

Origin of efficient luminescence from GaN:Eu³⁺ epitaxial films revealed by microscopic photoluminescence imaging spectroscopy

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We have studied photoluminescence (PL) properties of Eu³⁺-doped GaN (GaN:Eu³⁺) epitaxial films by microscopic PL imaging spectroscopy. The GaN:Eu³⁺ epitaxial films exhibit efficient red luminescence related to intra-4*f* transitions of Eu³⁺ ions. The intensity and the spectral shape of the Eu³⁺-related PL are sensitive to the Eu³⁺ concentration, the excitation wavelength, and the monitored position. Microscopic PL imaging spectroscopy revealed that efficient red luminescence of GaN:Eu³⁺ epitaxial films is due to Eu³⁺ ions around point defects and dislocations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2385180]

Recently, there has been much interest in optical and magnetic properties of wide-band-gap semiconductors doped with functional impurities because these materials are expected to be used in light-emitting or spintronics devices.^{1–6} In particular, high-quality GaN is one of the most interesting materials to be used as host crystals for impurity doping and GaN films doped with rare-earth ions are promising materials for light emitters in the visible and infrared spectral regions.^{7–11} It has been demonstrated that Eu³⁺-doped GaN (GaN:Eu³⁺) epitaxial films exhibit highly efficient red luminescence and stimulated emission due to intra-4*f* transitions of Eu³⁺ ions.^{10,11} The spatial distribution of the doped Eu³⁺ ions in heavily doped GaN:Eu³⁺ films may determine the luminescence properties of such films. In fact, spectroscopic studies of the photoluminescence (PL) properties of GaN:Eu³⁺ epitaxial films suggest the presence of several Eu sites that give rise to different peaks in PL spectra.¹² The determination of the Eu³⁺ positions for efficient PL in GaN:Eu³⁺ epitaxial films is very important for the development of red-light-emitting diodes and lasers.

In this work, we have investigated PL properties and acquired images of GaN:Eu³⁺ epitaxial films using a home-built confocal optical microscope. The intensity and the spectral shape of the Eu³⁺-related PL were found to be strongly dependent on the Eu³⁺ concentration, the excitation wavelength, and the monitored position. Microscopic PL (μ -PL) imaging spectroscopy clearly revealed that efficient red luminescence of GaN:Eu³⁺ epitaxial films is produced by the Eu³⁺ ions located around defects and dislocations.

The GaN:Eu³⁺ thin films were grown on sapphire (0001) substrates by gas-source molecular beam epitaxy using NH₃ gas as the nitrogen source.¹⁰ The Eu³⁺ concentration were determined by Rutherford backscattering spectrometry and energy dispersive x-ray spectroscopy. The Eu³⁺ ions are almost uniformly doped in the epitaxial films. The conven-

tional PL spectra were measured under the monochromatic light excitation from a Xe lamp through a 25 cm monochromator, using a charge-coupled device (CCD) detector and a 32 cm monochromator. The spatially resolved PL spectra were acquired using a home-built confocal optical microscope. An objective lens with a numerical aperture of 0.55 was used to focus the excitation light on the samples and for collecting the PL signals from the samples. The spatial resolution of this system was approximately 1 μ m. For the spatially resolved PL measurements, a He–Cd laser (325 nm) and a laser diode (405 nm) were used as excitation sources. The PL signals from the samples were detected using a 50 cm monochromator and a cooled CCD detector. The two-dimensional images consist of a series of PL spectra measured in 1 μ m steps across a 25 \times 25 μ m² area. The spectral sensitivities of the measurement systems were calibrated using a standard tungsten lamp.

