

Microstructural properties of Eu-doped GaN luminescent powders

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(Received 11 March 2002; accepted for publication 23 July 2002)

GaN powders doped with europium have been prepared using Eu and Ga nitrates and N_2H_4 as reactants. The resulting particles have dimensions ranging from 0.5 to 1.0 μm . The crystalline structure was studied by transmission electron microscopy, and it consisted of single crystals with a hexagonal (wurtzite) structure containing small cubic domains (zinc blende) and a high density of stacking faults, all aligned along the [0001] and $\langle 111 \rangle$ directions, respectively. Cathodoluminescence measurements show strong light emission in the red region. This luminescence corresponds to transitions of Eu with the strongest emission in the 611 nm line, which is associated to the $Eu^{3+} 4f$ transition from 5D_0 to 7F_2 . These results demonstrate the feasibility of GaN:RE powders for luminescent applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507355]

The group III nitrides and their alloys have vast potential applications for optical devices emitting in the ultraviolet and in the full range of the visible spectrum. High-efficiency GaN-based materials for blue, green, and amber light emitting devices have been successfully demonstrated by Nakamura.¹ However, red emission has not been realized yet in these materials because of difficulties in the synthesis of high In-content InGaN.² The growth of high quality InGaN with In concentration higher than 20% is considered very challenging.

Luminescence from materials doped with rare earth (RE) elements has generated much interest in recent years. The special characteristics of the rare-earth elements are due to their outer electron configuration. Following the Aufbau principle, the $5s^2$ and $5p^6$ subshells are completely filled in the lanthanide series. The electrons in the $4f$ subshell are strongly localized and do not participate in chemical bonding. Thus, the optical and magnetic characteristics of these elements are independent of the nature of their host environment.^{3,4}

In recent years, GaN doped with RE elements has become some of the most extensively studied RE-doped luminescent materials. RE-doped GaN is a promising candidate for optoelectronic devices, high-efficiency low-cost solar cells, optical coatings, and various types of sensors.⁵⁻⁷ Eu has been used extensively to achieve red light emission.⁸⁻¹⁰ RE-doped GaN materials are typically grown in thin films, where the RE doping of GaN is carried out *in situ* or *ex situ*.

In this work, the microstructural properties of Eu-doped GaN luminescent powders grown by a different method are

presented. The growth technique employed here is a modification of the method developed by Hahn and Juza for obtaining GaN by thermal decomposition of ammonium hexafluorogallate using ammonia as a carrier gas.¹¹

The Eu-doped GaN powders were produced using $Eu(NO_3)_3$, $Ga(NO_3)_3$, and N_2H_4 as the reactant materials. The required amount of each precursor was calculated from the desired mass of the product according to the chemical reactions involved in the synthesis. The Eu concentration in the GaN powders can be controlled down to 0.1% of Eu by varying the initial mass of the $Eu(NO_3)_3$ precursor. A more detailed description of the growth process is given elsewhere.^{12,13}

The Eu concentration was estimated by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Cathodoluminescence (CL) spectra were acquired using a commercial Gatan MonoCL2 spectrometer in a JEOL JSM 6300 scanning electron microscope (SEM). The kinetic energy of electrons used for CL excitation was 5 keV with an electron beam current of 60–300 pA. The CL measurements were performed at 5.7 K. In the spectral range of these measurements there was no significant change in system response and the behavior of the blaze angle was very flat. Therefore no correction for system response was applied to the CL spectra.

The microstructural properties of GaN:Eu powders were studied by transmission electron microscopy (TEM). A small amount of GaN:Eu powder was uniformly mixed with epoxy and then encapsulated between two silicon wafers. The sample preparation for TEM analysis was done by conventional cross-section techniques. The sample was examined in a JEOL 4000EX TEM operating at 400 kV.

