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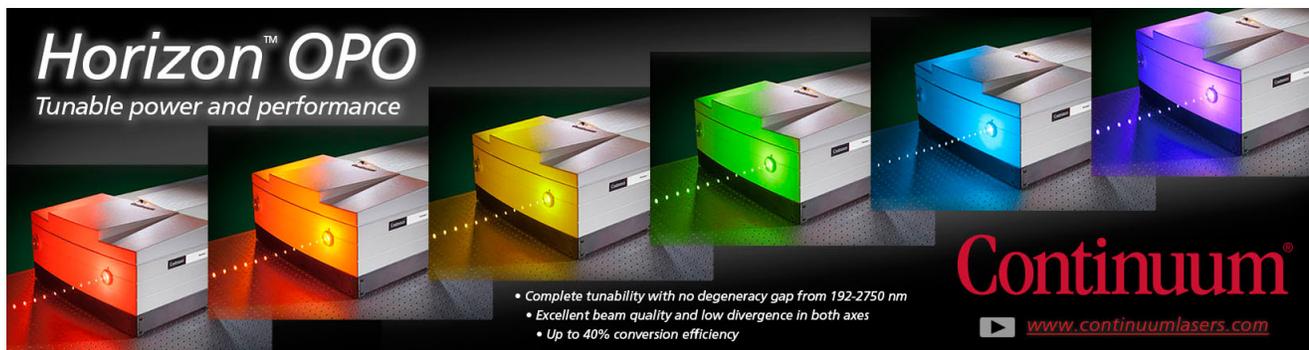
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Selectively excited photoluminescence from Eu-implanted GaN

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The intensity of Eu-related luminescence from ion-implanted GaN with a 10 nm thick AlN cap, both grown epitaxially by metal organic chemical vapor deposition (MOCVD) is increased markedly by high-temperature annealing at 1300 °C. Photoluminescence (PL) and PL excitation (PLE) studies reveal a variety of Eu centers with different excitation mechanisms. High-resolution PL spectra at low temperature clearly show that emission lines ascribed to ${}^5D_0\text{-}{}^7F_2$ (~622 nm), ${}^5D_0\text{-}{}^7F_3$ (~664 nm), and ${}^5D_0\text{-}{}^7F_1$ (~602 nm) transitions each consist of several peaks. PL excitation spectra of the spectrally resolved components of the ${}^5D_0\text{-}{}^7F_2$ multiplet contain contributions from above-band-edge absorption by the GaN host, a GaN exciton absorption at 356 nm, and a broad sub-edge absorption band centred at ~385 nm. Marked differences in the shape of the ${}^5D_0\text{-}{}^7F_2$ PL multiplet are demonstrated by selective excitation via the continuum/exciton states and the below gap absorption band. The four strongest lines of the multiplet are shown to consist of two pairs due to different Eu^{3+} centers with different excitation mechanisms. © 2005 American Institute of Physics. [DOI: 10.1063/1.2045551]

In recent years, GaN doped with rare earth (RE) elements has become attractive because of the higher efficiency of its room temperature luminescence when compared with that of narrow band semiconductor hosts.¹⁻³ The most prominent Eu-related luminescence occurs in the red spectral range around 620 nm and is ascribed to the *intra-4f* shell ${}^5D_0\text{-}{}^7F_2$ transition. While InGaN-based devices are suitable UV-blue-green light emitters they are much less efficient for red emission.⁴ Eu-doped GaN offers a potential alternative for red light emission from a III-nitride device structure. However, although GaN:Eu devices have been demonstrated,^{1-3,5} the Eu^{3+} lattice location and the detailed energy transfer process from host to dopant in GaN are still open questions.

