APPLIED PHYSICS LETTERS **88**, 011111 (2006)

Site specific Eu^{3+} stimulated emission in GaN host

J. H. Park and A. J. Steckl[a)]
Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030

(Received 29 September 2005; accepted 5 December 2005; published online 4 January 2006)

We report the observation of *site-specific* Eu^{3+} stimulated emission in GaN:Eu laser structures. Two main Eu sites have been identified from emission peaks associated with the $^5D_0 \rightarrow {}^7F_2$ transition during above band gap optical pumping with a pulsed N_2 laser (337 nm): (a) Eu_x emitting at ~620 nm—present in short cavities (~100 μm), exhibiting stimulated (side) emission threshold and a fast decay time constant (30–35 μs); (b) Eu_y emitting at ~621 nm—present in long cavities (~7 mm) and in surface emission, exhibiting no stimulated emission threshold and a slow decay time constant (150–250 μs). *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2161159]

Rare earth doped GaN (and related III–N alloys) have been reported[1,2] to be very versatile emitters of light at wavelengths covering the visible and near infrared (IR) range. In particular, Eu-doped GaN has been shown[3] to be an excellent choice for red emission ($\lambda \approx 620$ nm). This has led to a significant effort on the part of several groups to understand and model the mechanisms for photoemission in the GaN:Eu system using various techniques: (a) spectral photoluminescence (PL), PL excitation, and time-resolved photoluminescence (TRPL);[4–6] (b) Fourier transform IR spectroscopy;[7,8] (c) extended x-ray absorption fine structure (EXAFS) analysis;[9] (d) excitation energy emission spectroscopy.[10] Most of the mechanisms investigations were carried out on samples grown using molecular beam epitaxy (MBE). In addition, luminescence studies of GaN:Eu grown by interrupted growth epitaxy[11–13] (IGE) and Eu-implanted GaN (Ref. 14) have been reported. Many of the spectroscopy studies report the presence of multiple Eu sites with different emission spectra.

Recently, stimulated emission from Eu-doped GaN on sapphire[15] and silicon[16] substrates has been demonstrated. The emission spectra indicated that the peak wavelength was constant at ~620 nm below and above threshold. The peak wavelength of lasing emission is shifted by ~1 nm compared to that of the PL spectrum. In this letter, we report on an effort to identify the Eu site responsible for lasing.

GaN:Eu samples were grown on sapphire substrates by solid source (MBE) with a N_2 plasma source. An AlN buffer layer was grown for 5 min followed by the growth of GaN:Eu active layer for 1 h. Finally, an AlN capping layer was grown for 5 min. To investigate the effect of the different III–V ratios on the emission characteristics the Ga flux was varied from 2.5 to 4.5×10^{-7} Torr. The other growth parameters were kept constant: substrate and Eu cell temperature of 800 and 470 °C, and N_2 gas flow of 1.8 sccm. The total film thickness is approximately 500 nm for all samples.

Channeling Rutherford back-scattering (RBS/C) measurements have indicated[17,18] that for most GaN:RE^{3+} materials the great majority (>80%–90%) of RE^{3+} ions are located on Ga-substitutional sites. However, for GaN:Eu^{3+} both RBS/C (Ref. 19) and EXAFS (Ref. 9) measurements have revealed that most Eu^{3+} ions are located in *near* Ga-substitutional locations, with a displacement from the Ga site of 0.2 Å along the *c* axis. Optical studies have also indicated the presence of several Eu sites with different emission spectra and with significantly different lifetimes.[12,14,20] Each reported Eu site exhibited a peak shift from the standard $^5D_0 \rightarrow {}^7F_2$ wavelength, distinct lifetime characteristics and a different excitation mechanism. The number of Eu sites also depends on the incorporation method and growth conditions. For example, Eu implanted into GaN has been shown[20] to occupy two distinct sites. One site (with main emission peaks at ~621.8, 622.6 nm) is located on the Ga sublattice, while the second site (~620.8 nm) that has a larger effective excitation cross section is located in a more distorted local environment. Eu *in situ* doped during GaN growth by conventional solid state MBE on Si has also been reported[4] to have two distinct Eu^{3+} sites, evidenced by the presence of different $^5D_0 \rightarrow {}^7F_2$ peaks (622.3 and 624.9 nm) with above band gap and near-resonant excitation, which also exhibit different decay constants.