The GaN:Eu³⁺ films have a sharp PL peak at about 622 nm; this peak has been assigned to the intra-4*f* (⁵D₀ – ⁷F₂) transition of the Eu³⁺ ions.^{10,11} Figure 1 shows the spatial images of the spectrally integrated PL intensity from 615 to 635 nm for four samples having different Eu³⁺ concentrations: (a) 0.1, (b) 1, (c) 3, and (d) 8 at. % under 3.81 eV excitation at room temperature. The 25 \times 25 μ m² images of Fig. 1 consist of 25 \times 25 points with 1 μ m separation between points due to the scanning steps. The excitation energy (3.81 eV) is higher than the band-gap energy of GaN (3.39 eV).¹³ The host GaN crystals are initially excited by laser light, and then energy transfer from the host crystal to the Eu³⁺ ions occurs. The intensity of the PL peak due to the Eu³⁺ ions is sensitive to the monitored position for the low Eu³⁺ concentration samples (the 0.1 and 1 at. % Eu³⁺ samples); inhomogeneous PL intensity images are observed in the low concentration samples. By contrast, the spatial fluctuation of the Eu³⁺-related PL peak intensity is quite small and is not clearly observed in the high Eu³⁺ concentration samples (the 3 and 8 at. % Eu³⁺ samples). The spatial distribution of light-emitting Eu³⁺ ions becomes uniform in

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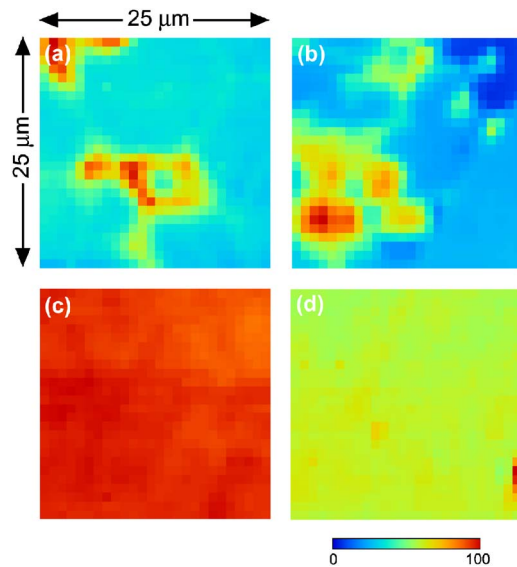


FIG. 1. (Color online) Two-dimensional images of spectrally integrated PL intensity from 615 to 635 nm of the GaN:Eu³⁺ epitaxial films having different Eu³⁺ concentrations: (a) 0.1, (b) 1, (c) 3, and (d) 8 at.% under the 3.81 eV excitation at room temperature.

the high concentration samples. However, concentration quenching of the PL intensity occurs in the 8 at.% Eu³⁺ sample. Out of the samples we used, the most efficient Eu³⁺-related PL occurred in the sample having a Eu³⁺ concentration of 2–3 at.%.¹⁰ In the high concentration sample [Fig. 1(d)], the reduction in the PL intensity is spatially uniform. However, it is interesting to note that the PL intensity from the sample is proportional to the bright emission area and has a maximum value at 3 at.%. The concentration dependence of the PL intensity demonstrates that there exist specific Eu³⁺ positions for efficient PL.

The spectral shape of the Eu³⁺-related PL at about 622 nm depends on the excitation photon energy. Figure 2 shows the macro-PL spectra of the (a) 1 and (b) 3 at.% Eu³⁺ samples under different excitation energies at room temperature. This figure shows that the Eu³⁺-related PL spectrum at about 622 nm consists of several PL lines and that the intensity ratio between the PL lines is sensitive to the Eu³⁺ concentration and the excitation energy. It is well known that the PL spectrum due to the ⁵D₀–⁷F₂ transitions of Eu³⁺ ions is

