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Concentration quenching of Eu-related luminescence in Eu-doped GaN

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The dependence of Europium (Eu)-related luminescence intensity on the Eu concentration in Eu-doped GaN was studied. This luminescence is observed at 622 nm and originates from the intra- $4f$ transition of the Eu^{3+} ion. The intensity of the luminescence increased with increasing Eu concentration, up to about 2 at. %, and then abruptly decreased. It was found that polycrystalline growth began to be induced at Eu concentrations of more than 2 at. %. In addition, clear evidence for the formation of EuN compounds was obtained by x-ray diffraction and extended x-ray absorption fine structure analysis. The cause of the concentration quenching is likely to be related to the polycrystalline growth as well as EuN formation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1771806]

GaN doped with rare-earth elements (RE) hold significant potential for applications in optical devices, since they show sharp intense luminescence which is only minimally affected by temperature variations.^{1–5} Among the various RE dopants, Eu seems to be the most interesting, since it yields red luminescence (622 nm) which has not been realized in commercially available light emitting devices (LEDs) that use InGaN active layers. We have earlier reported single crystalline growth of Eu-doped GaN and nearly temperature-independent red luminescence at 622 nm originating from the intra- $4f$ – $4f$ transition of the Eu^{3+} ion.^{4,5}

The red luminescence was analyzed and determined to be generated through trap-level-mediated energy transfer from the host GaN, and the external emission efficiency was estimated to be about 0.18 at room temperature when the Eu concentration was about 2 at. %.^{6,7} These results revealed that Eu-doped GaN could be a potential material for an active LED layer. However, the luminescence intensity abruptly decreased when the Eu concentration exceeded 2 at. %.⁸ The cause of this luminescence quenching is not well understood. In this study, structural properties of Eu-doped GaN were examined by x-ray diffraction (XRD) measurements and local structures around Eu atoms in Eu-doped GaN were investigated by extended x-ray absorption fine structure (EXAFS) measurements with fluorescence mode, in order to study the cause of the concentration quenching of Eu-related luminescence in Eu-doped GaN.

The Eu-doped GaN thin films were grown on sapphire (0001) substrates by gas-source molecular beam epitaxy (GSMBE) using uncracked NH_3 gas with 6N purity as the nitrogen source. Metallic Ga with 6-nine purity and Eu with 3N purity were evaporated from conventional Knudsen effusion cells. Details of the growth sequences are given elsewhere.^{4–6} The films were grown at 700 °C and the Eu doping concentration was controlled by varying the Eu cell

temperature from 390 to 500 °C. Eu concentrations in GaN were estimated using Rutherford back scattering (RBS) spectrometry to range from 0.1 to 16 at. %. The film thickness was about 1.0 μm for all samples.

Photoluminescence (PL) measurements at room temperature (RT) were carried out using a He–Cd laser (325 nm) as the excitation source. The structural properties of the Eu-doped GaN were studied by XRD with θ – 2θ mode using both $\text{Cu } K\alpha_1$ and $K\alpha_2$ radiation. Eu L_{III} -edge EXAFS measurements were carried out for the samples with Eu concentrations of about 0.1, 2, and 16 at. % in fluorescence mode using beamline 12C at the High Energy Accelerator Research Organization (KEK) to study the local structures around Eu atoms. Analysis of the EXAFS data was performed using a general procedure as follows.^{9,10} The EXAFS spectra were obtained in fluorescence detection mode at room temperature. A Fourier filtering technique was applied to the first nearest neighbor peak in the Fourier transform and the extracted $k^3\chi(k)$ on the shell was curve fitted using the parameters calculated with the FEFF8¹¹ program. The bond lengths, coordination numbers, and Debye–Waller factor were used as fitting parameters to yield optimum values.

Figure 1(a) shows PL spectra of Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B), 5 (C) and 16 at. % (D). Near band-edge emission of GaN was observed in sample (A) together with red emission at 622 nm which can be assigned to the 5D_0 – 7F_2 transition of Eu^{3+} . In samples (B), (C), and (D), red emission at 622 nm was observed without the band-edge emission of GaN. The intensity ratio of the red emission in these four samples is 312:6250:3503:1.0 for samples (A)–(D), respectively. The PL intensity at 622 nm of various Eu concentrations is plotted in Fig. 1(b). The PL intensity linearly increased up to an Eu concentration of 2 at. %, and then it was abruptly quenched for Eu concentrations of more than 2 at. %.

