

# Luminescence spectroscopy of Eu-implanted zincblende GaN

I. S. Roqan<sup>\*1</sup>, K. P. O'Donnell<sup>1</sup>, C. Trager-Cowan<sup>1</sup>, B. Hourahine<sup>1</sup>, R. W. Martin<sup>1</sup>, K. Lorenz<sup>2</sup>, E. Alves<sup>2</sup>, D. J. As<sup>3</sup>, M. Panfilova<sup>3</sup>, and I. M. Watson<sup>4</sup>

<sup>1</sup> Department of Physics, SUPA, University of Strathclyde, Glasgow G4 0NG, UK

<sup>2</sup> Department of Physics, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal

<sup>3</sup> Department of Physics, Universität Paderborn, 33098 Paderborn, Germany

<sup>4</sup> Institute of Photonics, SUPA, University of Strathclyde, Glasgow G4 0NW, UK

Received 27 July 2007, revised 11 September 2007, accepted 2 October 2007

Published online 21 November 2007

PACS 61.72.Vv, 78.55.–m, 78.60.Hk

\* Corresponding author: e-mail iman.roqan@strath.ac.uk

Cathodoluminescence (CL) and Photoluminescence (PL) of Eu-implanted zincblende-GaN (ZB-GaN:Eu) and wurtzite-GaN (W-GaN:Eu) are compared in order to investigate the optical activation of GaN by Eu. The Eu<sup>3+</sup> emission spectrum depends critically on the crystal structure of the GaN host;

implantation and post-annealing at 800 °C partially converts implantation-damaged ZB-GaN:Eu to W-GaN:Eu. Selective excitation of PL at wavelengths below the ZB-GaN band edge reveals a new sharp emission line at 627 nm, together with a number of satellites, which we ascribe to ZB-GaN:Eu.

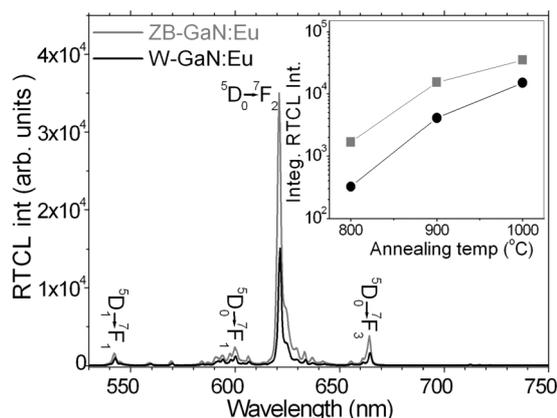
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Recent research on single crystalline wurtzite GaN:Eu (W-GaN:Eu) has revealed a strong and sharp red emission near 622 nm [1]. At least two different optical centres with different excitation pathways contribute to this emission [2]. Theoretical modelling [3] and optical spectroscopy [4] both suggest the occurrence in general of such 'site multiplicity' for RE defects in W-GaN; however, lattice location studies of W-GaN:RE show that RE ions preferentially occupy the substitutional Ga site in GaN. The optically active centres are therefore likely to be structurally similar RE<sub>Ga</sub> – intrinsic defect complexes. Recently, Park and Steckl reported that two different Eu<sup>3+</sup> sites are involved in stimulated emission (lasing) in W-GaN:Eu optical cavities [5]. A reported blue-shift of the dominant Eu<sup>3+</sup> peak in W-GaN powder, to 611 nm, ascribed to the existence of stacking faults and cubic structures [6], was not reproduced in later work [7]; moreover, aggregation of nanocrystalline powder into micrometer-sized conglomerates reportedly causes a significant red-shift of Eu<sup>3+</sup> emission spectra [8]. Despite many investigations, the luminescence spectroscopy of RE-doped GaN and the energy transfer from the wide bandgap host to the optically active RE centres are not well understood. A physical understanding of these mechanisms will perhaps emerge from a comparison of the

spectra of Eu ions in closely related hosts. In this paper, we attempt the first investigation of the red Eu emission from implanted and annealed cubic GaN:Eu (ZB-GaN:Eu).