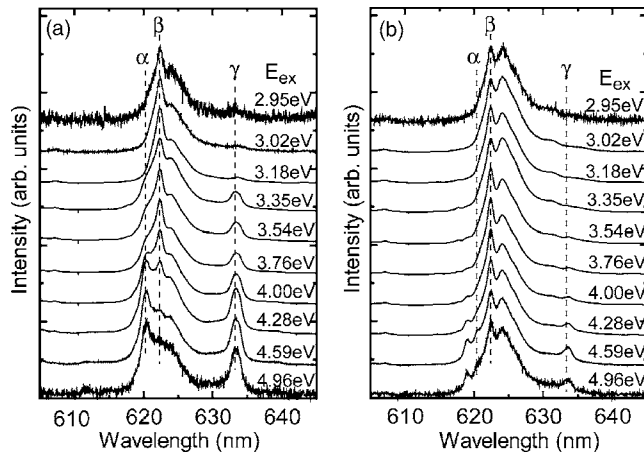


FIG. 2. Excitation energy dependence of the Eu³⁺-related PL spectra of (a) 1 and (b) 3 at.% Eu³⁺ films at room temperature. The excitation photon energies are shown.

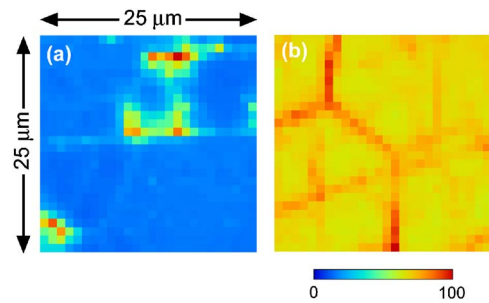


FIG. 3. (Color online) Two-dimensional images of spectrally integrated PL intensity from 615 to 635 nm of the GaN:Eu³⁺ epitaxial films under the 3.06 eV excitation at room temperature, (a) 1 and (b) 3 at.% Eu³⁺ samples.

split into three lines when Eu³⁺ ions are incorporated into the Ga²⁺ sites having a C_{3v} symmetry.¹⁴ Furthermore, the distortion of the local fields around the Eu³⁺ ions causes an energy shift in the PL peaks and gives rise to a complicated PL spectrum.¹⁴ Therefore, several PL peaks between 615 and 630 nm in Fig. 2 are assigned to the ⁵D₀–⁷F₂ transition split and shifted by the crystal field in the vicinity of the Eu³⁺ ions. On the other hand, the PL peak at 633.5 nm is due to the energy shift of the ⁵D₀–⁷F₂ transition or of the ⁵D₁–⁷F₄ transition.^{11,12,15} The Eu³⁺ concentration and the excitation energy dependences of the PL spectral shape clearly show that there are several Eu³⁺ sites having different local environments. In particular, the intensities of the PL peaks denoted by indices α, β, and γ (*I*_α, *I*_β, and *I*_γ) in the figure are sensitive to the Eu³⁺ concentration and the excitation energy. In the 1 at.% Eu³⁺ sample, the peaks α and γ are observed at 620.4 and 633.5 nm, respectively, under 4.96 eV excitation. When the excitation energy is reduced, the intensity of the peak β at 622.2 nm is enhanced. The peak β is clearly observable even under low-energy excitation that is less than the band-gap energy of the GaN host crystals, while the peaks α and γ are observable only under high-energy excitation exceeding the band-gap energy of the GaN host crystals. For the 3 at.% Eu³⁺ sample, the peak β is clearly observable under all the excitation energies used in our experiments, while *I*_α and *I*_γ are very weak. Our observations show that *I*_β increases as the Eu³⁺ concentration increases.