The majority of Eu ions in GaN host appear to occupy Ga substitutional sites, as might be expected,⁶ although a recent Rutherford backscattering study indicates that some Eu ions may be displaced by a small amount from the on-site position.⁷ Nyein *et al.* have inferred the existence of different Eu-related optically active centers from the observation that the PL decay dynamics and thermal quenching process depend on the energy of excitation.⁸ PL excitation (PLE) measurements on the 622 nm emission by the same group revealed five absorption lines in the spectral region from 570 to 590 nm associated with the ${}^7F_0\text{-}{}^5D_0$ transition. Selective excitation of PL by resonant pumping into these lines changed the envelope of the 620 nm spectral emission, although individual lines were not resolved.⁹

In addition to the resonant excitation of Eu ion, PL excitation is also a useful technique to study the excitation transfer from the host GaN, via such processes as carrier-mediated excitation, resonant excitation by excitons, and defect-mediated excitation. For example, PLE studies of GaN:Eu at 300 K identified the existence of a broad subgap absorption band at ~400 nm.⁸ By using the systematic ap-

proach of combined excitation-emission spectroscopy (CEES), Dierolf *et al.* present a detailed assignment of PL and PLE peaks for two dominant Er^{3+} sites and several minor ones in GaN:Er.¹⁰ The identified sites differ strongly in their excitation and energy transfer efficiencies.

In this letter we present new PLE and selectively excited PL results on the fine structure of the ${}^5D_0\text{-}{}^7F_2$ multiplet in Eu:GaN which show that the four main lines resolve into two distinct pairs. One pair is selectively excited via a broad absorption band centred near 385 nm indicating that different excitation mechanisms and different types of optically active Eu ions coexist within the sample.

Epilayers of GaN, approximately 2 μm thick, were grown by MOVCD on *c*-plane sapphire at 1090 °C following a low temperature GaN buffer layer. They were capped with a 10 nm thick monocrystalline layer of AlN, grown epitaxially at 1160 °C. Eu ions were implanted at normal incidence through the cap at 500 °C using an energy of 300 keV and a fluence of 2×10^{15} at/cm². The AlN cap allowed the implanted samples to be annealed for 20 min at the very high temperature of 1300 °C in a conventional tube furnace with a moderate overpressure of 4 bar nitrogen gas. The structural properties of the samples and the increased optical activation of the Eu ions compared to samples annealed at low temperature were reported previously.¹¹

PL and PLE spectra were recorded from samples maintained at approximately 15 K in a closed-cycle helium cryostat. The luminescence was analyzed by a 0.67 m focal length monochromator and detected using a cooled photomultiplier tube. The excitation source for PLE was a 1000 W short arc xenon lamp combined with a 0.25 m focal length monochromator. The incident power on the sample averages 0.6 mW on a surface area of about 2×5 mm². PLE spectra were obtained by fixing the detection monochromator at the peak of a particular emission line and scanning the excitation

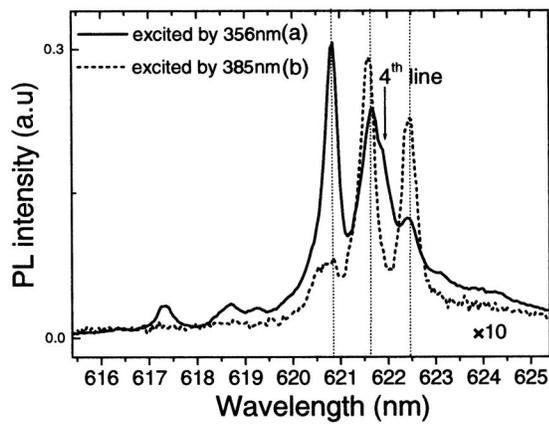


FIG. 1. 15 K PL spectra of AlN-capped GaN implanted with 2×10^{15} Eu/cm², after annealing at 1300 °C. Excited above band gap (solid line) and below band gap (dotted line) by a xenon lamp.

monochromator. The spectral resolution in the emission spectra was ~ 0.1 nm and that in the excitation spectra was ~ 4 nm. Selectively excited PL spectra were obtained using the Xe lamp with the excitation monochromator set at particular wavelengths. All the PLE spectra were corrected for the output of the xenon lamp and the throughput of the excitation monochromator, and normalized to the intensity of a PLE peak at 356 nm, which was a common feature of all PLE spectra.