ZB-GaN films, 820 nm thick, were grown at 710 °C by molecular beam epitaxy (MBE) on 3C-SiC substrates under N-rich growth conditions [9]. W-GaN layers, 1100 nm thick, were grown, nominally at ~1140 °C, by metalorganic vapor phase epitaxy (MOVPE) on sapphire (0001) substrates. All films were implanted at room temperature to a fluence of  $1 \times 10^{15} \text{ cm}^{-2}$  using 300 keV ion beams channelled along the surface normal. Depth-profiling by Rutherford Backscattering (RBS) showed a maximum Eu concentration at a depth of ~70 nm. Following implantation, samples of both sets of films were annealed for 20 minutes at 800 °C, 900 °C or 1000 °C under 3.8 bar of N<sub>2</sub>.

Cathodoluminescence (CL) was detected from samples mounted at room temperature in a modified Electron Probe Microanalyser (EPMA); the CL spectra were acquired with a CCD-spectrograph, using an electron beam energy of 5 keV and a current of 35 nA. Photoluminescence (PL) was excited at low temperature (15–20 K) using the 325 nm line of a ~5 mW He–Cd laser, and analyzed with a spectral resolution of 0.2 nm. Energy-selective Photolumi-

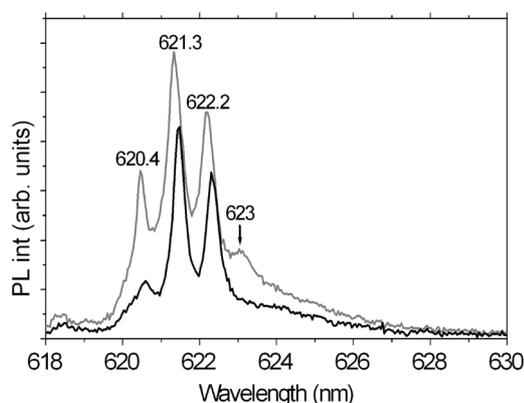


**Figure 1** CL spectra at RT of ZB-GaN:Eu and W-GaN:Eu samples (annealed at 1000 °C). The inset shows integrated RTCL intensity as a function of annealing temperature for (■) ZB-GaN:Eu and (●) W-GaN:Eu (log scale).

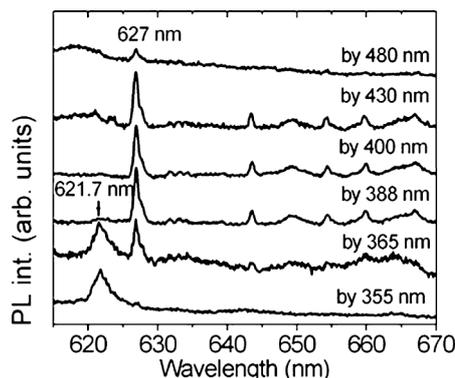
nescence Excitation (PLE) was carried out on samples at low temperature, using the output of a xenon (Xe) lamp (~1000 W) filtered by a 1/4-metre monochromator. All of the PLE spectra were corrected for the variation of monochromator output with wavelength.

Figure 1 shows that the intensity of CL at room temperature (RTCL) of the red emission is stronger for ZB-GaN:Eu, compared to W-GaN:Eu. Figure 2 shows high resolution PL spectra, excited by the 325 nm laser line. The ZB-GaN:Eu sample is again brighter and exhibits a small blueshift for spectral lines of ZB-GaN:Eu, compared to W-GaN:Eu, and an additional peak at 623 nm. The ratio of intensity of the dominant PL peak at ~621 nm to the peak at ~620 nm is larger in the W-GaN film. No PL related to  $\text{Eu}^{3+}$  emission lines was observed from W-GaN:Eu annealed at 800 °C, whereas it was observed from ZB-GaN:Eu annealed at the same temperature.