Figure 1 shows a SEM image of the GaN:Eu powder. The morphology of the powders consists of aggregates formed of fine particles with sizes ranging between 0.5 and

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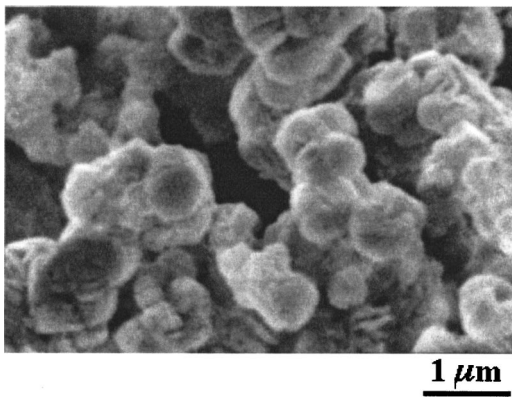


FIG. 1. Microcrystalline morphology of the GaN:Eu³⁺ powder observed in SEM image.

1.0 μm. The Eu concentration measured by AES and XPS was approximately 5 at. %.

A CL emission spectrum of GaN:Eu powder is shown in Fig. 2. The spectrum exhibits two groups of emission lines associated to Eu³⁺ (*4f* configuration⁶) *4f*–*4f* transitions from ⁵*D*₁ and ⁵*D*₀ levels to the ⁷*F*_{*J*} ground state. The red emission at 611–622 nm corresponds to the ⁵*D*₀→⁷*F*₂ transition and is the strongest in the CL spectrum. Peaks at 536, 591, and 663 nm are attributed to the ⁵*D*₁→⁷*F*₁, ⁵*D*₀→⁷*F*₁, and ⁵*D*₀→⁷*F*₃ transitions, respectively. The CL emission at 360 nm corresponds to the band-to-band transition of GaN. The intensity of this emission is relatively strong for powders of this type, and its sharpness is indicative of the high crystallinity of the GaN matrix.

Electron diffraction patterns from single GaN:Eu³⁺ particles indicated a hexagonal (wurtzite) structure. Diffraction patterns along a $\langle 11\bar{2}0 \rangle$ zone axis indicate disordering in the basal plane stacking sequence along the [0001] direction. This disordering is seen by a continuous intensity line that connects the diffraction spots along the *c* direction. Low-magnification TEM imaging reveals planar faults uniformly distributed over the whole particle, with some of the planar faults terminating within the particle.

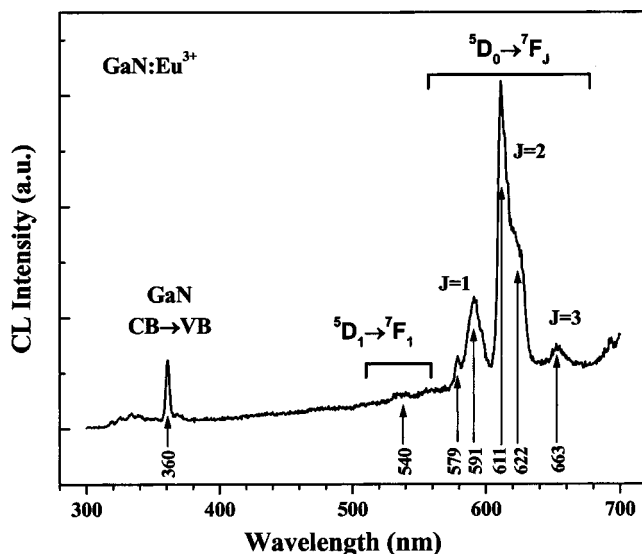


FIG. 2. Cathodoluminescence spectrum of GaN:Eu³⁺ at 5.7 K.

