AIP Conference Proceedings

Temperature-dependent hysteresis of the emission spectrum of Eu-implanted, Mg-doped HVPE GaN

K. P. O'Donnell, R. W. Martin, P. R. Edwards, K. Lorenz, E. Alves, and M. Boćkowski

Citation: AIP Conference Proceedings **1566**, 63 (2013); doi: 10.1063/1.4848286
View online: http://dx.doi.org/10.1063/1.4848286
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1566?ver=pdfcov
Published by the AIP Publishing

Temperature-Dependent Hysteresis of the Emission Spectrum of Eu-implanted, Mg-doped HVPE GaN

K.P. O'Donnell[1], R.W. Martin[1], P.R. Edwards[1], K. Lorenz[2], E. Alves[2] and M. Boćkowski[3]

[1]*SUPA Department of Physics, University of Strathclyde, Glasgow, Scotland, UK;* [2]*Instituto Tecnológico e Nuclear, Instituto Superior Técnico, Sacavém, Portugal;* [3]*Unipress, Warsaw, Poland.*

Abstract. A red emission site (hereafter, Eu0), with its main $^5D_0$ to $^7F_2$ peak at 619 nm, is observed by photoluminescence (PL) spectroscopy of Eu-implanted, Mg-doped GaN, in samples annealed at high temperature and pressure (up to 1400 °C, 1 GPa) in order to remove lattice damage. The PL spectrum is strongly *temperature-hysteretic* between room temperature and ~20 K: below 30 K, photochromic switching occurs between Eu0 and the usually dominant Eu1 center; upon warming the sample, the Eu0 signal does not recover until the temperature reaches ~150 K. Photobleaching of Eu1 takes place at low temperatures after cooling, while photo-enhancement of Eu0 takes place at high temperatures after re-warming. These observations suggest a microscopic model of charge-driven defect interconversion in p-type GaN:Eu, Mg.

Keywords: GaN, Eu doping, photoluminescence, hysteresis.
PACS: 78.55Cr, 61.72uj

INTRODUCTION

Red light emission from GaN:Eu light emitting diodes is driven by electron-hole recombination in the active region[1]. In an attempt to improve the efficiency of the red GaN:Eu LED, which has a p-i(Eu)-n structure[2], we set out to study the possibility of Eu incorporation into p- and n-type GaN by implanting Eu into commercial doped GaN wafers.

EXPERIMENTAL

GaN films, ~3 μm thick, grown by hydride vapor phase epitaxy (HVPE) on (0001) sapphire substrates and doped with Si (n-type), Zn or Mg (p-type), were purchased from TDI. Samples were implanted with 300 keV Eu ions to a fluence of 10^{13} to 10^{15} at/cm^2 with the surface normal tilted 10º away from the beam. Post-implant annealing was performed for 30 min at 1100 ºC-1400 ºC under 1 GPa of nitrogen.

Samples were mounted in a closed-cycle helium refrigerator, equipped with a temperature controller, and illuminated by monochromatic light from a Xe lamp passed through a ¼-metre monochromator. In a typical cycle of observation a sample was continuously cooled from RT to below 20 K and then continuously warmed, after a brief waiting period at base temperature, to ~280 K whilst under constant illumination with ~1 mW of 350 nm superbandgap light. Spectra were obtained with a cooled CCD camera attached to a ⅔-metre monochromator with input slit set to match the 25 μm pixel width. A one second camera exposure was programmed at 0.5 K intervals automatically. The cooling or heating rate was held below 5 K per minute.

RESULTS

The dominant $^5D_0$ to $^7F_2$ transitions of Eu sites in III-N semiconductors split into a pair of sharp lines (A+E) near 622 nm and an outlier (E) near 635 nm[3]. Site multiplicity may produce confusing overlapping spectra in certain circumstances[1]; for simplicity, we focus upon the outlier region from 630 nm to 636 nm, where each individual site should produce an unsplit doublet in C_{3v} symmetry.

Figure 1 shows the temperature dependence of luminescence lines of GaN(Mg):Eu in this spectral region for a sample cooled from RT to 18 K. The line at 632 nm (Eu0 hereafter,) *vanishes* in a narrow temperature range near 25 K, to be replaced by a line due to the normally dominant Eu1 site at 634.4 nm. Upon warming the sample from base temperature, Eu0 emission does not reappear until the sample temperature reaches ~150 K (Figure 2).

The Eu0/Eu1 system therefore provides a classic, perhaps unique, example of *luminescence hysteresis*. To accompany the bistability of hysteresis, we have observed several other features that are characteristic of metastability, including photo-bleaching, photo-enhancement and luminescence transients. These will be described in detail elsewhere.

