J. Indian Inst. Sci., Sept.–Oct. 2001, **81**, 579–583.

Short Communication

Luminescence properties of Eu-implanted GaN for full color micro light-emitting diode array†

A. WAKAHARA,* Y. NAKANISHI, T. OHSHIMA‡ AND H. ITOH‡
Department of Electrical and Electronics Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan. ‡Japan Atomic Energy Research Institute.
email: wakahara@eee.tut.ac.jp

Abstract

Europium (Eu) was implanted into GaN epitaxial layer and its films were annealed at 0.1 atm NH_3 diluted with N_2 at a temperature range of 950−1100°C to remove any 'implantation damages'. Photoluminescence (PL) properties were measured in the temperature range 80−280 K by using He-Cd laser as an excitation source. Strong emission at 621 nm, corresponding to the transition from $^5D_0$ to $^7F_2$ states of Eu^{3+}, was observed and the thermal quenching of the PL intensity was very small.

Keywords: GaN, Eu, ion implantation, photoluminescence properties.

1. Introduction

GaN and related compounds are attactive materials for optoelectronic devices in a UV-visible region as its bandgap can be varied from 6.2eV for AlN to 1.9eV for InN.[1] Recent progress on crystal growth resulted in bright blue/green light-emitting-diodes (LEDs)[2] and violet laser diodes (LDs). Nitride-based LEDs have a full color LED display. They consist of GaInN blue and green LEDs and InGaP or AlGaAs red LED. It is difficult to obtain red-light emission from the nitrides due to a mismatch of temperature and lattice constants between GaN cladding and InGaN active layers. To realize a monolithic full-color LED display, red emission from the nitrides is most important. It is a challenging technological problem.

Rare earth impurities in a semiconductor act as effective luminescence centers. They have very narrow line width and very small thermal quenching.[3] Nitrides have wide bandgap and thus allow transition in visible region. They seem to be useful material for rare earth impurity from the viewpoint of the host material. Some researchers have reported that Tm, Er, and both Eu and Pr doped into GaN result in blue[4], green[5], and red[6,7] emissions, respectively. Rare earths have been introduced into GaN by *in-situ* doping during molecular beam epitaxy (MBE) or ion implantation. Heikenfeld *et al*.[6] have observed red emission from Eu-doped GaN grown by solid source MBE, but little work describing Eu doping using ion implantation has been published. Ion implantation technique has been widely used for Si device technology. Moreover, it is suitable for fabrication of a monolithic LED array by using masked process. In this study, we introduce Eu into GaN by using ion implantation technique and investigate the photoluminescence properties.

*Author for correspondence.
†Presented at the Indo-Japanese Workshop on Microsystem Technology held at New Delhi during November 23–25, 2000.

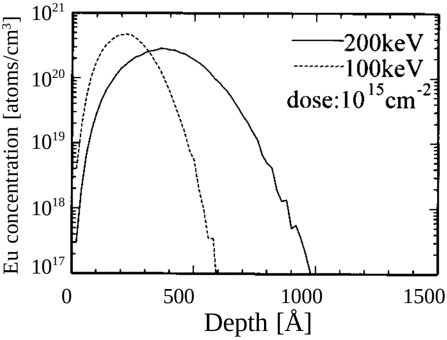

FIG. 1. Simulated Eu distribution by TRIM95.

Table I
Parameters for Eu-implantation and the simulated results using TRIM95

Acceleration energy [keV]	Dose $[cm^{-2}]$	Projected range [nm]	Peak concentration $[cm^{-3}]$
100	10^{14} 10^{15}	~60 nm	4.3×10^{19} 4.3×10^{20}
200	10^{13} 10^{14} 10^{15}	~100 nm	2.7×10^{18} 2.7×10^{19} 2.7×10^{20}