The μ-PL spectral shape depends on the excitation photon energy, similar to the case of macro-PL spectra. Figure 3 shows the spatial images of spectrally integrated PL intensity from 615 to 635 nm for the (a) 1 and (b) 3 at.% Eu³⁺ samples under 3.06 eV excitation. In the μ-PL spectra, the PL peak β is dominant under 3.06 eV excitation. The high contrast PL images are observed under 3.06 eV excitation, in contrast with the PL images under 3.81 eV excitation shown in Fig. 1. In the 1 at.% Eu³⁺ samples, the bright regions appear as small spots. Under 3.06 eV excitation, localized states in the GaN host crystals are directly excited since the incident photon energy is lower than the band-gap energy of GaN. The Eu³⁺ ions are then excited by energy transfer from the localized states. It is therefore concluded that the Eu³⁺ ions around point defects cause the small bright spots in Fig. 3(a). In addition, the positions of the bright spots under the 3.06 eV excitation almost coincide with those under the 3.81 eV excitation; the Eu³⁺-related PL is efficient in the vicinity of the point defects, even if the spatially uniform excitation of the GaN host crystals occurs under high-energy excitation above the band-gap energy. In the 3 at.% Eu³⁺ samples, several bright lines are clearly observed under the

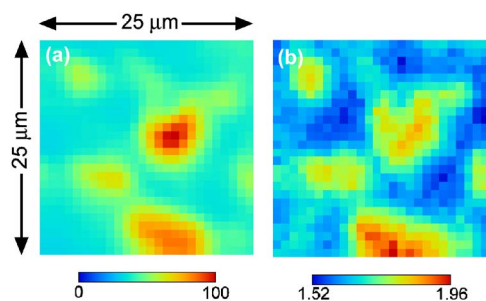


FIG. 4. (Color online) Dependence of the spectral shape of the 1 at.% Eu^{3+} sample under the 3.81 eV excitation at room temperature on monitored position. (a) Spatial image of spectrally integrated PL intensity from 615 to 635 nm. (b) Spatial image of the intensity ratio I_β/I_γ .

3.06 eV excitation in Fig. 3(b), while the PL intensity is spatially uniform under the 3.81 eV excitation in Fig. 1(c). These bright lines are due to dislocations. It has been reported that transmission electron microscope observations show the presence of stacking faults and twins in samples having a high Eu^{3+} concentration (>2 at. %).¹⁰ Heavy doping of Eu^{3+} introduces the dislocations and disorder into GaN crystals. Our μ -PL studies provide further support for such structural change in high Eu^{3+} concentration samples.

In the μ -PL spectra of the 1 at. % Eu^{3+} sample, the three PL peaks (α , β , and γ) are clearly observable under the 3.81 eV excitation at any monitored position, but the spectral shape depends on the monitored position. Figure 4 shows (a) the spectrally integrated PL intensity image and (b) the spatial image of the intensity ratio I_β/I_γ in the 1 at. % Eu^{3+} sample under the 3.81 eV excitation at room temperature. There is a good correlation between the PL intensity image [Fig. 4(a)] and the I_β/I_γ image [Fig. 4(b)]. The GaN: Eu^{3+} epitaxial films show enhancement in the intensity of peak β at positions that have efficient luminescence located around the point defects. The point defect induces distortion of the crystal lattice in its vicinity. The electric dipole intra- $4f$ transitions become partially allowed due to mixing with orbitals having different parities because they have an odd crystal field component.¹⁶ Therefore, it is concluded that the Eu^{3+} ions exhibit efficient luminescence when they are incorporated into Ga lattice sites that are distorted by the point defects and that the PL peak β is due to the Eu^{3+} ions located in the distorted Ga lattice sites.

In the samples having concentrations of Eu^{3+} above 3 at. %, the PL peak β is dominant in the μ -PL spectrum at any monitored positions even under the 3.81 eV excitation, and there is no correlation in the spatial image between the I_β/I_γ intensity ratio and the spectrally integrated PL intensity. Our observations indicate that Eu^{3+} -ion doping induces stacking faults and twins with the dislocations in the GaN host crystal and that the distortion of the crystal lattice occurs over the entire GaN: Eu^{3+} films as a result of these dislocations. Thus, it is concluded that the total luminescence intensity of the film is determined by the PL intensity I_β due to the Eu^{3+} ions located in Ga lattice sites that are distorted by the point defects and the dislocations and that spatially