Figure 3 shows PL spectra of ZB-GaN:Eu, with selective excitation. (The effective bandgap of ZB-GaN, estimated from PLE spectra (not shown here), is ~3.33 eV,



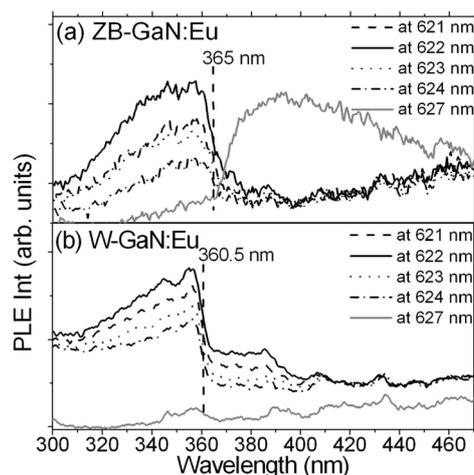
**Figure 2** High resolution PL spectra of ZB-GaN:Eu annealed at 1000 °C (grey upper spectrum) compared to that of W-GaN:Eu (black lower spectrum), at 20 K ( $\lambda_{\text{ex}} = 325$  nm).



**Figure 3** PL spectra of ZB-GaN:Eu (annealed at 1000 °C) excited by different wavelengths at 15 K. A dominant new line appears at 627 nm. Note, the satellite lines which can also be selectively excited by ~388 nm light.

whereas that of W-GaN is ~3.49 eV). Typical red wurtzite GaN:Eu emission near 622 nm is observed when the sample is excited at wavelengths below 360 nm (above the W-GaN band edge). When the sample is excited at wavelengths between 365 nm and 480 nm, however, a new emission line emerges at 627 nm, accompanied by a series of minor satellites at longer wavelengths, up to about 670 nm.

The PLE spectrum in Fig. 4(a) confirms that the 627 nm line is excited mainly below the bandgap of ZB-GaN:Eu; a broad asymmetric excitation band extends from just above the bandgap of ZB-GaN (<370 nm) to well below it (>480 nm) with a peak near 390 nm. The  $\text{Eu}^{3+}$  emission lines from 620.5 nm to 624 nm have similar PLE spectra to those of the W-GaN:Eu sample, which are shown for purposes of comparison in Fig. 4(b). PLE of



**Figure 4** PLE spectra monitored at 621–622 nm and 627 nm (at 15 K) for (a) ZB-GaN:Eu (annealed at 1000 °C) and (b) W-GaN:Eu (annealed at 1300 °C for obtaining a strong signal). The dashed vertical lines indicate the effective bandgaps (the 'background' PLE spectrum for 627 nm detection shows only experimental artefacts and noise).

W-GaN:Eu confirm that the 621–624 nm lines can be excited above and/or below the bandgap of W-GaN (at ~360 nm) as explained in detail in Ref. [2]. The effective bandgap of the ZB sample, indicated on the figure, is found to be red-shifted, by ~5 nm, or ~50 meV, compared to the W-GaN sample.

To further investigate the nature of the implanted materials, PL spectra were acquired, using 325 nm laser excitation, in the band edge regions of ZB-GaN:Eu and W-GaN:Eu samples, both annealed at 1000 °C, and compared with bandedge PL spectra of untreated samples. The 378.4 nm and 355 nm (not shown) band edge emissions of ZB-GaN and W-GaN, respectively, disappear, after implantation and are not recovered by annealing at 1000 °C.

All of the spectroscopic results reported above are consistent with the inference that ZB-GaN is partially converted to W-GaN as a result of implantation and post-annealing. A probable cause is the effect of implantation on the sample quality, through the creation of stacking faults that are stable upon annealing at high temperatures [10], which is necessary in order to activate the RE<sup>3+</sup> emission [11]. Type conversion may in fact start during implantation [12]; total implantation fluence has the greatest negative effect on crystal quality which is partially recovered by annealing [11]. Furthermore, Sun et al. reported the formation of wurtzite inclusions in *poor quality* ZB-GaN material when it was annealed at temperatures from 800 °C to 1000 °C [13].