2. Experimental

Undoped GaN epilayers of 2 μm thickness were used as the host crystal for Eu implantation. The GaN epilayers were grown on sapphire(0001) substrate by using organometallic vapor phase epitaxy (OMVPE) using trimethylgallium and ammonia at 1000°C. Full width at half maximum of GaN (0002) X-ray rocking curve was in the range of 250–350 arc s. Ion implantation of Eu was carried out at room temperature with the acceleration energy of 100–200 keV, and the dose density was in the range of 10^{13}–10^{15} cm^{-2}. The implantation rate of Eu was approximately 3×10^{11} atoms/cm^2 s. Figure 1 shows the implanted Eu profile calculated using TRIM95 simulator.[8] The projected length of Eu was in the range of 60–100 nm and the calculated peak concentration was 10^{19}–10^{20} cm^{-3} (Table I). After the implantation, the samples were annealed to remove implantation damages in a hot-wall type furnace using 10% NH_3 diluted with N_2 atmosphere to prevent the decomposition of GaN. The annealing temperature and time were 950–1100°C and 10–60 min, respectively. The crystalline quality of the implanted samples was evaluated by reflection high-energy electron diffraction (RHEED), atomic force microscope (AFM), and photoluminescence (PL). PL properties were measured in the temperature range 80–280 K with He-Cd laser as an excitation light. The excitation power density was about 2 W/cm^2.

3. Results and discussion

Figure 2 shows the RHEED patterns of (a) as-grown GaN, (b) as implanted, and (c) after annealing at 1050°C for 60 min. In this case, the acceleration energy and the Eu dose were 200 keV and 10^{15} cm^{-2}, respectively. If the implanted sample indicates a halo pattern, it means that the crystal-

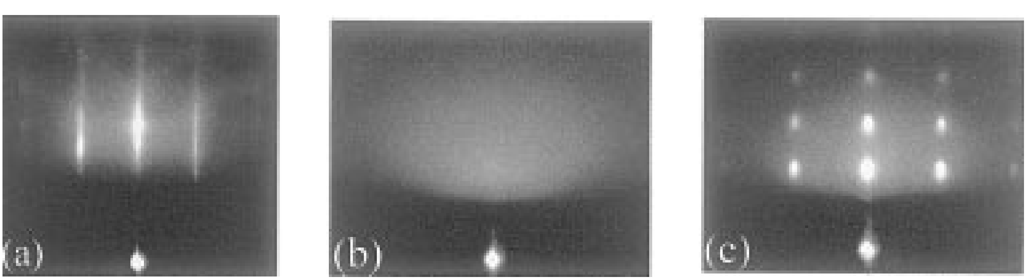

FIG. 2. RHEED pattern of (a) as-grown GaN, (b) Eu-doped GaN after ion implantation with acceleration energy of 200 keV and Eu dose of 10^{15} cm^{-2}, and (c) after ion implantation and annealing at 1050°C for 60 min.

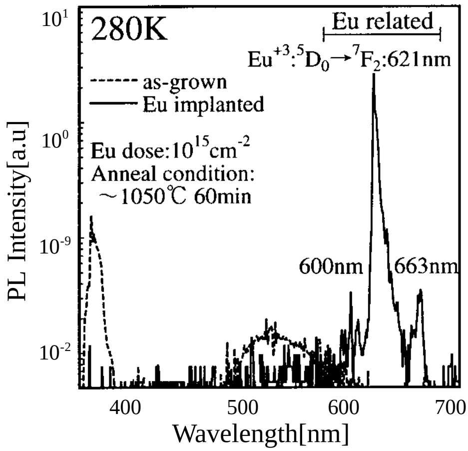

FIG. 3. Photoluminescence spectrum of Eu-doped GaN (solid line) and as-grown GaN (dotted line) at 280 K.

