**Optical and structural properties of Eu-implanted In$_x$Al$_{1-x}$N**


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Off-axis implantation of 80 keV Eu ions into epitaxial c-plane InAlN/GaN bilayers confines rare-earth (RE) doping largely to the InAlN layer. Rutherford backscattering spectrometry and x-ray diffraction show good correlations between the Eu$^{3+}$ emission linewidth and key structural parameters of In$_x$Al$_{1-x}$N films on GaN in the composition range near lattice matching ($x \approx 0.17$). In contrast to GaN:Eu, selectively excited photoluminescence (PL) and PL excitation spectra reveal the presence of a single dominant optical center in InAlN. Eu$^{3+}$ emission from In$_0.17$Al$_{0.83}$N:Eu also shows significantly less thermal quenching than GaN:Eu. InAlN films are therefore superior to GaN for RE optical doping. © 2009 American Institute of Physics. [doi:10.1063/1.3245386]

**I. INTRODUCTION**

A key issue in the development of rare-earth (RE)-based optical devices is their efficient operation at room temperature; this consideration prompts the study of semiconductor hosts with wide bandgaps according to the well-known “Favennec principle.” Recently, the III-nitride compounds GaN and AlN and, to a much lesser extent, the alloys AlGaN and InAlN have been doped with RE ions for potential application in light-emitting diodes, optical amplifiers, and solid state lasers. As expected, RE-doped AlGaN shows less thermal quenching of the impurity ion emission than GaN. Furthermore, AlN-containing III-N alloys prove resistant to both the high-temperature annealing, which enables luminescence of ion-implanted samples, and to surface amorphization during implantation. Special motivation for studying RE-doped InAlN comes from the close lattice match of InAlN to GaN (falling within $\sim 1\%$ for InN molar fractions between 14% and 22%), which leads to the prospect of RE-doped lattice-matched heterostructures, for example, microcavities. The spectroscopic investigation of similar optical centers in a range of III-nitride hosts may also lead to a better general understanding of the mechanism of optical energy transfer from the semiconductor host to ions in these materials. In this work, we report the influence of InN fraction $x$ on the Eu$^{3+}$ emission from implanted In$_x$Al$_{1-x}$N films in the composition range near lattice matching to GaN ($x \approx 0.17$). We investigate the influence of the structural quality of the films on the linewidth and intensity of Eu$^{3+}$ emission. We also present the photoluminescence (PL) and PL excitation (PLE) spectra of InAlN:Eu, which may contribute to a general understanding of the excitation mechanisms of RE-

doped III-nitrides. Finally, we confirm significant improvements of temperature quenching behavior for InAlN:Eu samples compared to GaN:Eu.

**II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES**

InAlN samples were grown by metal organic vapor phase epaxy on 1 μm thick GaN buffer layers on (0001)-oriented sapphire substrates at the different setpoint temperatures listed in Table I. Lorenz and co-workers gave further details on the growth conditions and described the characterization of as-grown InAlN samples, including information on how the InN content depends on the growth temperature.

Rutherford backscattering spectrometry (RBS) was used to determine both the mean InN fraction and the crystal quality of the InAlN material used as an implant host. $X_{\text{min}}$ is the ratio of backscattered yield in the aligned RBS spectrum to that in a spectrum taken on a rotating, misaligned sample. A lower $X_{\text{min}}$ implies better crystal quality: for III-N materials, 2%–3% is typical for good single-crystal layers, and 100% indicates an amorphous or polycrystalline target. $X_{\text{min}}$ can never be zero, due to backscattering by surface atoms. High-resolution x-ray diffraction (HR-XRD) measurements were performed in a Bruker D8 Discover system, using a Cu source operating at 40 kV and 40 mA. In order to improve the angular resolution, a monochromator with four Ge (002) crystals and a scintillator detector were used. In these mea-