A typical Eu³⁺ PL spectrum for excitation at 356 nm (3.48 eV) is shown in Fig. 1(a). The PL spectrum shows three main peaks, at 620.8 nm, 621.7 nm, 622.5 nm and three minor peaks are resolved at 617.2 nm, 618.7 nm, and 619.3 nm on the shorter wavelength side of the main peaks. Shoulders also appear in the wavelength range 623–625 nm. The first main peak at 620.8 nm is the dominant emission with full-width at half maximum (FWHM) 0.4 nm, and the third line at 622.5 nm is weak. More interestingly, the middle line is seen to consist of two components with a peak at 621.7 nm and a shoulder at 621.9 nm. In previously published works, only the three main peaks with a broadened middle peak have been reported and the splitting of the central peak has not been clear.^{7,8} Our results show the emission due to the 5D_0 - 7F_2 transition to consist of 4 main emission lines.

Normalized PLE spectra taken at the three main emission peaks (Fig. 2) clearly demonstrate above-gap excitation (below ~ 355 nm) and an excitonlike absorption peak at 356 nm (3.48 eV). The main difference between the three PLE traces is the appearance of a broad excitation band from 360 nm to 410 nm centered at about 385 nm for the emission lines at 621.7 nm (unresolved doublet) and 622.5 nm (singlet). Some weak structures can also be observed within this band at ~ 372 nm and ~ 385 nm. The PLE spectrum detected at 621.7 nm collects light from two emission peaks to produce an excitation spectrum, which is roughly the average of the other two. Hence, only the line pair at 621.7 nm and 622.5 nm is excited in the broad band. It is interesting to note further that PL spectra of luminescent Eu:Ga₂O₃ samples generally show a set of near-band-edge luminescence peaks in the wavelength range from 370 nm to 400 nm.¹²

Figure 1(b) confirms that the PL spectrum excited below the bandgap is markedly different from the spectrum excited at 356 nm. The line at 620.8 nm is now the weakest of the

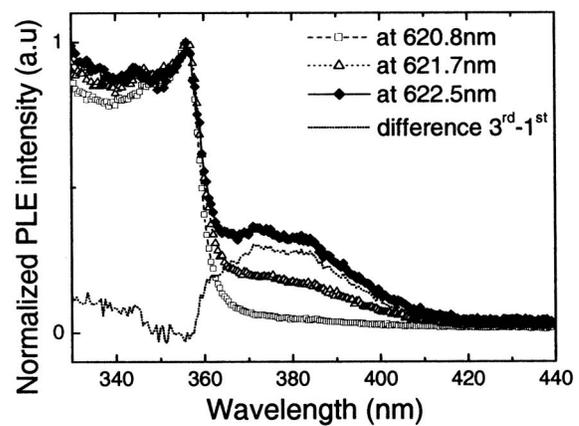


FIG. 2. 15 K normalized PLE spectra of AlN-capped GaN implanted with 2×10^{15} Eu/cm², after annealing at 1300 °C, detected at the three main peaks, 620.8 nm, 621.7 nm, and 622.5 nm. Also shown (dotted line) is the difference between the first and last PLE spectra.

four and the peak at 622.5 nm is enhanced. Moreover, the middle peak becomes much sharper and is slightly blue-shifted to 621.6 nm. This is due to the selective enhancement of one of the pair of unresolved lines. The minor peaks in the shorter wavelength range from 617 nm to 620 nm disappear completely from the PL spectrum, and the intensity of the shoulders in the longer wavelength range from 623 nm to 625 nm is also reduced.

The PLE and PL results discussed above provide information about the different energy transfer processes in Eu:Ga₂O₃. First, band to band Ga₂O₃ absorption followed by carrier-mediated energy transfer to the Eu ions leads to the intra $4f$ shell transition with subsequent light emission. Secondly, excitation of luminescence from the Eu ions via a process involving the Ga₂O₃ bound exciton peak at 356 nm is a feature common to all the PLE spectra, as shown by Fig. 2. Thirdly, a pair of PL emission lines at 621.6 nm and 622.5 nm can be excited below the band gap at ~ 385 nm, indicating an excitation pathway involving defect levels or complexes associated with a fraction of Eu ions. It is interesting to note that a broad absorption band at ~ 400 nm, observed for Er-implanted Ga₂O₃,¹³ can be enhanced by Mg co-doping which selectively increases the intensity of emission at 1554.8 nm from one of the Er³⁺ centers in Ga₂O₃.¹⁴ For Eu doped Ga₂O₃, the control of defect levels within the Ga₂O₃ band gap by, for example, co-doping could possibly be used to increase the efficiency of Eu related luminescence.