The energy transfer from the host to intra 4f shell in W-GaN:Eu can occur in 2 different processes, either by above band gap excitation, which also involves the GaN bound exciton at 356 nm, as shown in Fig. 4b, implying the carrier-mediated energy transfer to Eu<sup>3+</sup> ions; or by below band gap excitation which may involve either defect levels or complexes related to Eu<sup>3+</sup> ions [2, 14]. At least 2 distinct centres luminesce, but the physical model for these centres is not clear. We have argued that Eu<sub>Ga</sub>-V<sub>N</sub> or Eu<sub>Ga</sub>-Ga<sub>i</sub> centres are the most likely candidates, on account of the site multiplicity [4, 15]. The new sharp line at 627 nm is clearly related to cubic phase material; in previous work on W-GaN:Eu crystals and powders, no such line was observed. It is unlikely that the type conversion from cubic to wurtzite material can ever be effected to completion. Hence, we assume that some cubic material must remain in our samples. Furthermore, the line at 627 nm does not appear in RTCL spectra. Nor is it seen when the sample is excited above the ZB-GaN band edge, a mode of excitation which also presumably operates through carrier mediation [16]. Furthermore, PL temperature dependence studies (figure not shown) reveal that the Eu<sup>3+</sup> emission lines related to W-GaN:Eu persist at room temperature, whereas the Eu<sup>3+</sup> lines related to ZB-GaN quench and disappear at 200 K. PL and PLE spectra of converted ZB-GaN:Eu (Figs. 3 and 4) show that the 627 nm line is preferentially excited by a broad excitation band, which could represent, according to accepted excitation models, an ‘Eu-associated defect’ or ‘charge-transfer

state’ localized in the bandgap. The absence of above-gap excitation is probably due to optical ‘masking’ of the cubic material by the predominant wurtzite phase; the excitation spectrum dips as the wavelength of the exciting light decreases to below ~355 nm. Therefore, PLE confirms that the new line at 627 nm is related to an optical centre created in ZB-GaN. However, there is obviously strong competition between phases for excitation capture in the spectral range between the ZB- and W-GaN band edges. Since the excitation conditions differ so much between ZB-GaN and W-GaN, it is not possible to estimate the relative abundances of the two phases in our samples by purely spectroscopic means. Likewise, optical techniques alone cannot provide a physical model for the defect responsible. However, the large number of satellite lines observed together with the 627 nm line and sharing its excitation mechanism, once more point to the involvement of a family of defects with similar morphology, as proposed for W-GaN:Eu. Future work will be necessary to investigate the origin of these lines and their physical model, using higher quality cubic GaN and careful control of the implantation/annealing process in order to avoid the ZB-to-W conversion.

PL and CL spectra of converted ZB-GaN:Eu show a dependence of the Eu<sup>3+</sup> emission intensity on the growth method; the intensity of ~622 nm lines is actually *stronger* in the converted material. We note in this context that the residual doping density in MBE ZB-GaN is expected to be smaller than in MOVPE W-GaN:Eu films on account of the lower growth temperature, and this should improve the luminescence efficiency of converted material as a result of an increase in electron–hole pairs. The rapid temperature quenching of the luminescence in cubic material points however to a deterioration of the remaining cubic phase as a result of implantation and annealing.

In conclusion, the Eu<sup>3+</sup> emission spectrum in implanted and annealed GaN has been shown to depend critically on the crystal structure of the GaN host. Implanting ZB-GaN samples with a moderate fluence of heavy ions may produce W-GaN material, which makes spectroscopic analysis initially difficult. The ~622 nm CL emission from converted ZB-GaN:Eu is stronger than that from W-GaN:Eu. Selective PLE spectroscopy reveals a new 627 nm line and a large number of satellites which we attribute to new Eu-related optical centres in ZB-GaN.

**Acknowledgment** D.A. and M.P. would like to thank Dr. H. Nagasawa and Dr. M. Abe from SiC Development Center, HOYA Corporation, for supplying the 3C-SiC substrates for the ZB-GaN samples. K. Lorenz thanks FCT, Portugal for their grants (BPD/18958/2004 and POCI/FIS/57550/2004).

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