To investigate the peak shift of stimulated emission, we developed the variable virtual cavity (VVC) method, which is based on the variable stripe length[21] method utilized in the measurement of optical gain. In this method a pump beam forms a virtual cavity incident on the top surface of the sample. The resulting Eu emission is measured either at the cavity side (side emission) or top surface (top emission). The principle of this method is to control the side emission from the sample by the adjustment of optical pump beam size on the sample surface with a variable slit. For relatively large pump beam dimensions and long virtual cavities, the side emission measured includes edge emission from the GaN:Eu layer as well as emission reflected from the top surface and the substrate. For very small virtual cavity dimensions, the side edge emission measured contains only the edge emission from the GaN:Eu layer. The side emission was collected by a 10× objective lens and analyzed with a 0.5 m spectrometer. The sample was pumped by N_2 laser (337.1 nm, 600 ps). A more detailed description of emission related to beam size has been previously reported.[15]

Figure 1(a) shows the side emission spectrum from a 100 μm virtual cavity using a GaN:Eu sample grown with a Ga flux of 3.6×10^{-7} Torr. The side emission measured from this short cavity consists predominantly of emission from the cavity edge, with a peak wavelength of ~619.9 nm. The dashed lines in Fig. 1(a) are Gaussian profiles fit to the experimental data. The side spectrum from a 7 mm long cavity

---

[a)] Author to whom correspondence should be addressed; electronic mail: a.steckl@uc.edu

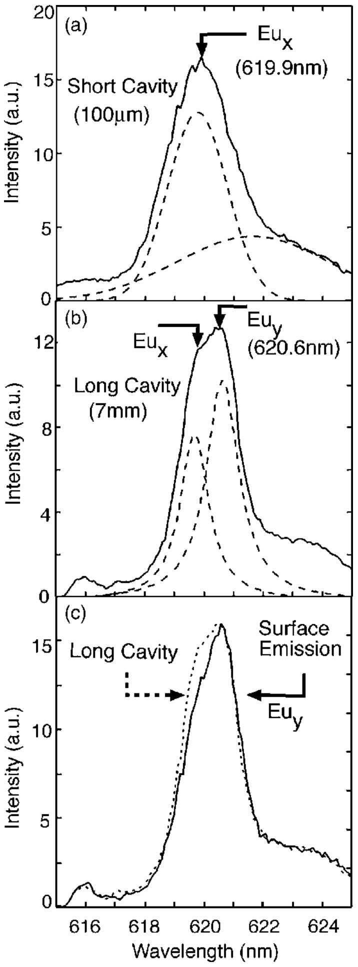

FIG. 1. Emission spectra from: (a) the side of the GaN:Eu structure for short (100 μm—Eu$_x$) cavity; dashed lines are Gaussian fit curves; (b) the side of the GaN:Eu structure for long (7 mm—Eu$_x$) cavity; dashed lines are Gaussian fit curves; and (c) the edge of the long cavity and surface emission with N$_2$ laser.

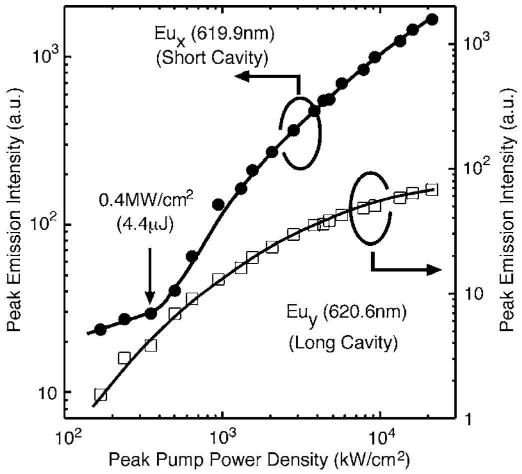

FIG. 2. Eu$_x$ and Eu$_y$ peak intensity as a function of peak pump power density. Only Eu$_x$ shows a threshold for stimulated emission, at ~400 kW/cm^2 (4.4 μJ).