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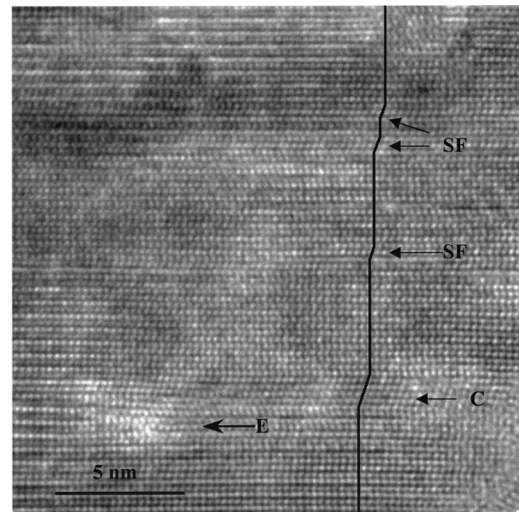


FIG. 3. HRTEM image showing the typical structure of the GaN:Eu³⁺ particles. The vertical segments are due to the stacking sequence of the hexagonal structure, and the tilted segments are associated with stacking faults or small cubic domains (C). An edge dislocation appears in the image (E).

Figure 3 shows a high-resolution TEM (HRTEM) image of a GaN:Eu³⁺ particle. The material has a hexagonal structure with many stacking faults (SFs). The black line traces the arrangement in the stacking sequence. The planar faults can be clearly seen in Fig. 3; the stacking sequence of the hexagonal structure ...*ABABABA*... (vertical segment), is interrupted by a single extra plane that is out of sequence. The extra plane gives rise to a stacking fault ...*ABABCABA*... (tilted portion). In the region of the SFs, there are three planes following the ...*ABC*... sequence. If during growth of the material, this sequence repeats again, a small cubic domain is formed (...*ABCABCA*...) like that identified with *C* in Fig. 3. Other kinds of defects observed are edge dislocations, however they are not as common as the SFs.

Figure 4 shows the microstructure of two single GaN:Eu³⁺ particles that have coalesced during the synthesis

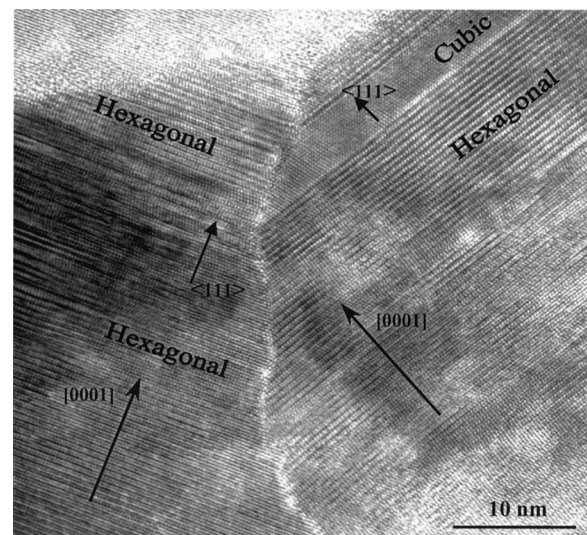


FIG. 4. HRTEM image of the coalescence of two GaN:Eu³⁺ particles. Both particles show small cubic domains along a $\langle 111 \rangle$ direction.

process. Note the sharp grain boundary, it is evidence that no segregation of material at particle boundaries occurs during growth. In addition to stacking faults, small cubic GaN domains are also observed on both particles. The cubic domains have thickness of up to 4.15 nm (16 stacking planes) and occur sporadically.

In summary, europium-doped GaN luminescent powders were successfully grown by a different synthesis method. A microstructural study of the powders reveals the wurtzite structure of submicron particles with a high density of stacking faults. Light emission observed by cathodoluminescence indicates high-quality GaN band edge emission. Characteristic Eu^{3+} emissions corresponding to intra- $4f$ -shell transitions are observed in the 540–664 nm range. A strong emission line occurs at 611 nm (red in color) and corresponds to the 5D_0 to 7F_2 transition.

This work was partially supported by Durell Corporation, CONACYT and DGAPA (México), and the DOE

(Grant No. DE-FC26-01NT41202). Technical help provided by E. Aparicio, F. Ruiz, I. Gradilla, and J. A. Diaz is gratefully acknowledged.

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