# Depth profiling of ion-implanted AlInN using time-of-flight secondary ion mass spectrometry and cathodoluminescence

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Investigation of the depth profiles and luminescence of Eu and Er-ions implanted into AlInN/GaN bilayers differentiates between ions located in the two different III-N hosts. Differences between samples implanted using channeling or off-axis geometries are studied using time-of-flight secondary ion mass spectometry. A fraction of ions have crossed the AlInN layer (either 130 or 250 nm thick) and reached the underlying GaN. Cathodoluminescence spectra as a function of incident electron energy and photoluminescence excitation data distinguish between ions within AlInN and GaN. The RE emission from the AlInN is broader and red-shifted and the dependence of the intensity on host is discussed.

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## **1** Introduction

Rare Earth (RE) doped III-nitride materials offer potential for light emitting devices with notable benefits arising from the use of wide bandgap, robust hosts for the luminescent ions [1]. GaN has been widely used as a RE host and AlGaN layers shown to offer further advantages [2]. In this work we describe investigations of AlInN ternary layers, which can be lattice matched to GaN [3, 4]. Europium and erbium ions have been ion-implanted into MOCVD grown GaN and AlInN/GaN bilayers. A high temperature anneal is employed to repair damage and optically activate intra-4f-shell transitions of the RE ions, which for Eu and Er give strong emission in the red and green spectral regions, respectively. The optical and structural properties of the samples were characterized using cathodoluminescence (CL), time-of-flight secondary ion mass spectrometry (TOF-SIMS), photoluminescence (PL), wavelength dispersive X-ray (WDX) analysis, Rutherford back-scattering spectrometry (RBS) and X-ray diffraction (XRD). In particular we will compare investigations of the depth profile of the Eu / Er ions within the AlInN/GaN layers using TOF-SIMS, CL and PL excitation (PLE).

# 2 Experimental details

A series of  $Al_xIn_{1-x}N$  epilayers was grown on GaN-on-sapphire buffer layers in an Aixtron 200-series MOVPE reactor and subsequently implanted with RE ions. In this work we will consider two nearly

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lattice-matched AlInN/GaN samples with an AlInN growth temperature of 820 °C. Simulations of RBS data gave thicknesses of  $130\pm5$  and  $250\pm10$  nm, in good agreement with values estimated from growth rates. AlInN elemental compositions were measured using WDX and RBS. For both samples the InN fraction was estimated to be  $17\pm2$  at.%. It should be noted that for the thinner sample the WDX data, measured with electrons of energy 4.5 keV gave a higher result than that from the RBS. The RBS channelling spectrum and high-resolution SE images indicate a high crystal quality. This is confirmed by X-ray reciprocal space mapping which also showed the AlInN to be very nearly lattice-matched to the underlying GaN. The thicker sample was produced by simply increasing the flow rate of the Al and In metal-organics by x2.5 and is expected to be of lower crystal quality. This is confirmed by SE imaging and by the RBS/C and X-ray data. In fact these measurements indicate a variation in the InN fraction with depth, as discussed further below.

Pieces from both samples were implanted with Eu and Er ions at room temperature. The Eu implantation was channelled along the c-axis and performed at 80 keV with a nominal dose of  $5x10^{14}$  at/cm<sup>-2</sup>. The Er implantation was randomly aligned (10° off the c-axis) using 120 keV and a nominal dose of  $1x10^{15}$  at/cm<sup>-2</sup>. The implanted samples were then annealed at 800 °C for 20-30 minutes under a N<sub>2</sub> ambient and with GaN proximity caps. In RE:GaN we have shown that RE luminescence is very weak or absent in unannealed samples but increases dramatically for high temperature anneals (>1200 °C) [5]. In the present case we selected an annealing temperature just below the AlInN growth temperature to avoid decomposition but subsequent work has shown similar samples to withstand annealing at 1200 °C.

Light emission from as-implanted and annealed samples was investigated using CL and PL and their structural properties analysed by TOF-SIMS and SE imaging. The CL data were collected as a function of electron beam energy using a CCD spectrograph with the sample at approximately 20 K or at RT. PL(E) data were measured using a Xe-lamp based system [6]. The TOF-SIMS depth profiles were collected using an ION-TOF TOF-SIMS 5 with a 2 pA Bi<sup>+</sup> (or a 4 pA Au<sup>+</sup>) ion beam for analysis of an area of  $\approx 100 \times 100 \mu m^2$ . Sample erosion was achieved by a 1 keV,  $\approx 250$  nA, O<sub>2</sub> sputter beam on an area of  $300 \times 300 \mu m^2$ . Similar data, differing only in a x2 reduced sputter energy, from AlN / GaN samples confirm the depth resolution to be approximately 1 nm.