is shown in Fig. 1(b). Fitting of the spectrum with Gaussian profiles indicates the presence of two closely spaced but distinct Gaussian distributions: (a) a small peak with a wavelength identical to that of short cavity (619.9 nm) and (b) a larger peak with a wavelength of 620.6 nm. The two peaks indicate the presence of two different Eu sites in the GaN host. We have assigned as Eu$_x$ the site with emission at 619.9 nm and as Eu$_y$ the site with emission at 620.6 nm. Figure 1(c) shows the comparison of spectra obtained from long cavity side emission [also shown in Fig. 1(b)] and surface emission. Whereas side emission from the long cavity contains both Eu$_x$ and Eu$_y$ peaks, surface emission exhibits only the Eu$_y$ peak. Interestingly, PL spectra obtained with conventional low power continuous wave above band gap optical pumping (He–Cd laser, 325 nm) show the same peak at 620.6 nm as the surface emission obtained with high peak power pumping (N$_2$ laser). Since the PL emission obtained with above band gap GaN:Eu excitation is generally considered to be due to the majority of Eu^{3+} ions (which are located on Ga sites), the results shown in Fig. 1 point to Eu$_y$ emission being linked to the Ga-substitutional Eu site. We, therefore, tentatively assign the Eu$_x$ site to an environment different from the Ga-substitutional location of Eu$_y$, where different local fields and symmetry yield a slightly higher $^5D_0 \rightarrow {}^7F_2$ transition energy ($\Delta E \approx 2$ meV) occurring at 619.9 nm. As discussed later, these assignments are supported by associated lifetime characteristics.

In order to investigate the site dependence of stimulated emission, we measured the side emission intensity of Eu$_x$ and Eu$_y$ peaks as a function of pump power dependence. For emission from the Eu$_x$ site we used the 619.6 nm peak from the 100 μm cavity [Fig. 1(a)] and for the Eu$_y$ site emission we used the 620.6 nm peak from the 7 mm long cavity [Fig. 1(b)]. Figure 2 shows that the two sites experience a different dependence on the pumping power. Emission from the Eu$_x$ site exhibits a threshold for stimulated light at 0.4 MW/cm^2, whereas the Eu$_y$ site emission increases continuously with peak pumping power. This indicates that only the Eu$_x$ site contributes to stimulated emission in Eu-doped GaN thin films. These results point to the advantage of developing growth techniques such as IGE that can selectively enhance Eu incorporation[22] into certain sites.

Figure 3 illustrates the usefulness of the VVC method. The side emission from very short cavities contains only edge emission from the GaN:Eu thin film, in other words the contribution from the Eu$_x$ site emission at ~619.9 nm. As the virtual cavity length increases, however, the peak wavelength of side emission increases due to increasing contribution from the Eu$_y$ sites (~620.6 nm). Therefore, we are able

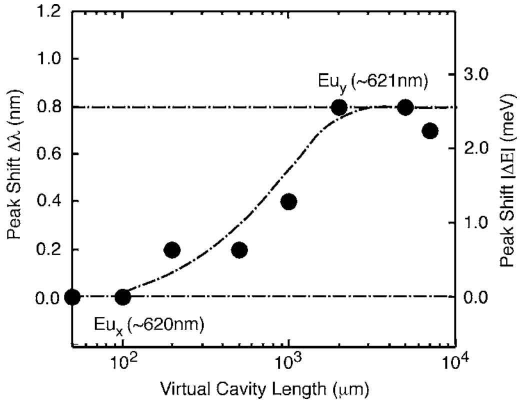

FIG. 3. Eu emission peak wavelength shift as a function of virtual cavity length. The Eu$_x$ site dominates side emission from short cavities, whereas emission from long cavities and the top surface (PL) is dominated by the Eu$_y$ site.