**TABLE I. Summary of growth parameters for the Al$_x$In$_{1-x}$N samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth temp. (°C)</th>
<th>InAlN thickness (nm)</th>
<th>XRD InN fraction ($x$)</th>
<th>RBS $X_{\text{min}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S760</td>
<td>760</td>
<td>130 ± 5</td>
<td>0.19 $\pm$ 0.24</td>
<td>43 ± 2</td>
</tr>
<tr>
<td>S800</td>
<td>800</td>
<td>125 ± 5</td>
<td>0.19 ± 0.01</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>S820</td>
<td>820</td>
<td>128 ± 5</td>
<td>0.16 ± 0.01</td>
<td>4.0 ± 0.5</td>
</tr>
<tr>
<td>S840</td>
<td>840</td>
<td>122 ± 5</td>
<td>0.13 ± 0.01</td>
<td>4.4 ± 0.5</td>
</tr>
</tbody>
</table>

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measurements, the main parameter of interest is the halfwidth (full width at half maximum height) of the 2θ-ω line profile.

In order to minimize penetration of the Eu implant, c-plane InAl₁₋ₓN/xGaN samples were “randomly” implanted with an 80 keV Eu ion beam tilted 10° away from the surface normal to a fluence of 5 × 10¹⁴ cm⁻². Ion implantation channelled along the (0001) crystal direction can readily penetrate InAlN overlayers 100 nm thick, as was clearly shown in previous work by elemental depth profiling using secondary ion mass spectrometry. The randomly implanted samples were annealed at 1000 °C for 30 min in flowing N₂ at atmospheric pressure. A GaN:Eu film was prepared for purposes of comparison using the same implantation and annealing conditions.

Room temperature cathodoluminescence (RT-CL) spectra were acquired in a modified electron probe microanalyzer (EPMA) using a beam energy of 3 keV and a current of 35 nA. The CL is collected using an optical microscope built into the EPMA and detected using a 0.125 m optical spectrometer equipped with a cooled silicon charge-coupled device 1024 detector array. At 3 keV, 90% of the beam is deposited within ~95–100 nm of the surfaces of our layers according to Monte Carlo simulations of the electron trajectories. PL and PLE spectra were acquired at sample temperatures of ~25–300 K, using the monochromated output of a 1000 W Xe arc lamp as the excitation source. The raw PLE spectra were corrected for the variation in monochromator output with wavelength.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 compares the RT-CL spectra of several InAl₁₋ₓN/xEu samples (for InN fractions between 0.13 and 0.22) with that of a GaN:Eu sample prepared under identical conditions, and identifies the main Eu³⁺ transitions. Figure 2 shows the integrated intensity of the dominant ⁷D₂ to ⁷F₂ emission (near 623 nm for InAlN:Eu) as a function of InN fraction, normalized to that from GaN:Eu. A significant enhancement of the Eu³⁺ emission intensity is observed for Eu-implanted InAlN compared to GaN. Figures 1 and 2 indicate that the sample with an InN fraction of 0.13 has the largest output for our set. The much weaker emission from sample S760 reflects the much poorer crystalline quality of InAlN grown at low temperatures, as will be discussed later. The emission lines of InAlN:Eu are considerably broader than those of GaN:Eu and the peaks are redshifted by about 1 nm (3 meV). The crystal field of different hosts influences the RE transition energies, but not in a straightforward way; the influence of the crystal field on the Eu³⁺ line position is weak in RE-doped III-nitrides.¹⁴,¹⁵

Figure 3(a) shows at a glance that the variations with InN fraction in the Eu³⁺ emission linewidth and in χмин are similar. The observed values of χмин (4%–6%) represent good crystalline quality for samples with InN fractions <0.20. The emission linewidth increases slowly as the InN fraction increases in this range. Overall, the emission linewidth increases nearly linearly with χмин, as shown in Fig. 3(b); the residual width of ~20 meV, obtained by extrapolating the linewidth dependence to χмин equal to zero, represents the alloy broadening due to random composition fluctuations in the absence of structural disorder; this appears to be quite large but should vary relatively little with composition in a restricted range of composition [scaling approximately as x(1−x)].¹⁵ The additional effects of structural disorder, usually associated with unannealed crystal defects, on the values of χмин and the linewidth of Eu³⁺ emission appear to be comparable.

