

## Lattice site location of optical centers in GaN:Eu light emitting diode material grown by organometallic vapor phase epitaxy

K. Lorenz, E. Alves, I. S. Roqan, K. P. O'Donnell, A. Nishikawa, Y. Fujiwara, and M. Boćkowski

Citation: [Applied Physics Letters](#) **97**, 111911 (2010); doi: 10.1063/1.3489103

View online: <http://dx.doi.org/10.1063/1.3489103>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/97/11?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Enhancement in light efficiency of a GaN:Eu red light-emitting diode by pulse-controlled injected charges](#)  
Appl. Phys. Lett. **105**, 171903 (2014); 10.1063/1.4900840

[Afterglow of Eu-related emission in Eu-doped gallium nitride grown by organometallic vapor phase epitaxy](#)  
J. Appl. Phys. **116**, 043515 (2014); 10.1063/1.4891232

[Effect of thermal annealing on luminescence properties of Eu,Mg-codoped GaN grown by organometallic vapor phase epitaxy](#)  
Appl. Phys. Lett. **102**, 141904 (2013); 10.1063/1.4800447

[Improved luminescence properties of Eu-doped GaN light-emitting diodes grown by atmospheric-pressure organometallic vapor phase epitaxy](#)  
Appl. Phys. Lett. **97**, 051113 (2010); 10.1063/1.3478011

[High-temperature annealing and optical activation of Eu-implanted GaN](#)  
Appl. Phys. Lett. **85**, 2712 (2004); 10.1063/1.1801686

---

An advertisement for Oxford Instruments Atomic Force Microscopy (AFM) is shown. It features a blue background with three images: a mobile phone, a desktop computer, and an AFM. Text on the left asks 'You don't still use this cell phone or this computer' and 'Why are you still using an AFM designed in the 80's?'. On the right, it says 'It is time to upgrade your AFM' and 'Minimum \$20,000 trade-in discount for purchases before August 31st'. Below that, it states 'Asylum Research is today's technology leader in AFM'. The Oxford Instruments logo and tagline 'The Business of Science' are at the bottom right, along with the email 'dropmyoldAFM@oxinst.com'.

# Lattice site location of optical centers in GaN:Eu light emitting diode material grown by organometallic vapor phase epitaxy

K. Lorenz,<sup>1,a)</sup> E. Alves,<sup>1</sup> I. S. Roqan,<sup>2,b)</sup> K. P. O'Donnell,<sup>2</sup> A. Nishikawa,<sup>3</sup> Y. Fujiwara,<sup>3</sup> and M. Boćkowski<sup>4</sup>

<sup>1</sup>Instituto Tecnológico Nuclear, Estrada Nacional 10, 2686-953 Sacavém, Portugal and CFNUL, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal

<sup>2</sup>Department of Physics, SUPA, University of Strathclyde, Glasgow G4 0NG, Scotland, United Kingdom

<sup>3</sup>Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

<sup>4</sup>Institute of High Pressure Physics, Polish Academy of Sciences, 01-142 Warsaw, Poland

(Received 21 June 2010; accepted 23 August 2010; published online 16 September 2010)

Eu-doped GaN was grown by organometallic vapor phase epitaxy at temperatures from 900 to 1100 °C. Eu incorporation is influenced by temperature with the highest concentration found for growth at 1000 °C. In all samples, Eu is incorporated entirely on substitutional Ga sites with a slight displacement which is highest ( $\sim 0.2$  Å) in the sample grown at 900 °C and mainly directed along the *c*-axis. The major optical Eu<sup>3+</sup> centers are identical for *in situ* doped and ion-implanted samples after high temperature and pressure annealing. The dominant Eu<sup>3+</sup> luminescence lines are attributed to isolated, substitutional Eu. © 2010 American Institute of Physics. [doi:10.1063/1.3489103]

Rare earth (RE) doping of GaN has been intensively studied using *ex situ* ion implantation<sup>1,2</sup> or *in situ* doping during epitaxial growth, mainly by molecular beam epitaxy (MBE).<sup>3</sup> The light emission of optically active RE ions spans a wide spectral range including the visible spectrum allowing the production of all-nitride light emitting devices (LEDs) in all primary colors. The growth of Eu-doped GaN by organometallic vapor phase epitaxy (OMVPE) is challenging due to the small number of appropriate precursors and their low vapor pressure.<sup>4,5</sup> Recently, the first current injection LED, operating at low voltages, based on OMVPE GaN:Eu was realized by some of the present authors.<sup>6</sup> However, neither the incorporation site of Eu nor the nature of optical Eu centers in OMVPE layers has been studied in detail.