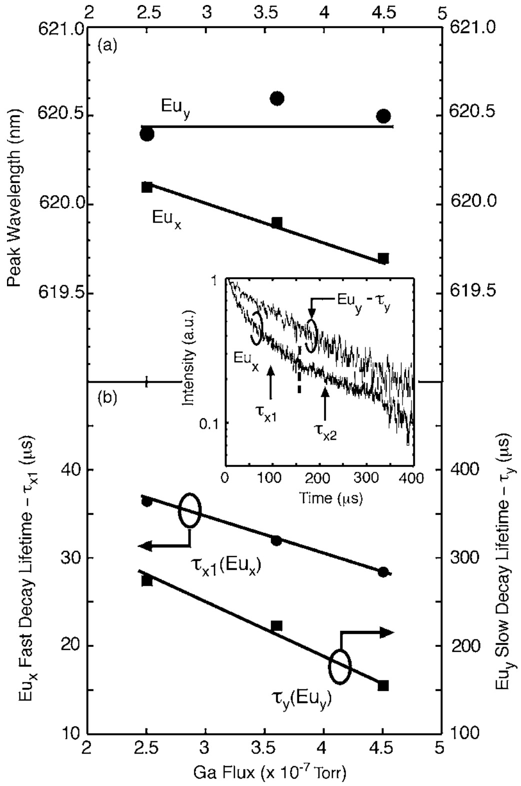

FIG. 4. The effect of Ga flux during GaN:Eu MBE growth on: (a) peak emission wavelength of Eu_x and Eu_y sites and (b) emission decay time constants from Eu_x and Eu_y sites.

to separate transitions from the two sites by controlling the beam size on the sample surface.

Additional insight into the Eu sites can be gained by studying their dependence on the Ga flux during growth of the GaN:Eu layer. The Ga flux dependence of the emission wavelength from each site is shown in Fig. 4(a). The wavelength of the Eu_y site emission is independent of the Ga flux, whereas the wavelength of Eu_x emission decreases with Ga flux, showing an increasing difference from the Eu_y emission. The constant wavelength of the Eu_y site suggests that it preserves the same physical location in the GaN host. On the other hand, the fact that the Eu_x emission wavelength varies with Ga flux indicates that the physical location of the Eu_x site in the GaN host is influenced by the Ga flux. As the Ga flux increases not only are fewer Ga vacancies available for Eu substitution but also fewer N vacancies are present due to increasing Ga–N bonding opportunities. This in turn could force Eu ions into slightly different interstitial locations. Figure 4(b) shows the PL decay time constant of each site as a function of Ga flux. The insert shows the emission intensity time decay characteristics of each site in the sample grown with Ga flux of 3.6×10^{-7} Torr. The Eu_y site exhibits a single exponential decay with $\tau_y\approx224$ μs decay time constant. The Eu_x site experiences a more complex decay behavior. Fitting the time dependence of Eu_x emission to a biexponential decay revealed a fast decay component with a time constant $\tau_{x1}\approx32$ μs and a slow decay component with a time constant $\tau_{x2}\approx240$ μs (which is close to the value of τ_y). The existence of a fast decay time constant is another indication that the physical location of the Eu_x site is different from that of Eu_y site. These decay constants are surprisingly close to the GaN:Eu results reported[4] by Nyein *et al.* with conventional TRPL: τ_{x1} and τ_{x2} are a good match for the biexponential decay which they obtain for above band gap excitation ($\tau_{\text{fast}}\approx30$ μs and $\tau_{\text{slow}}\approx240$ μs), while τ_y is a good match for their below band gap excitation single exponential decay ($\tau\approx240$ μs). Interestingly, the value of τ_{x1} is also nearly the same as that obtained by Lee *et al.*[23] for the nonradiative back transfer process between Eu^{3+} ions and a trap state in GaN ($\tau_{\text{IE}}\approx36$ μs). Surprisingly, the decay constants of both sites decrease with increasing Ga flux. Based on simple energy transfer considerations, one can interpret the reduction in decay time constant as being due to an exponential decrease in the activation energy of the process given by $1/\tau=(1/\tau_0)e^{-\frac{\Delta E}{kT}}$. The energy reduction is calculated to be ~6.5 meV for the fast Eu_x decay and ~15.4 meV for the slow decay of Eu_x and for Eu_y. These are relatively large values in comparison to the activation energy of the Eu-trap forward transfer calculated[23] by Lee *et al.* A more complete understanding of the energetics of the Eu_x and Eu_y sites requires temperature dependent and excitation energy dependent measurements.