Figure 2 shows XRD profiles of samples (A)–(D). A peak at $2\theta=34.60^\circ$ for sample (A) is the same as that for the (0002) reflection of undoped GaN. Although the Eu ion has a larger covalent radius than the Ga ion, 0.185 nm for Eu and

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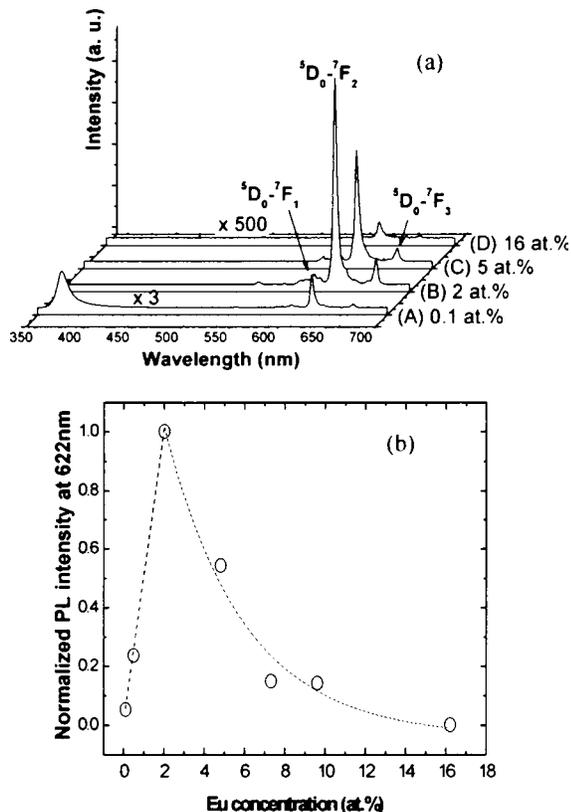


FIG. 1. (a) Photoluminescence (PL) spectra of Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B), 5 (C), and 16 at. % (D) measured at room temperature. (b) PL intensities at 622 nm vs various Eu concentrations.

0.126 nm for Ga,¹² no clear peak shift was observed between samples (A) and (B). From our recent transmission electron microscopy (TEM) observations, a high density of stacking faults and twins was detected for sample (B), and it is likely that the strain caused by Eu doping was relaxed by the introduction of these stacking faults and twins.¹³ In the XRD profile of sample (C), polycrystalline growth was confirmed since the 36.4° peak which can be assigned to (10-10) reflection appeared together with (0002) reflection. And for sample (D), two kinds of materials, GaN and EuN, were detected. That is, peaks at 34.60°, 36.4° and 39.5° can be assigned to (0002), (10-10) reflection of hexagonal GaN and (002) reflection of cubic GaN, respectively. The peak at 36.0° can be assigned to the (200) reflection of EuN.¹⁴ In comparing the peak intensities of GaN with those of EuN, a relatively large

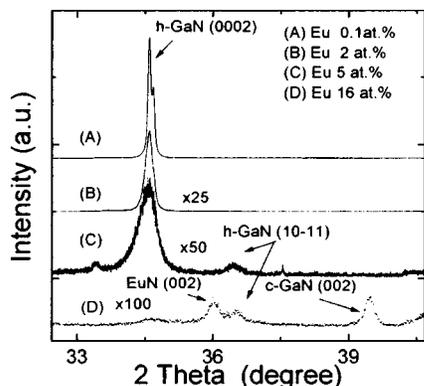


FIG. 2. X-ray diffraction data measured with θ - 2θ mode for Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B), 5 (C), and 16 at. % (D).

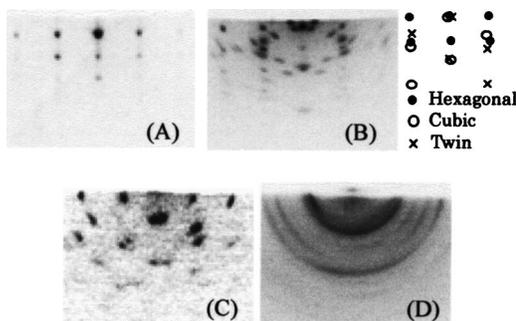


FIG. 3. RHEED patterns after 2 h growth of Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B), 5 (C), and 16 at. % (D).

amount of Eu atoms were distributed and formed EuN compounds.

Reflection high energy electron diffraction (RHEED) patterns for the samples are shown in Fig. 3. Sample (A) shows a typical pattern for hexagonal GaN, while sample (B) reveals a mixed spotty pattern of cubic and hexagonal phases of GaN consistent with the results of TEM observations.¹³ The interpretation of spots is shown next to sample (B). The RHEED pattern for sample (C), however changed to ring-like pattern suggesting polycrystalline growth and for sample (D), the pattern changed completely to a ring pattern. From the RHEED observations, it is clear that polycrystalline growth began to be induced at an Eu concentration of more than 2 at. %. Generally, a grain boundary acts as a nonradiative center. Therefore, one of the reasons for the concentration quenching of Eu-related luminescence could be the formation of a polycrystalline microstructure.