In this paper Rutherford backscattering/channeling (RBS/C) and photoluminescence (PL) measurements are combined in order to analyze the incorporation sites and optically active centers of GaN:Eu doped *in situ* during OMVPE growth using layers similar to those deployed in the red LED.<sup>6</sup> Eu was found on near-substitutional Ga-sites with slight displacements in particular for samples grown at low temperatures. The optical centers are found to be identical to those of an implanted sample annealed at high temperature and pressure, viz. the isolated Eu<sub>Ga</sub> impurity which provides the dominant PL emission at low temperatures with above-gap excitation.<sup>7</sup>

GaN:Eu layers,  $\sim 400$  nm thick, were grown by OMVPE on GaN/sapphire at different growth temperatures  $T_G$  as described previously.<sup>8</sup> In the following the samples grown at 900 °C, 950 °C, 1000 °C, 1050 °C, and 1100 °C are named S900, S950, S1000, S1050, and S1100, respectively. The optical properties of these samples are compared to a GaN sample, named I1450, implanted with 300 keV Eu ions to a fluence of  $1 \times 10^{13}$  cm<sup>-2</sup> and annealed at 1450 °C for

30 min in 1 GPa nitrogen pressure leading to a complete recovery of the crystal as confirmed by RBS/C and x-ray diffraction. A detailed spectroscopic investigation of implanted and high pressure annealed GaN was reported previously.<sup>7</sup>

RBS/C measurements were performed using a 2 MeV He<sup>+</sup> beam, a two axes goniometer and Si surface barrier detectors at  $\sim 180^\circ$  and  $140^\circ$  backscattering angle. Full angular scans were fitted using the Monte Carlo code FLUX.<sup>9</sup> PL spectra were acquired at 20 K using a 1000 W Xe lamp/1/4 m monochromator combination for excitation and a 2/3 m spectrometer/photomultiplier combination for detection.

Figure 1 shows the random and  $\langle 0001 \rangle$  aligned RBS/C spectra for sample S1000. The Eu signal, visible for the first  $\sim 100$  nm of the GaN:Eu layer, reveals a homogeneous Eu distribution with depth. A fit to the random spectrum using the NDF code<sup>10</sup> yields a Eu concentration of 0.11(2) at. %. The Eu concentration and Ga minimum yield for the five GaN:Eu films are summarized in the inset of Fig. 1. In agreement with secondary ion mass spectrometry measurements,<sup>8</sup>

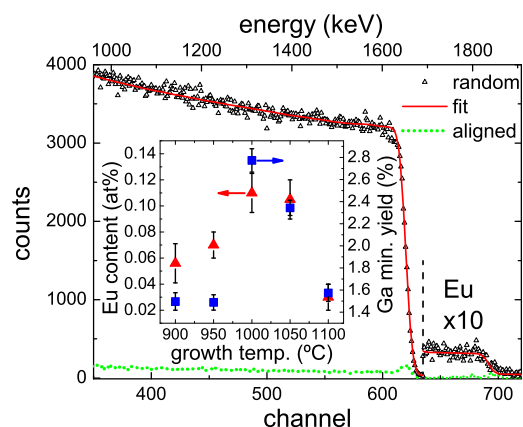


FIG. 1. (Color online) RBS/C random and  $\langle 0001 \rangle$  aligned spectra and the fit to the random spectrum of sample S1000. The inset shows Eu concentration and Ga minimum yield as a function of  $T_G$  for all *in situ* doped samples.

<sup>a)</sup>Electronic mail: lorenz@itn.pt.

<sup>b)</sup>Present address: Physical Science and Engineering Division 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia.

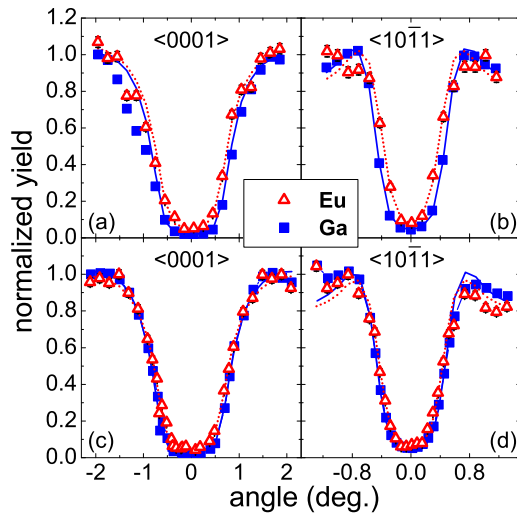


FIG. 2. (Color online) Full angular scans (symbols) and fits (lines) for Eu and Ga across the  $\langle 0001 \rangle$  and the  $\langle 10\bar{1}1 \rangle$  axes for samples S900 [(a) and (b)] and S1000 [(c) and (d)].