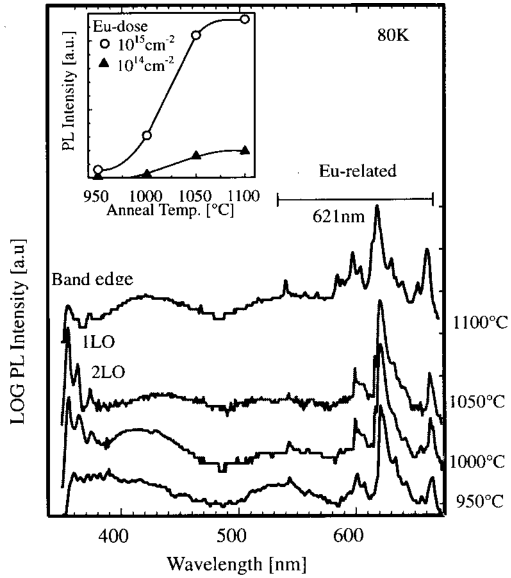

FIG. 4. Annealing temperature dependence on PL spectra of Eu-doped GaN at 80 K. The Eu-dose was 1015 cm^{-2}. The insert shows the intensity of 621 nm emission as a function of the annealing temperature.

line structure of the implanted region is destroyed. On the other hand, after annealing, RHEED pattern becomes spotty, indicating that the implantation damage is removed. However, the observed spot pattern suggests roughening of the surface. According to AFM measurement, the root mean square (RMS) value of the surface roughness of as-grown GaN is approximately 0.3 nm, which, after annealing, increases to 4 nm.

Figure 3 shows typical PL spectrum of Eu-implanted sample compared with nondoped GaN measured at room temperature. It is clearly seen that band edge and yellow-band emissions of GaN disappear and new strong and narrow red emission peaks around 600 nm from the Eu-implanted sample. These peaks are assigned as 4*f*-4*f* core level transitions of Eu^{3+}. The strongest peak observed at 621 nm corresponds to the transition between $^5D_0$ and $^7F_2$ states in Eu^{3+}. The intensity of 621 nm emission is much stronger than that of bang-edge emission obtained from as-grown GaN layer and the emission can be seen with naked eye in day light.

To ascertain the optimum annealing temperature for activating the implanted Eu, PL properties were used. Figure 4 shows the PL spectra as a function of annealing temperature. PL intensity of the transition increases from $^5D_0$ to $^7F_2$ with increasing annealing temperature but saturates above 1050°C. For the near-band-edge emission of GaN, the intensity also increases with annealing temperature up to 1050°C, but decreases at 1100°C. Moreover, the linewidth becomes narrow and well resolved near band-edge emission and its LO phonon replicas can be seen at 1050°C. Therefore, the optimum annealing temperature of the present work is 1050°C.

Figure 5 shows the PL intensity of the Eu-implanted GaN as a function of the Eu dose at 621 nm. The PL intensity increases with the dose. The slope of the PL intensity seems to be approximately 0.63. Chao *et al*.[9] also reported similar effect on 564 nm upconversion luminescence from

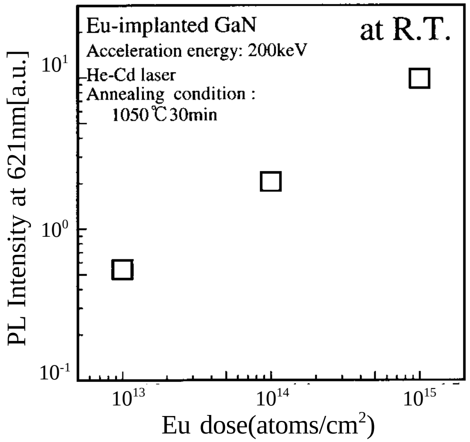

FIG. 5. PL intensity of the EU-implanted GaN (grown by OMVPE) as a function of the Eu dose at 621 nm.

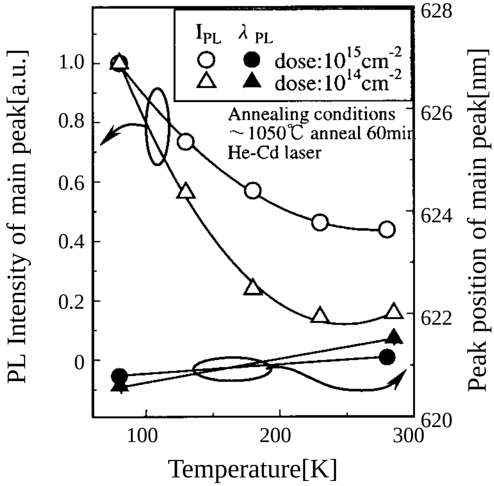

FIG. 6. PL intensity (open circle and triangle) and peak position (solid circle and triangle) of main emission as a function of the PL measurement temperature.