uniform doping of the Eu^{3+} ions with PL peak β occurs in the 3 at. % Eu^{3+} film. In the 1 and 3 at. % Eu^{3+} samples, the peak β appears at almost the same energy, but spectral shapes are slightly different from each other. Then, it is speculated that atomic configuration around the point defects is not significantly different from that around the dislocations. Further experimental studies are needed for the understanding of atomic configurations around the Eu^{3+} ions. However, excessive doping of Eu^{3+} ions induces nonradiative centers and increases interactions between the Eu^{3+} ions, and consequently the intensity of Eu^{3+} -related PL is quenched, as shown in Fig. 1.¹⁰ The intensity of Eu^{3+} -related PL is strongly correlated with the spatial distribution of the point defects and the dislocations.

The site-dependent Eu^{3+} luminescence in GaN: Eu^{3+} epitaxial films has been studied by μ -PL spectroscopy. From spatially resolved PL spectra and intensity images, it was found that efficient red luminescence in GaN: Eu^{3+} epitaxial films is due to Eu^{3+} ions located in the Ga lattice sites distorted by the point defects and the dislocations. Control of the density and the positions of the defects and the dislocations in GaN host crystals will be important in applications in which GaN: Eu^{3+} is used as a red-light emitter. Such control is possible by using modified substrates and by modifying GaN structures such as quantum wells and dots. It has been demonstrated that the spatially resolved PL spectroscopy is one of the most useful methods for characterizing semiconductor films doped with functional impurities.

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- ¹J. D. Bryan and D. R. Gamelin, *Prog. Inorg. Chem.* **54**, 47 (2005), and references therein.
- ²A. Ishizumi, C. W. White, and Y. Kanemitsu, *Appl. Phys. Lett.* **84**, 2397 (2004).
- ³A. Ishizumi and Y. Kanemitsu, *Appl. Phys. Lett.* **86**, 253106 (2005).
- ⁴R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, and L. W. Molenkamp, *Nature (London)* **402**, 787 (1999).
- ⁵Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, *Nature (London)* **402**, 790 (1999).
- ⁶T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).
- ⁷A. J. Steckl, J. Heikenfeld, D. S. Lee, and M. Garter, *Mater. Sci. Eng., B* **B81**, 97 (2001).
- ⁸J. D. MacKenzie, C. R. Abernathy, S. J. Pearton, U. Hömmerich, J. T. Seo, R. G. Wilson, and J. M. Zavada, *Appl. Phys. Lett.* **72**, 2710 (1998).
- ⁹H. J. Lozykowski, W. M. Jadwisieniczak, and I. Brown, *Appl. Phys. Lett.* **74**, 1129 (1999).
- ¹⁰H. Bang, S. Morishima, J. Sawahata, J. Seo, M. Takiguchi, M. Tsunemi, K. Akimoto, and M. Nomura, *Appl. Phys. Lett.* **85**, 227 (2004).
- ¹¹J. H. Park and A. J. Steckl, *Appl. Phys. Lett.* **88**, 011111 (2006), and references therein.
- ¹²E. Nyein, U. Hömmerich, J. Heikenfeld, D. S. Lee, A. J. Steckl, and J. M. Zavada, *Appl. Phys. Lett.* **82**, 1655 (2003).
- ¹³H. P. Maruska and J. J. Tietjen, *Appl. Phys. Lett.* **15**, 327 (1969).
- ¹⁴A. A. Kaminskii, *Laser Crystals*, Springer Series in Optical Science Vol. 14, 2nd ed. (Springer, Berlin, 1990), p. 120.
- ¹⁵T. Andreev, E. Monroy, B. Gayral, B. Daudin, N. Q. Liem, Y. Hori, M. Tanaka, O. Oda, and D. L. S. Dang, *Appl. Phys. Lett.* **87**, 021906 (2005).
- ¹⁶*Phosphor Handbook*, edited by S. Shionoya and W. M. Yen (CRC, Boca Raton, FL, 1999), Chap. 3, p. 179.