the Eu concentration is first found to increase with  $T_G$  up to a maximum at 1000 °C indicating an incomplete pyrolysis of the Eu precursor at lower  $T_G$ . For higher  $T_G$  the Eu concentration decreases and in particular for sample S1100 it is very low pointing to a strong desorption of Eu from the surface. The surface morphology was shown to be smoothest for growth at 1000–1050 °C which facilitates the Eu incorporation.<sup>11</sup> V/III flux ratio, carrier gas and reactor pressure may further influence the Eu incorporation and were kept constant in this study. The minimum yield,  $\chi_{\min}$ , (ratio of the yield in the aligned to that of the random spectrum) serves as a measure of single crystalline quality. A typical value for state-of-the-art undoped OMVPE GaN is  $\chi_{\min} = 2\%$ .<sup>12</sup>  $\chi_{\min}$  values for all samples are comparable to undoped GaN films. The best values of  $\sim 1.5\%$  are observed for the samples with low Eu content while crystal quality is slightly worse for the samples grown at 1000 and 1050 °C which have the highest Eu incorporation. In the case of MBE grown GaN:RE layers and high voltage electroluminescence devices the optimum RE concentration was reported to be 0.5–1 at.%,<sup>3</sup> considerably higher than in the present samples. Increasing RE incorporation in OMVPE layers could possibly lead to increased luminescence but may at the same time deteriorate further the crystal quality.

RE are known to substitute for Ga atoms in implanted as well as *in situ* doped samples grown by MBE.<sup>7,13</sup> In early experiments on implanted samples, Eu was found slightly displaced from the substitutional site.<sup>2</sup> The substitutional fraction  $f_s$  can be estimated from the random and aligned spectra using  $f_s = (1 - \chi_{\min}^{\text{Eu}}) / (1 - \chi_{\min}^{\text{Ga}})$ , where  $\chi_{\min}^{\text{Eu}}$  and  $\chi_{\min}^{\text{Ga}}$  are the minimum yields for Eu and Ga, respectively. This analysis yields a substitutional fraction close to 100% in all OMVPE samples. However,  $\langle 0001 \rangle$  aligned spectra are not sensitive to displacements of the Eu ions along this direction. In order to study in detail the incorporation site of Eu, full angular scans across the  $\langle 0001 \rangle$  and the  $\langle 10\bar{1}1 \rangle$  axes were performed and are presented in Fig. 2 for samples S900 and S1000 together with their FLUX fits. For S1000 the scans for Eu and Ga almost perfectly overlap for both axes showing that Eu is incorporated on substitutional Ga sites. For S900 a clear narrowing of the Eu scan is observed for the tilted axis,

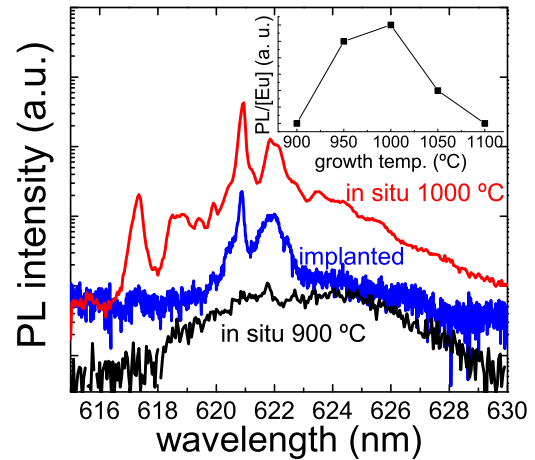


FIG. 3. (Color online) PL spectra ( $\lambda_{\text{exc}} = 348$  nm) of samples S900, S1000, and I1450. The inset shows the integrated PL intensity within the sharp emission lines normalized to the Eu content.

The displacement perpendicular to the  $\langle 10\bar{1}1 \rangle$  direction derived with FLUX is  $\sim 0.17(2)$  Å corresponding to a displacement of  $0.24(3)$  Å along the *c*-axis assuming that this is the major direction of displacement. This assumption is supported by the  $\langle 0001 \rangle$  scan showing only a small narrowing of the Eu scan.

