Eu–Mg defects and donor–acceptor pairs in GaN: photodissociation and the excitation transfer problem

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Abstract
We have investigated the temperature-dependent photoluminescence (TDPL) profiles of Eu\(^{3+}\) ions implanted in an HVPE-grown bulk GaN sample doped with Mg and of donor–acceptor pairs (DAP) involving the shallow Mg acceptor in GaN(Mg) (unimplanted) and GaN(Mg):Eu samples. Below 125 K, the TDPL of Eu\(^{3+}\) in GaN(Mg):Eu correlates with that of the DAP. Below 75 K, the intensity of Eu\(^{3+}\) emission saturates, indicating a limitation to the numbers of Eu–Mg defects available to receive excitation transferred from the host, while the DAP continues to increase, albeit more slowly in the implanted than the unimplanted sample. Prolonged exposure to UV light at low temperature results in the photodissociation of Eu–Mg defects in their Eu\(_1\)(Mg) configuration, with a corresponding increase in shallow DAP emission and the emergence of emission from unassociated Eu\(_{Ga}\) (Eu2) defects.

Keywords: photoluminescence, energy transfer, gallium nitride, rare earth

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

Rare-earth (RE)-doped wide bandgap semiconductors have potential applications in light emitting diodes and display devices [1–4]. When incorporated in III-nitride semiconductors, RE\(^{3+}\) ions exhibit characteristic sets of sharp \textit{intra-4f shell} emission lines; Eu-doped GaN attracts special attention for intense red emission near 621 nm, due to \(^{5}D_{0} \rightarrow ^{7}F_{2}\) multiplet transitions [5–10]. In recent years, a number of studies have shown that Mg co-doping of GaN:Eu significantly increases the luminescence intensity of samples measured at room temperature [11, 12]. For example, Sekiguchi et al have compared the quantum efficiencies of GaN:Eu and GaN(Mg):Eu samples which were found to be 6.8\% and 77\%, respectively [13]. In the absence of Mg, Eu-implanted GaN features two main luminescence centres, which we call Eu2 (Eu\(_{Ga}\), the unassociated ‘prime’ defect [14]) and Eu1 (Eu\(_{Ga},X\), where \(X\) is a lattice defect, possibly a nitrogen vacancy [8]). In contrast to GaN:Eu, which shows Eu\(^{3+}\) emission from many different ‘RE sites’ [15], the photoluminescence (PL) spectrum of ion-implanted GaN(Mg):Eu is apparently dominated by emission from a single, albeit photochromic centre with a unique set of emission lines at room temperature, labelled Eu0 [9]; a variety of experimental results indicates that the Eu0...
defect comprises a single Mg atom in close association with an Eu2 defect [9, 16].

The luminescence of Eu$^{3+}$ is often excited indirectly through energy transfer (ET) from the GaN host, necessarily so in electroluminescence (EL) applications, but also by photoexcitation with above-bandgap or near-bandgap light [6]; several mechanisms for ET have been proposed: RE-defect-related Auger excitation [17, 18]; excitation through charge transfer states of Eu$^{3+}$/Eu$^{2+}$ ions [19–21]; excitation via bound excitons [22]; Mishra et al [23] proposed ET from donor–acceptor pairs (DAP) to Eu$^{3+}$; Mitchell et al [8] further speculated that ET from DAP, formed either by unintentionally doped oxygen O$_N$ and V$_{Ga}$, or by V$_N$ and V$_{Ga}$, might be responsible for emission from Eu2 and Eu1 defects, respectively. However, to the best of our knowledge, there is only a single report [24] that provides spectroscopic evidence of deep-level interaction with Eu$^{3+}$ by demonstrating the below-gap photoluminescence excitation (PL/E) of a single sample.

In this paper, we have investigated and compared TDPL of Eu$^{3+}$ ions in GaN(Mg):Eu and of DAP in GaN(Mg) and GaN(Mg):Eu. Our investigation shows that below 125 K, TDPL of Eu$^{3+}$ in GaN(Mg):Eu correlates with that of the DAP, suggesting a competition between DAP emission and excitation transfer to Eu$^{3+}$ ions. Prolonged UV light exposure at low temperature partially converts Eu–Mg centres to Eu2 through light-induced Mg migration. The Eu–Mg centres recover to a great extent after sample reannealing.