#### **3** Results and discussion

CL spectra from the thinner AlInN on GaN layer implanted with Eu are shown in Fig. 1. At low electron beam energies, below 3 keV, a single broad peak is resolved with a full width at half maximum of approximately 4 nm. With increasing beam energy a series of sharper lines, characteristic of the  ${}^{5}D_{0}{}^{-7}F_{2}$  transition of Eu<sup>3+</sup> ions implanted into GaN [1,6], appear on top of this broader band. Monte-Carlo simu-



**Fig. 1 (left)** CL spectra at 20 K as a function of excitation energy for the  ${}^{5}D_{0}$ – $F_{2}$  transition of Eu<sup>3+</sup> in the sample with thinner AlInN (normalised to the broad peak). **Fig. 2 (right)** RT CL spectra measured from the Er implanted AlInN/GaN structure and a comparative Er:GaN sample.

lation for a 4.5 keV electron beam indicates that 90 % of the electron energy is deposited within a depth of 150 nm. This indicates that those Eu ions resident in the AlInN generate the broad, unresolved peak in the region of the  ${}^{5}D_{0}-{}^{7}F_{2}$  luminescence but that a fraction of the Eu ions have reached into the underlying GaN and, when excited, these generate the sharper lines. The centre of the Eu:AlInN band is near 623 nm, slightly red-shifted from that for Eu:GaN. CL spectra from the thicker sample show a similar behaviour although the beam energy required to produce the sharp line transitions is of course higher. Figure 2 shows room temperature 3 keV CL data from the Er-implanted AlInN/GaN and a comparative Er:GaN sample. A similar broadening of the RE luminescence lines within the ternary host can be seen.

CL data from the implanted AlInN samples and from GaN samples implanted and annealed under identical conditions show the RE luminescence to be significantly more intense (typically by a factor of x3) in the wider gap ternary and indeed can be detected before annealing. However, the results below will show that the extremely small fraction of RE ions that cross the AlInN layer into the underlying GaN generate comparatively very strong RE-luminescence. This may relate to the degree of implantation damage in the buried layer but further work is required to understand the relative intensities for Eu in AlInN and GaN.

The signature of RE ions within the buried GaN is perhaps surprising when considering simulation of their expected range using TRIM [7], although this will not account for the effects of ion channelling which we expect to increase the range of ions within the Eu-implanted samples by a considerable factor. The dashed lines in Fig. 3 show the TRIM profiles for Eu (or Er) implanted into AlInN at 80 and 120 keV. The depths at which the ion concentrations have decreased by 2 orders of magnitude from their peak concentration are approximately 50 and 70 nm, respectively. To obtain details about the depth profile of the implanted RE ions the samples were studied using TOF-SIMS. Figure 3 shows semilog plots for both AlInN on GaN samples, using the <sup>69</sup>Ga<sub>2</sub>, and <sup>113</sup>In mass channels as representative of the III-N elements. In all cases the <sup>27</sup>Al<sub>2</sub> signal shows similar features to the <sup>113</sup>In signal. The start of the GaN layer is clearly visible and the RBS-measured depth is used to produce the depth scales. In the thicker AlInN sample the <sup>113</sup>In signal varies with depth, showing two near-step-like increases as suggested by simulation of the RBS and XRD data. For both the channelled Eu-implantation and random Er implantation the data confirm that the rare earth profile has reached the AlInN/GaN interface. As expected there is indication that the channelled Eu ions have penetrated deeper than the Er ions and there is indication of a small build up of Eu just above the interface. The depth of the peak Eu / Er concentration is quite similar for the measurement and the simulation but the SIMS data show tails extending much deeper into the sample than the TRIM prediction. This is the case even for the off-axis implantation and the increased range due to channelling is not as great as expected. The long tails are characteristic of channelled implantation and



**Fig. 3** TOF-SIMS spectra from the Eu- (upper panel) and Er- (lower panel) implanted AlInN/GaN structures. The thicker and thinner AlInN layers correspond to the left (right) plots with the depth scales constructed using the measured AlInN thicknesses. The dashed lines show the RE profile generated by a TRIM simulation.

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suggest that some ion channelling has occurred even for the off-axis Er implantation. It is possible that some ions have undergone small angle scattering and been steered into the c-axis. The data for the thinner samples reinforces the above observations. A greater number of channelled Eu ions have now reached the AlInN/GaN interface and there is a clear peak indicating a build-up of ions at the interface. The data also suggest that implanted Eu ions have displaced some In (and Al) ions through the interface. It is important to note that in both Eu-implanted samples the concentration of RE within the GaN remains very low and the intensity of luminescence that can be excited from Eu:GaN in this cases seems to indicate an extremely high excitation efficiency of these ions.

Further distinction between the RE ions located within the AlInN or GaN regions is resolved in PLE and selectively excited PL data (Fig. 4). The PLE spectrum is detected using Eu-luminescence near 622 nm. The peak near 350 nm is due to absorption in the GaN and lamp excitation at this wavelength gives PL with the sharp red luminescence lines expected for Eu:GaN. Tuning the excitation to shorter wavelengths causes the PL spectrum to broaden and become characteristic of Eu:AlInN. The absorption onset in the region below 300 nm could then be associated with the band-gap of the AlInN, the value of which is currently not unambiguously known [3]. However, care is needed since PLE studies of Eu:GaN reveal a below-band-gap absorption edge [6] and furthermore the system response below 260 nm is complicated.



**Fig. 4** (Left) PLE spectrum at 15 K from Eu-implanted AlInN/GaN detected at 617.2 nm. The arrows indicate the excitation wavelengths used to produce the PL spectra (right).

In summary, AlInN/GaN bilayers have been implanted with RE ions under different conditions and the resulting RE depth profile and luminescence studied using TOF-SIMS, RBS, CL and PLE. The results demonstrate a higher than expected range for the implanted ions. A fraction of ions have crossed the AlInN (either 130 or 250 nm in thickness) and reached the underlying GaN. CL and PLE spectra differentiate between ions located in the two different III-N hosts. Increasing the band-gap of the host has resulted in a broadening and shift of the RE-luminescence lines.

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