **212**, 39 (2000).
- ⁴J. M. Zavada and D. Zhang, Solid-State Electron. **38**, 1285 (1995).
- ⁵A. J. Steckl, J. C. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Wang, and R. Jones, IEEE J. Sel. Top. Quantum Electron. **8**, 749 (2002).
- ⁶P. N. Favennec, H. L'Haridon, D. Moutonnet, M. Salvi, and Y. LeGuillou, Electron. Lett. **25**, 718 (1989).
- ⁷H. Tostmann, E. DiMasi, O. G. Shpyrko, P. S. Pershan, B. M. Ocko, and M. Deutssh, Phys. Rev. Lett. **84**, 4385 (2000).
- ⁸H. Wu, J. Hunting, K. Uheda, L. Lepak, P. Konkapaka, F. J. DiSalvo, and M. G. Spencer, J. Cryst. Growth (in press).
- ⁹B. Predel, Z. Phys. Chem. (Munich) **24**, 206 (1960).
- ¹⁰S. P. Yatsenko and V. N. Danilin, Izv. Akad. Nauk SSSR, Neorg. Mater. **4**, 863 (1968).
- ¹¹A. Sieverts and W. Krumbhaar, Ber. Deut. Chem. Ges. **43**, 894 (1910).
- ¹²W. Janoff, Z. Phys. **142**, 619 (1955).
- ¹³T. M. Shkol'nikova, A. P. Basin, and V. V. Serebrennikov, Zh. Fiz. Khim. **46**, 804 (1972).
- ¹⁴P. H. Citrin, P. A. Northrup, R. Birkhahn, and A. J. Steckl, Appl. Phys. Lett. **76**, 2865 (2000).
- ¹⁵H. J. Lozykowski, W. M. Jadwisienczak, and I. Brown, Appl. Phys. Lett. **74**, 1129 (1999).
- ¹⁶R. H. Birkhahn, R. Hudgins, D. S. Lee, B. K. Lee, A. J. Steckl, A. Saleh, R. G. Wilson, and J. M. Zavada, MRS Internet J. Nitride Semicond. Res. **4S1**, G3.80 (1999).
- ¹⁷A. J. Steckl and R. Birkhahn, Appl. Phys. Lett. **73**, 1700 (1998).