Figure 4 shows the HR-XRD 2θ-ω scans around the (0002) planes for as-grown samples S840, S820, S800, S760, and GaN. The XRD halfwidths of S840, S820, and S800 (with InN fractions of 0.13, 0.16, and 0.19, respectively) are
all ∼400 arc sec, which represents a significant improvement over previously reported values. The good 2θ-ω halfwidths in samples with x < 0.2 reflect low compositional fluctuations. Together with the homogeneity of the In distribution with depth, evidenced by RBS, these results further show that PL line broadenings are caused by crystal defects rather than by compositional fluctuations or gradients. Reciprocal space mapping shows that samples S800, S820, and S840 have the same in-plane lattice constant as GaN, indicating pseudomorphic growth.9 As expected, the reflection from InAlN shifts to lower angles (larger c lattice parameter) with increasing InN fraction. The XRD peak of S760 shifts back toward the GaN peak and has a halfwidth of 800 arc sec. RBS of sample S760 shows a compositional grading with InN fractions of ∼24% near the interface and ∼19% at the surface;9 the excessive widths of its XRD and PL peaks partly reflect this composition anomaly. These results also confirm the poorer crystalline quality of sample S760. RBS/channeling measurements of samples S840, S820, and S800 (figures not shown) confirm the remarkable thermal stability of this material at annealing temperatures more than 160 K higher than the growth temperatures shown in Table I. Preliminary transmission electron microscopy analysis of similar samples indicates that no new dislocations form in the AlInN layers; threading dislocations from the GaN underlayer confirm the fact that almost all implanted ions stop within the overlayer.

Figure 5(b) shows the PLE detected by monitoring the In0.13Al0.87N:Eu3+ emission peak at 623.5 nm. The excitation band below 310 nm is associated with interband optical absorption of In0.13Al0.87N. This shows that energy transfer from the InAlN host to the RE 4f shell precedes optical emission from the ions. However, there is also a weak band centered at 350 nm, as shown more clearly in the inset of the figure on a logarithmic scale. It is the presence of such a “sub-bandgap” PLE band, albeit much stronger in relative intensity, that confirms the presence of other occupied sites “sub-bandgap” PLE band, albeit much stronger in relative intensity, that confirms the presence of other occupied sites.

Figure 6 shows the thermal quenching of the integrated Eu3+ emission intensity from In0.13Al0.87N:Eu. The ratio of PL intensity at 10 K to that at RT is only ∼1:4:1, which represents a significant reduction in thermal sensitivity compared to GaN:Eu, for which this ratio is typically 20:1 for samples prepared under identical conditions. The corresponding activation energy, ΔE, obtained by fitting the temperature dependence to the simple function is as follows:

\[ I(T) = I(0) e^{-\Delta E/kt} \]
where $k$, the Boltzmann constant, is $\approx 70$ meV, with a degeneracy factor $A$ of $\approx 5$. The dependence of temperature quenching on the host material may indicate suppression of the energy back transfer rate with increasing bandgap or a more efficient energy transfer from the host to RE$^{3+}$ ions in the defect-related energy transfer model proposed in Ref. 21 or to a lower incorporation rate of implantation defects acting as nonradiative recombination centers.

IV. CONCLUSIONS

RBS, XRD, and CL measurements demonstrate that the emission efficiency of Eu in InAlN varies strongly with the InN fraction, while the emission linewidth scales with key parameters of structural disorder. No spectroscopic evidence of phase separation is found: the strong In$_{0.13}$Al$_{0.87}$N bandgap feature shows no splitting. Moreover, In$_{0.13}$Al$_{0.87}$N:Eu PL emission has strongly enhanced thermal stability compared to GaN:Eu. We conclude that InAlN:Eu is a suitable material for the development of practical RE-doped III-nitride photonic devices.

ACKNOWLEDGMENTS

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