This work was supported in part by the U. S. Army Research Office (No. DAAD19-03-1-0101). The authors acknowledge the support, encouragement, and many technical discussions with J. M. Zavada.

[1] A. J. Steckl and J. M. Zavada, Mater. Res. Bull. **24**, 33 (1999).
[2] A. J. Steckl, J. C. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Wang, and R. A. Jones, IEEE J. Sel. Top. Quantum Electron. **8**, 749 (2002).
[3] J. C. Heikenfeld, M. Garter, D. S. Lee, R. Birkhahn, and A. J. Steckl, Appl. Phys. Lett. **75**, 1189 (1999).
[4] E. Nyein, U. Hommerich, J. Heikenfeld, D. S. Lee, A. J. Steckl, and J. M. Zavada, Appl. Phys. Lett. **82**, 1655 (2003).
[5] U. Hommerich, E. Nyein, D. S. Lee, J. Heikenfeld, A. J. Steckl, and J. M. Zavada, Mater. Sci. Eng., B **105**, 91 (2003).
[6] C. W. Lee, H. O. Everitt, D. S. Lee, A. J. Steckl, and J. M. Zavada, J. Appl. Phys. **95**, 7717 (2004).
[7] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, and E. Yagi, Phys. Status Solidi B **228**, 318 (2001).
[8] Z. Li, H. Bang, G. Piao, J. Sawahata, and K. Akimoto, J. Cryst. Growth **240**, 382 (2002).
[9] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, and E. Yagi, J. Cryst. Growth **237–239**, 1027 (2002).
[10] H. Y. Peng, C. W. Lee, H. O. Everitt, D. S. Lee, A. J. Steckl, and J. M. Zavada, Appl. Phys. Lett. **86**, 051110 (2005).
[11] C. Munasinghe, A. J. Steckl, E. Nyein, U. Hommerich, H. Y. Peng, H. O. Everitt, Z. Fleischman, V. Dierolf, and J. M. Zavada, Mater. Res. Soc. Symp. Proc. **866**, 41 (2005).
[12] E. Nyein, U. Hommerich, C. Munasinghe, A. J. Steckl, and J. M. Zavada, Mater. Res. Soc. Symp. Proc. **866**, 67 (2005).
[13] V. Dierolf, Z. Fleischman, C. Sandmann, A. Wakahara, T. Fujiwara, C. Munasinghe, and A. J. Steckl, Mater. Res. Soc. Symp. Proc. **866**, 73 (2005).
[14] K. Wang, R. W. Martin, K. P. O'Donnell, V. Katchkanov, E. Nogales, K. Lorenz, E. Alves, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **87**, 112107 (2005).
[15] J. H. Park and A. J. Steckl, Appl. Phys. Lett. **85**, 4588 (2004).
[16] J. H. Park and A. J. Steckl, J. Appl. Phys. **98**, 056108 (2005).
[17] 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).
[18] E. Alves, K. Lorenz, R. Vianden, C. Boemare, M. J. Soares, and T. Monteiro, Mod. Phys. Lett. B **15**, 1281 (2001).
[19] 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).
[20] L. Bodiou, A. Braud, J.-L. Doualan, R. Moncorge, K. Lorenz, and E. Alves, Opt. Mater. (Amsterdam, Neth.) (in press).
[21] K. L. Shaklee, R. E. Nahory, and R. F. Leheny, J. Lumin. **7**, 284 (1973).
[22] C. Munasinghe and A. J. Steckl, Thin Solid Films **496**, 636 (2006).
[23] C. W. Lee, H. O. Everitt, D. L. Lee, A. J. Steckl, and J. M. Zavada, J. Appl. Phys. **95**, 7717 (2004).