2. Methods

2.1. Sample preparation

A freestanding Mg-doped GaN sample, measuring 1 cm $\times$ 0.4 cm $\times$ 0.5 mm, was grown by hydride vapour phase epitaxy (HVPE) at Kyma Technologies, USA. The Mg doping level, measured by secondary ion mass spectrometry, averages $3 \times 10^{18}$ Mg cm$^{-3}$. In addition to Mg, the sample is also unintentionally doped with Si to a concentration of $\sim 1 \times 10^{15}$ atoms cm$^{-3}$. The concentrations of other unintentional dopants, for example, O, H and Fe, were below the detection limits of SIMS. The sample was implanted with Eu ions along the surface normal to a fluence of $2 \times 10^{13}$ cm$^{-2}$@300 keV, resulting in a maximum Eu concentration, $\sim$50 nm below the surface, of $\sim 3 \times 10^{18}$ cm$^{-3}$, closely matching the mean Mg level. To repair implantation damage, the sample was annealed at high temperature and pressure (HTHP): 1673 K, 10 GPa of N$_2$; during annealing, the sample surfaces were covered with bulk GaN powder to prevent the out-diffusion of nitrogen.

2.2. Optical measurements

Samples were mounted in a closed-cycle helium cryorefrigerator with base temperature of 12.5 K. TDPL spectra of GaN(Mg) and GaN(Mg):Eu were recorded during the cooling cycle at a 1 K temperature interval with a cooling rate of $\sim$6 K min$^{-1}$. PL excitation used either a 355 nm CW laser (with maximum power of 20 mW in a 1.5 mm spot) or a 1 kW Xe lamp filtered through a 1/4-m monochromator with $\lambda_{exc}$ = 350, 354 and 362 nm. Luminescence was dispersed using two monochromators (Andor Shamrock (model No.: SR-163) and McPherson (207)) in order to capture emission over the full visible range (350-750 nm) and in a 15 nm window around 622 nm, resolving the closely spaced $^5D_0 \rightarrow ^7F_2$ emission lines from Eu$^{3+}$ ions in different defects/defect configurations. Spectra were recorded using cooled 1024 $\times$ 127 pixel CCD cameras with effective spectral resolutions of about 1 nm and 0.04 nm, respectively and digital (pixel) resolutions of 0.4 nm and 0.015 nm, respectively.

3. Results

3.1. TDPL of Eu–Mg defects in GaN(Mg):Eu

Figure 1 shows the TDPL spectra of the GaN(Mg):Eu sample recorded during a cooling run from 295 to 14 K under 354 nm, 8 mW cm$^{-2}$ excitation, corresponding to a photon flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$. The RT PL spectrum comprises a weak near-band-edge emission, with a wavelength peak of $\sim$383 nm (3.24 eV), a green emission band, peaking at $\sim$530 nm (2.34 eV), corresponding to native GaN lattice defects, and strong Eu$^{3+}$ emission from the Eu0 defect, with its main peak at 618.9 nm (2.004 eV).

In the temperature range from 295 K to base temperature, the intensity of all bands and lines increases because of decreased non-radiative competition for the available excitation. Below 125 K, DAP luminescence corresponding to shallow donors and acceptors appears with a zero-phonon line at 379.3 nm (3.27 eV) and prominent LO-phonon replicas.
at 390 and 402 nm (3.18 and 3.09 eV). Upon further cooling, below ~50 K, Eu0 switches to Eu1(Mg) with a main peak at 621.8 nm (1.997 eV) [9, 25]. (Eu1(Mg) is different from the common Eu1 defect; it comprises a Mg atom in close association with Eu and, unlike Eu1, it does not show a sub-gap excitation band [20].) To illustrate this photochromic switching, the inset to figure 1 plots the mean spectral intensities of $5D_0 \rightarrow 7F_2$ emission lines of the Eu0 and Eu1(Mg) for the GaN(Mg):Eu sample (recorded at higher resolution than figure 1) as a function of temperature. Cooling the sample below 75 K results in a rapid decrease in Eu0 while the Eu1(Mg) signal rises to replace it. $T_{1/2} \approx 38$ K marks the temperature at which the defects are ‘half-switched’. In previous publications [9, 16, 25], we have reported that switching between Eu0 and Eu1(Mg) demonstrates the structural instability of GaN(Mg) at low temperature, with Eu ions acting as sensitive nanoprobes of the local environment. In a previous publication, ([25] and references therein) we also considered two other models advanced in the literature to explain temperature dependent PL of Eu$^{3+}$ in GaN(Mg). We ruled them out, mainly because of their inadequacy in explaining the emission behaviour during both the cooling and warming runs; details can be found in [25].