The most intense luminescence of GaN:Eu<sup>3+</sup> is known to arise from the  $^5D_0 \rightarrow ^7F_2$  transition near 620 nm. Eu-implanted GaN typically shows two majority optical centers named Eu1 and Eu2.<sup>14,15</sup> The latter was recently identified as the isolated substitutional Eu<sub>Ga</sub> impurity.<sup>7</sup> In general, both Eu1 and Eu2 are excited by above band gap light while Eu1 is additionally excited by a broad absorption feature below the band gap of GaN.<sup>14</sup> The Eu<sup>3+</sup> emission of sample I1450 was shown to be dominated by the Eu2 center using the same excitation conditions as in the present study.<sup>7</sup>

The low temperature PL spectra for samples S900, S1000, and I1450 are presented in Fig. 3. S1000 and I1450 have the same spectral shape in the 621–622 nm region suggesting that the same Eu<sup>3+</sup> center is dominant in both samples. The same spectral shape is also seen for samples S950 and S1050 (not shown). The most intense line is the one at 621 nm characteristic for the Eu2 center. Indeed, just as in implanted samples, PL excitation below the band gap (not shown) produces the typical spectral pattern for the Eu1 center but with much lower intensity. All samples except S900 show the typical sharp lines for Eu1 and Eu2 centers with highest intensity for the sample S1000. S900, in contrast, only shows a broad emission of much lower intensity around 623 nm. The inset in Fig. 3 shows the integrated PL intensity within the sharp emission lines normalized to the Eu content as a function of  $T_G$  and reveals the narrow growth window for optimized Eu emission. The strong broadening for sample S900 hints at Eu ions incorporated in a large number of sites with different microscopic environments. This is a surprising result bearing in mind the excellent crystalline quality of this sample and the complete incorporation of Eu into near-substitutional lattice sites. On the other hand, sample S900 reveals a greater displacement of Eu from the substitutional site.

It is worth to mention here that Eu in implanted samples is often found displaced from the substitutional site.<sup>2</sup> The

fact that this displacement is low in samples annealed under optimized conditions<sup>7</sup> indicates that in this case it is due to the interaction of Eu with residual implantation defects. However, even for heavily damaged material Eu emission from implanted samples always showed the typical sharp emission lines of the  $^5D_0 \rightarrow ^7F_2$  transition.<sup>16</sup>

In sample S900 a clustering of Eu ions may explain the observed behavior. Clustering occurs preferentially at low  $T_G$  where the diffusion length of adatoms on the surface is low. Such clusters may consist of two or more Eu ions incorporated on second nearest neighbor Ga-sites. They cause a local distortion of the lattice and a relaxation of the Eu ions into the crystal channels and can furthermore explain the apparent multiplicity of the local environment around  $Eu^{3+}$  emitting centers and possibly the decrease of emission efficiency in this sample due to cross relaxation between neighboring  $Eu^{3+}$  ions. Indications for Eu clustering in this sample were also reported by Woodward *et al.* based on site selective optical spectroscopy measurements.<sup>17</sup>

Finally it is interesting to compare the PL intensity in the best *in situ* doped (S1000) and the implanted sample I1450. S1000 shows an integrated PL intensity approximately 20 times stronger than I1450. Note, however, that S1000 contains  $\sim 400$  times more Eu ions. This observation suggests that a large fraction of incorporated Eu ions remain optically inactive.

In summary, we studied structural and optical properties of GaN doped with Eu during OMVPE at different  $T_G$ . All samples show excellent crystal quality comparable to state-of-the-art undoped GaN epilayers. The Eu incorporation is influenced by  $T_G$  with the highest Eu concentration of 0.11(2) at. % found for growth at 1000 °C pointing to a critical balance between incomplete pyrolysis of the Eu precursor at low temperatures and desorption of Eu from the surface at high temperatures. Despite a slight decrease of crystal quality in this sample it shows a complete substitutional incorporation of Eu on Ga sites with low displacements and the highest red  $Eu^{3+}$  PL intensity. For excitation above the band gap, the dominant Eu center in this sample, and therefore in the GaN:Eu LED,<sup>6</sup> is the Eu2 center assigned to isolated substitutional  $Eu_{Ga}$ . The sample grown at 900 °C, on the other hand, showed only a weak and broad red emission without the typical sharp lines. This and the fact that Eu is found displaced from the substitutional site in this sample was tentatively explained by the formation of Eu clusters promoted by a low diffusion length of adatoms at low  $T_G$ . Finally, the red PL intensity of the best *in situ* doped sample

is 20 times stronger than that of a low fluence implanted and fully annealed sample while the number of Eu ions is approximately 400 times larger pointing to a significant potential for optimization of luminescence efficiency in future GaN:Eu based LEDs.