Er-implanted GaN.[9] Moreover, they observed the concentration quenching of luminescence for the Er-dose to be higher than $1–2\times10^{15}$ cm^{-2}. To ascertain the activation mechanism for implanted Eu impurity, further investigations such as dose dependence of the incorporated lattice site are required in high doses (>10^{15} cm^{-2}).

Figure 6 shows the temperature dependence of the PL intensity and peak position of 621 nm emission. The amount of thermal quenching, I_{280k}/I_{80k}, is defined as the 621 nm PL intensity ratio at 280 and 80 K. In the case of Eu dose of 10^{15} cm^{-2}, the PL intensity decreases slightly with increasing temperature, thermal quenching being about 40%. On the other hand, it is approximately 15% only in the case of Eu-dose of 10^{14} cm^{-2}. The thermal quenching of the Eu-related emission is very small compared to those of the band-edge-emissions of GaN and GaAs, which are almost 1%. Eu-related emission indicates very small peak shift as the temperature is changed. The peak shifts between 80 and 280 K for Eu-dose of 10^{-15} cm^{-2} and 10^{14} cm^{-2} are -11.6×10^{-4}eV and -2.96×10^{-3}eV, which correspond to the peak shift rate of -5.8×10^{-6} eV/K and -14.8×10^{-6} eV/K, respectively. Morishima *et al*.[10] also observed red emission from the Eu-doped GaN grown by gas-source molecular beam epitaxy (GSMBE). The amount of thermal quenching and peak shift rate between 77 and 280 K was approximately 25% and -7×10^{-6} eV/K, respectively. Therefore, simultaneous use of ion implantation of Eu and high temperature hot-wall annealing in NH_3-contained N_2 atmosphere is suitable for fabrication of full-color LED microarray.

4. Conclusions

Eu has been incorported into GaN epilayer by ion implanation and its photoluminescence properties have been investigated. The impurities could be removed by thermal annealing in N_2 atmosphere containing 10% NH_3 at 1050°C. Strong and sharp red-emission peaks related to Eu^{3+} have been observed successfully. The red emission was visible with the naked eye. Moreover, the PL intensity ratio, I_{280K}/I_{80K}, was about 40% which is comparable to that reported by *in-situ* doping during MBE growth. The peak position is not dependent on the temperature.

References

1. STRITE. S., LIN, M. E. AND MORKOC, H. *Thin Solid Films*, 1993, **231**, 197–210.

2. NAKAMURA, S. *et al*. *Appl. Phys. Lett*., 1998, **72**, 2014–2016.

3. FAVENNEC, P. N., L'HARIDON, H., SALVI, M., MOUTONNET, D. AND GULLIOU, Y. L. *Electron. Lett*., 1989, **25**, 718–719.

4. STECKL, A. J., GARTER, M., LEE, D. S., HEIKENFELD, J. AND BIRKHAHN, R. *Appl. Phys. Lett.*, 1999, **75**, 2184–2186.

5. GARTER, M., SCOFIELD, J., BIRKHAHN, R. AND STECKL, A. J. *Appl. Phys. Lett.*, 1999, **74**, 182–184.

6. HEIKENFELD, J., GARTER, M., LEE, D. S., BIRKHAHN, R. AND STECKL, A. J. *Appl. Phys. Lett.*, 1999, **75**, 1189–1191.

7. CHAO, L. C. AND STECKL, A. J. *Appl. Phys. Lett.*, 1999, **74**, 2364–2366.

8. BIERSACK, J. P. AND HAGGMARK, L. G. *Nucl. Instrum. Methods*, 1980, **174**, 257–269.

9. CHAO, L. C. *et al.* *Appl. Phys. Lett.*, 1999, **75**,1833–1835.

10. MORISHIMA, S., MARUYAMA, T. AND AKIMOTO, K. *J. Cryst. Growth*, 2000, **209**, 378–381.