The Physics of Semiconductors
AIP Conf. Proc. 1566, 63-64 (2013); doi: 10.1063/1.4848286

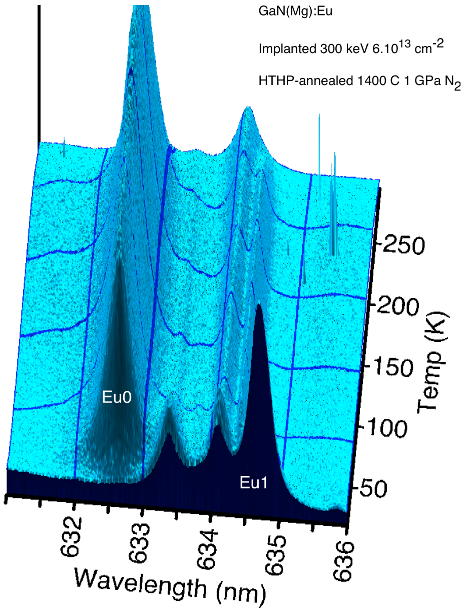

FIGURE 1. Showing the temperature dependence of luminescence for a cooling sample, GaN(Mg):Eu6a. Note the photochromic switching of Eu0 (632 nm) to Eu1 (634.4 nm) below 30 K.

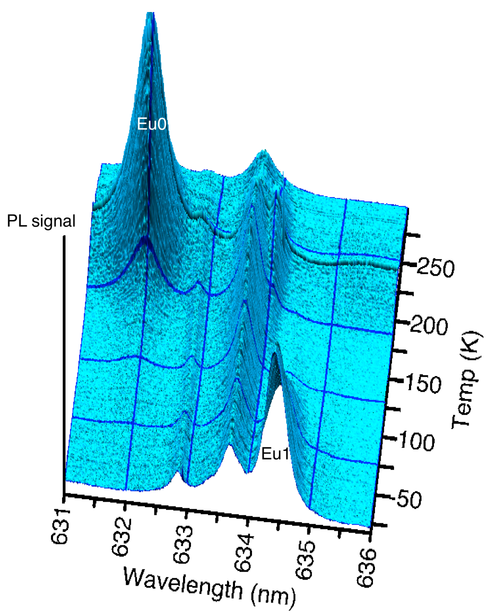

FIGURE 2. Showing the temperature dependence of luminescence for sample warming. The Eu0 signal does not fully recover until the temperature reaches ~250 K.

DISCUSSION AND CONCLUSION

For simplicity, we consider only the principal sites involved in the luminescence hysteresis of Eu-implanted GaN, represented by the dominant PL peaks Eu0 (632 nm) and Eu1 (634.4 nm). Our results for the warming phase of the cycle are consistent with Lee et al.[4], on the PL of (Eu, Mg) codoped GaN, grown by metalorganic vapour phase epitaxy, but different centers dominate in material grown by molecular beam epitaxy[5].

Since the Eu0 spectrum appears in Mg-doped samples, and not in Si-doped or Zn-doped samples, implanted with Eu and annealed in the same way, we conclude that Eu0 *requires* the presence of Mg and in fact that the site involved *contains* Mg. Mg forms two deep acceptors in GaN with an activation energy of 140-200 meV[6]. One of these acceptors, A1, is metastable at low temperature, suggesting a parallel with the spectroscopy of Eu0 as described above. However it is unlikely that the metastable acceptor survives our extreme annealing conditions. At the same time, recent calculations suggest that the stable Mg acceptor in GaN undergoes a strong distortion when neutral, due to localisation of charge on a neighbouring N atom[7].

We propose that such charge-induced local lattice relaxation provides a *mechanism* for the hysteretic behavior of the Eu0 luminescence. Carrier freeze-out at low temperatures, during the cooling phase, drives a lattice distortion of the (Eu, Mg) centre that renders it Eu1-like in structure and thus 'converts' Eu0 to Eu1. Upon subsequently warming the sample, the Eu0 signal cannot recover until holes are released from deep acceptors. This occurs only at fairly elevated temperatures above 150 K.

In summary, we have described the interesting, perhaps unique, temperature dependence of the Eu-related emission of Mg-doped GaN, and attributed the experimental results, including luminescence hysteresis, photo-bleaching and photo-enhancement, to conformational changes brought about by a change of charge state of (Eu,Mg)-related defects in p-type GaN. Further work, both experimental and theoretical, is required to verify or contradict the model.

REFERENCES

1. K.P. O'Donnell and V. Dierolf (Eds.), Rare-Earth Doped III-Nitrides for Optoelectronic and Spintronic Applications, Topics in Applied Physics Vol. 124 (Springer, 2010)
2. A. Nishikawa, T. Kawasaki, N. Furukawa, Y. Terai, and Y. Fujiwara, Appl. Phys. Express **2**, 071004 (2009)
3. J. B. Gruber, U. Vetter, T. Taniguchi, G. W. Burdick, H. Hofsäss, S. Chandra and D.K. Sardar, J. Appl. Phys. **110**, 023104 (2011)
4. D.-G. Lee, A.Nishikawa, Y. Terai and Y. Fujiwara, Appl. Phys. Lett. **100**, 171904 (2012)
5. Y. Takagi, T. Suwa, H. Sekiguchi, H.Okada, and A.Wakahara, Appl. Phys. Lett. **99**, 171905 (2011)
6. B. Monemar et al. Phys. Rev. Lett. **102**, 235501 (2009)
7. J. L. Lyons, A. Janotti, and C. G. Van deWalle, Phys. Rev. Lett. **108**, 156403 (2012).