The EXAFS function $k^3\chi(k)$ with a k weighting value of 3 was extracted from the L_{III} -edge fluorescence spectrum and is depicted in Fig. 4(a). The top two spectra in Fig. 4(a) are very similar. On the other hand, the third spectrum is clearly different from the other two. The Fourier transformed $k^3\chi(k)$ spectra for the three Eu concentrations are shown in Fig. 4(b). The relatively large peaks at about 1.6–2.5 and about 2.7–3.7 Å are attributed to the first and second nearest neighbor atoms, respectively, for all samples. Fourier filtering was carried out in the range of 1.68–2.52 and 2.63–3.63 Å for the first and second nearest neighbor atoms,

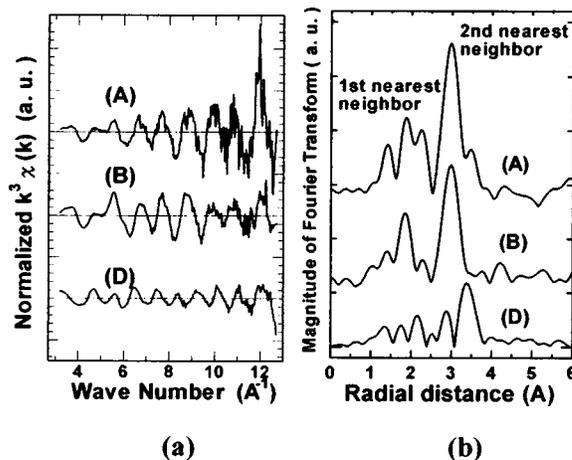


FIG. 4. (a) Normalized $k^3\chi(k)$ EXAFS oscillations of Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B), and 16 at. % (D). (b) Fourier transform of the k^3 -weighted EXAFS oscillation of Eu-doped GaN with Eu concentrations of 0.1 (A), 2 (B) and 16 at. % (D).

TABLE I. Analytical results of EXAFS from Eu-doped GaN.

Sample	Parameter	1st neighbor atoms		2nd neighbor atoms	
		N		Ga	Eu
(A) Eu: 0.1%					
	C.N	1.4	1.8	11.2	
	R(Å)	2.3	2.5	3.4	
(B) Eu: 2%					
	C.N	2.8	0.8	11.1	0.2
	C.N ratio			98%	2%
	R(Å)	2.3	2.5	3.3	3.3
(D) Eu: 16%					
	C.N	0.2	3.0	5.4	2.9
	C.N ratio			65%	35%
	R(Å)	2.3	2.4	3.3	3.6

respectively, in sample (A), from 1.55 to 2.38 and 2.63 to 3.63 Å in sample (B), and from 1.55 to 2.38 and 2.70 to 3.80 Å in sample (D). In order to analyze the EXAFS spectra, parameter fitting was conducted with theoretically calculated spectra using the FEFF8 program, which derives the scattering potentials and phase shifts by *ab initio* calculations. The fitting parameters for the optimum fit are shown in Table I.

The analytical results show that most of the Eu atoms formed bonds with nitrogen with two different bond lengths of 2.3 and 2.5 Å, and the total coordination number for nitrogen was nearly four for all samples. These results reveal that most of the doped Eu atoms were incorporated into Ga lattice sites with distorted tetrahedral symmetry.⁸ These results are consistent with previous reports. For the second nearest neighbor atom, these results suggest the existence of Eu in addition to Ga. The atomic ratios for the second nearest neighbor atoms represent the concentration of the mixed crystal if the constituent atoms were randomly distributed. The Eu concentration value obtained by EXAFS analysis for sample (B) is 2 at. %. This value is same as that determined by RBS and indicates that Eu ions are almost uniformly distributed over the entire film. On the other hand, the analyzed Eu concentration for sample (D) is about 35 at. % and this value is clearly different from the RBS result (16 at. %). The larger value of Eu content obtained by EXAFS compared with that by RBS suggests phase separation of EuN from GaN. These results are consistent with the XRD results.

As reported previously,^{4,6} most of the red emission is generated through excitation of GaN, therefore it may be difficult to generate red emission in EuN since energy transfer from GaN to EuN is not very efficient. Moreover, intrinsically, alloys formed with a component of the host matrix, EuN in this case, are generally known to evoke luminescence quenching either by increasing ion-ion interactions between rare-earth ions or by forming rare-earth compounds that are not optically active.^{15,16} For these reasons, concentration quenching of Eu related luminescence in heavily Eu-doped GaN may be caused by the formation not only of polycrystalline material but also of EuN compounds.

In summary, concentration quenching of Eu related luminescence from Eu-doped GaN was observed for Eu concentrations of over 2 at. %, and the cause of the quenching was studied. It was found that single crystalline Eu-doped GaN converted into polycrystalline form at Eu concentrations of more than 2 at. %. Formation of an EuN compound was also detected for an Eu concentration of 16 at. %. The cause of the quenching of Eu related luminescence is probably conversion to the polycrystalline form and the formation of EuN.

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