Financial support by FCT Portugal (Ciência 2007, Grant No. PTDC/CTM/100756/2008), by JSPS Japan, Grant-in-Aid for Creative Scientific Research under Grant No. 19GS1209, Grant-in-Aid for Young Scientists (B) under Grant No. 21760007, and by the Global Centre of Excellence Program “Advanced Structural and Functional Materials Design” from MEXT Japan is gratefully acknowledged.

- <sup>1</sup>H. J. Lozykowski, W. M. Jadwisieniczak, and I. Brown, *Appl. Phys. Lett.* **74**, 1129 (1999).
- <sup>2</sup>T. Monteiro, C. Boemare, M. J. Soares, R. A. Sa-Ferreira, L. D. Carlos, K. Lorenz, R. Vianden, and E. Alves, *Physica B* **308–310**, 22 (2001).
- <sup>3</sup>A. J. Steckl, J. C. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Wang, and R. Jones, *IEEE J. Sel. Top. Quantum Electron.* **8**, 749 (2002).
- <sup>4</sup>M. Pan and A. J. Steckl, *Appl. Phys. Lett.* **83**, 9 (2003).
- <sup>5</sup>J. Laski, K. Klinedinst, M. Raukas, K. C. Mishra, J. Tao, J. McKittrick, and J. B. Talbot, *J. Electrochem. Soc.* **155**, J315 (2008).
- <sup>6</sup>A. Nishikawa, T. Kawasaki, N. Furukawa, Y. Terai, and Y. Fujiwara, *Appl. Phys. Express* **2**, 071004 (2009).
- <sup>7</sup>I. S. Roqan, K. P. O'Donnell, R. W. Martin, P. R. Edwards, S. F. Song, A. Vantomme, K. Lorenz, E. Alves, and M. Boćkowski, *Phys. Rev. B* **81**, 085209 (2010).
- <sup>8</sup>T. Kawasaki, A. Nishikawa, N. Furukawa, Y. Terai, and Y. Fujiwara, *Phys. Status Solidi C* **7**, 2040 (2010).
- <sup>9</sup>P. J. M. Smulders and D. O. Boerma, *Nucl. Instrum. Methods Phys. Res. B* **29**, 471 (1987).
- <sup>10</sup>N. P. Barradas, C. Jaynes, and R. P. Webb, *Appl. Phys. Lett.* **71**, 291 (1997).
- <sup>11</sup>H. Kasai, A. Nishikawa, T. Kawasaki, N. Furukawa, Y. Terai, and Y. Fujiwara, *Jpn. J. Appl. Phys., Part 2* **49**, 048001 (2010).
- <sup>12</sup>J. G. Marques, K. Lorenz, N. Franco, and E. Alves, *Nucl. Instrum. Methods Phys. Res. B* **249**, 358 (2006).
- <sup>13</sup>K. Lorenz, R. Vianden, R. Birkhahn, A. J. Steckl, M. F. da Silva, J. C. Soares, and E. Alves, *Nucl. Instrum. Methods Phys. Res. B* **161–163**, 946 (2000).
- <sup>14</sup>K. Wang, R. W. Martin, K. P. O'Donnell, V. Katchkanov, K. Lorenz, E. Alves, S. Ruffenach, and O. Briot, *Appl. Phys. Lett.* **87**, 112107 (2005).
- <sup>15</sup>L. Bodiou, A. Braud, J.-L. Doualan, R. Moncorgé, J. H. Park, C. Munasinghe, A. J. Steckl, K. Lorenz, E. Alves, and B. Daudin, *J. Appl. Phys.* **105**, 043104 (2009).
- <sup>16</sup>K. Lorenz, N. P. Barradas, E. Alves, I. S. Roqan, E. Nogales, R. W. Martin, K. P. O'Donnell, F. Gloux, and P. Ruterana, *J. Phys. D: Appl. Phys.* **42**, 165103 (2009).
- <sup>17</sup>N. Woodward, A. Nishikawa, Y. Fujiwara, and V. Dierolf, “Site and sample dependent electron-phonon coupling of Eu ions in epitaxial-grown GaN layers,” *Opt. Mater.* (to be published).