3.2. Comparing TDPL profiles of DAP and total Eu$^{3+}$

Figure 2 compares the TDPL profiles of several emission signals recorded during cooling: (1) the wavelength-integrated emission intensities of DAP from GaN(Mg); (2) the integrated emission intensities of DAP from GaN(Mg):Eu; (3) the difference of integrated emission intensities of DAP from GaN(Mg) and GaN(Mg):Eu (i.e. (3) = (1)−(2)); and (4) the integrated emission intensities of Eu$^{3+}$ emissions from GaN(Mg):Eu (= Eu0 + Eu1(Mg) + Eu2 (see later)). (Above 50 K, samples also show weak emission corresponding to e-A° recombination (see figure S1 in the supporting information (stacks.iop.org/JPhysD/51/065106/mmedia)) which overlaps the DAP zero-phonon line; hence the wavelength-integrated emission intensities of DAP include emission corresponding to e-A°). For unimplanted GaN(Mg), the DAP emission increases rapidly below 125 K; for GaN(Mg):Eu the rate of increase is somewhat moderated. While the Eu$^{3+}$ TDPL saturates below ~75 K, that of the DAP continues to increase. The difference between the two DAP profiles is similar to the temperature profile of Eu$^{3+}$ emission, suggesting that the DAP excitation ‘missing’ in GaN(Mg):Eu transfers in some way to Eu$^{3+}$.

Figure 3 shows the wavelength-integrated intensities of DAP and Eu$^{3+}$ emissions as functions of excitation density at 13 K. Both dependences seem anomalous: the DAP emission increases linearly in both the implanted and unimplanted samples while total Eu$^{3+}$ emission shows an approximate square-root dependence on excitation power.

3.3. UV light-induced photo-dissociation of Eu–Mg defects

To study any light-induced alteration in emission spectra, as expected from previous studies [26], we stabilised the sample in the dark at the base temperature of the cryostat for 30 min, and recorded a kinetic series of PL spectra at intervals of 0.5 s.
During continuous illumination from time zero, Figure 4 shows that the wavelength-integrated intensity of the DAP emission in unimplanted GaN(Mg) remains constant, ignoring small lamp fluctuations over the long experimental duration. On the other hand, for the Eu-implanted sample, the integrated emission intensity of the DAP increases as that of Eu$^{3+}$, mainly due to the fact that Eu1(Mg) near base temperature decreases.

Light soaking also produces fundamental changes in the spectrum (figure 5). After repeated and prolonged UV light soaking at low temperature, the intensity of the line corresponding to Eu2 defects at 620.8 nm grows from near-zero to a substantial fraction of that of the Eu1(Mg) defect at 621.7 nm.

### 4. Discussion

With the abrupt rise of intensity in the temperature range 150–100 K, figure 1 shows an exponential correlation, at least, between DAP and Eu$^{3+}$ emission in GaN(Mg):Eu. At higher temperatures, where DAP emission is absent, we must look for another process to increase the Eu$^{3+}$ signal; this may be due to reduced competition from non-radiative processes [27, 28]. The inset to figure 1 shows Eu0 switching to Eu1(Mg) below ~75 K. In previous publications, we have described this one-to-one transformation as a nanoscale phase instability [9, 16, 25]. We proposed that at low temperatures, localisation of holes on the axial N neighbours of Mg atoms drives a lattice distortion that increases Eu–Mg separation [25]. Sample warming above 150 K, not shown here, triggers the release of holes by Mg acceptors. Eu0 reappears as the lattice relaxes locally to its starting configuration [16, 25].