To make clear the relationship between the 4 main emission lines near 622 nm, different excitation sources, viz., He-Cd laser at 325 nm, argon ion laser at 364 nm and 457 nm, xenon lamp at 356 nm and 385 nm, have been used to excite the sample. Fitting four Lorentzian peaks to these PL spectra confirms that the peaks can be divided into two pairs whose intensities are correlated. Figure 3 shows the intensities of the four peaks for the different excitation sources. The integrated intensity is normalized to the intensity at 620.8 nm for each excitation source. The intensities of the pair at 620.8 and 621.9 nm follow roughly parallel lines and are clearly related. The intensities of the pair at 621.6 and 622.5 nm follow a similar trend, but one that is markedly different from the first pair.

The observation of two pairs of PL emission peaks and the excitation band below the band gap at ~ 385 nm demon-

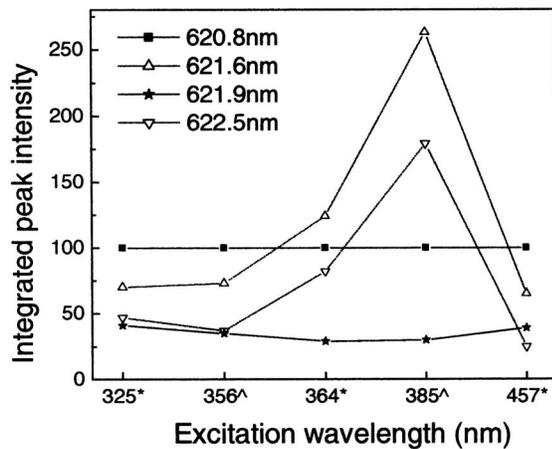


FIG. 3. Integrated PL peak intensity for different excitation sources. The intensity is calculated from a fitting of four Lorentzian peaks to each of the PL spectra and is normalized to the intensity at 620.8 nm for each excitation source. (* refers to laser excitation and ^ refers to lamp excitation.)

strates direct evidence of at least two kinds of luminescent Eu ion sites in the GaN host. Eu ions at one set of sites are responsible for the 620.8 nm and 621.9 nm PL peaks and can be excited mainly by interband absorption of the host. Their luminescence efficiency is very low when excited through the broad excitation band below band gap. However Eu³⁺ ions at the other set of sites, corresponding to the 621.6 nm and the 622.5 nm PL peaks, can be efficiently excited not only by interband absorption but also by the broad excitation band below band gap.

It is expected that the 4f shell energy levels of Eu ions at both sets of Eu³⁺ sites would be further split by the crystal field. Thus, it is possible that the observed emission structure is a mixture of emission lines from different RE sites, each split by the crystal field. If Eu³⁺ ions occupy substitutional Ga sites, which have C_{3v} symmetry, the ⁵D₀ level is nondegenerate and the ⁷F₂ level is predicted to be split into three levels by the crystal field.¹⁵ This means that three emission lines from one kind of Eu³⁺ ions are possible. Since there are at least two kinds of Eu sites, the emission lines may fall on top of each other, like the middle peak in Fig. 1(a).

Temperature dependent measurements show different thermal quenching behavior for the three peaks in our previous work,¹² and also consistent with the results in the report by Nyein *et al.*⁸ We have also investigated selectively excited PL in the regions near 664 nm (⁵D₀-⁷F₃) and 602 nm (⁵D₀-⁷F₁) and seen effects similar to those for ⁵D₀-⁷F₂, with

the relative strength of the lines within the observed multiplets strongly modified when the excitation energy is changed from above to below the GaN band gap.

In summary, we have studied PL and PL excitation spectra of Eu-implanted and high-temperature annealed GaN with an AlN capping layer. The dependence of the PL spectra on the excitation mode (above band gap excitation and below band gap excitation) reveals contributions of at least two kinds of optically active Eu³⁺ centers to the emission near 622 nm. PL excitation spectra demonstrate that one kind of Eu center is excited following a broad absorption band centered at around ~385 nm. These results clearly confirmed the existence of different Eu³⁺ centers with distinct contribution to the main emission at 622 nm. Further work has to be done to make clear the origin of these Eu³⁺ centers in order to optimize the red luminescence.

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