The difference in DAP TDPL profiles of GaN(Mg) and GaN(Mg):Eu samples shown in figure 2 suggests that the addition of Eu$^{3+}$ ions introduces a new physical process that impacts upon the emission intensity. In particular, the difference profile, obtained by subtracting that of GaN(Mg):Eu DAP from that of GaN(Mg), closely resembles that of the Eu$^{3+}$ emission below 125 K, implying that the additional physical process could be an ET from DAP to Eu$^{3+}$ ions. On the other hand, simple competition between independent excitation paths would lead to the same result. Above 125 K, since there is no DAP emission, the excitation transfer might occur via the several different processes suggested in the introduction. Our group previously suggested a possible excitation route through the charge transfer states of Eu ions [20].

A striking feature of figure 2 is the saturation of difference profile and the Eu$^{3+}$ temperature profile below ~75 K. This limiting behaviour is further observed in the integrated emission intensity versus impinging light intensity plots shown in Figure 3, which depicts a square-root and linear dependence for Eu$^{3+}$ ions and DAP emission intensities, respectively. Since the thickness of the GaN(Mg) sample is ~0.5 mm and Eu$^{3+}$ ions are implanted only within 100 nm of the surface, saturation of Eu$^{3+}$ emission indicates the presence of a limited number of Eu–Mg pairs to receive excitation from any active channel. It is important to recall that Eu implantation results in a non-uniform concentration profile with a peak concentration of ~3 × 1019 cm$^{-3}$ (closely matching the mean Mg level) ~50 nm below the surface. A simple analysis suggests that ~50% of the Mg atoms in the implanted region are not associated with Eu atoms. Furthermore, at 355 nm excitation, ~37% of incident photons penetrate to depths (beyond 100 nm) where Eu is hardly present. As the penetration depth is not a steep function of photon energy above the band gap, the use of available shorter wavelengths might not create a significant difference in Eu and DAP emission versus excitation intensity plots. In order to study the effect of excitation penetration depth on Eu and DAP emission, we recorded PL using 362 and 350 nm excitation (respectively slightly below and slightly above the band gap) at 13 K. Figure S2 of the supporting information reveals that the PL intensity versus the excitation intensity plot show the same square-root and linear dependence for Eu$^{3+}$ ions and DAP emission intensities, respectively. Noticeably, as 362 nm photons penetrate deeper in the sample, the integrated emission intensity of DAP is higher than observed for 350 nm excitation, whereas the reverse is true for Eu emission.

Figure 4 reveals that prolonged UV light soaking at 13 K causes a decrease in emission intensity of Eu$^{3+}$ (mainly of Eu1(Mg) at this low temperature) and a simultaneous increase in DAP emission intensity, once more suggesting a competition between DAP and Eu$^{3+}$ excitation. The accompanying spectral changes, with the emergence of the characteristic Eu2 line, suggests strongly that prolonged exposure to UV light causes photo-dissociation of Eu–Mg pairs with the direct consequence, at least in part, of producing Eu2 defects. This conjecture finds support in a further experimental result shown in figure 5. After reannealing the sample at high temperature and high pressure, the PL of Eu2 defects decreases while that of Eu1(Mg) is partially restored, clearly indicating the recovery of Eu–Mg defects, through the re-association of Eu and Mg ions, upon HTHHP reannealing. These findings are entirely consistent with the model that Eu0 and Eu1(Mg) configurations comprise a Eu atom in close association with a Mg acceptor [9, 16, 25].
5. Summary and conclusions

The RT PL spectrum of ion-implanted HVPE Kyma GaN(Mg):Eu shows band-edge emission, a green emission band corresponding to native GaN lattice defects and Eu$^{3+}$ emission from Eu0 defects, all of which increase in intensity on sample cooling. Cooling below 125 K elicits DAP emission with LO-phonon replicas. Upon further cooling below 75 K, Eu–Mg defects switch configuration from Eu0 to Eu1(Mg) and the total Eu$^{3+}$ emission saturates. The differences in the TDPL of DAP in GaN(Mg) and GaN(Mg):Eu, which matches the profile of Eu$^{3+}$ emission, may suggest excitation transfer from DAP to Eu$^{3+}$ ions or simple competition between the two processes. Continuous UV light soaking at 13 K leads to photo-dissociation of Eu–Mg pairs, resulting in the appearance of Eu2 and a simultaneous increase in DAP emission. After prolonged UV soaking, a sample can be partially restored by re-annealing at HTHP: in line with the results of recent structural studies [29], Mg appears to be a labile defect in GaN.

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