Structural and optical characterisation of Eu implanted Al$_x$Ga$_{1-x}$N

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Abstract

Al$_x$Ga$_{1-x}$N films grown on sapphire substrates with AlN contents from 0 to 100% were implanted with $8 \times 10^{14}$ at/cm$^2$ Eu ions. The structural properties and damage accumulation were studied by Rutherford backscattering and channelling spectrometry. The implantation damage decreases considerably for all samples containing Al with AlN showing the best radiation hardness. Despite a high damage level, the fraction of Eu incorporated in near-substitutional sites is highest for GaN. Photoluminescence spectra after annealing at 1100 °C show Eu related luminescence lines in the red spectral region for all samples. The PL intensity at room temperature increases strongly when the AlN content is increased from 0 to 30% and drops steeply for higher AlN contents.

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1. Introduction

Emissions from optically active rare earth (RE) ions span a wide range of the electromagnetic spectrum from UV to IR including the whole visible spectrum. Favennec et al. showed that thermal quenching of RE luminescence in semiconductors is reduced for materials with wide band gap [1]. Therefore, group III nitrides with their wide and direct band gap seem to be ideal hosts. In fact, the development of electroluminescent devices based on RE doped GaN that emit in all primary colours has been reported recently [2].

By changing the Al content in Al$_x$Ga$_{1-x}$N ternary alloys it is possible to engineer the band gap within a range of $\sim$3.4 (GaN) to $\sim$6.2 eV (AlN). Besides the decrease of thermal quenching, increasing the band gap of the host material allows energetically higher lying RE levels to be exploited as shown for example for Tm implanted and in-situ doped Al$_x$Ga$_{1-x}$N [3,4]. Furthermore, Al containing nitrides are more resistant to radiation damage than GaN which can facilitate the RE doping by ion implantation [5]. It was reported recently that the luminescence intensity of implanted Eu can be increased significantly when the AlN content in Al$_x$Ga$_{1-x}$N is raised up to $\sim$50% while it decreases for higher AlN contents [6]. However, the excitation mechanisms that lead to an energy transfer from the nitride host matrix to the RE ions are not well understood and probably native or implantation defects play an important role. In this work we study the damage introduced in Al$_x$Ga$_{1-x}$N layers by Eu implantation and present first photoluminescence measurements.

2. Experimental details

Al$_x$Ga$_{1-x}$N films (with $x = 0, 0.30, 0.6, 0.74$ and 1), grown by metal organic chemical vapour deposition in the case of GaN and by halide vapour phase epitaxy$^1$ in

$^1$ HVPE material was purchased from Technologies and Devices International Inc., 12214 Plum Orchard Drive, Silver Spring, MD 20904, USA.
the case of AlGaN and AlN on (0001) sapphire substrates, were implanted with $8 \times 10^{14}$ at/cm$^2$ Eu ions with 300 keV. The implantation was performed with a $10^6$ tilt between the surface normal and the ion beam in order to minimise channelling effects. Post implant annealing was performed in a tube furnace in 3.8 bar N$_2$ overpressure at 1100 °C for 20 min; the samples were protected by an unimplanted piece of AlN placed face to face as a proximity cap to inhibit out-diffusion of nitrogen from the surface. The GaN sample was additionally protected by an epitaxial AlN capping layer grown prior to the implantation to allow annealing at temperatures exceeding 1000 °C [7].

Rutherford backscattering/channelling (RBS/C) studies were performed with a 1 mm diameter collimated beam of 2 MeV He$^+$ ions. The backscattered particles were detected at 140° and close to 180° with respect to the incoming beam direction using silicon surface barrier detectors with resolutions of 13 and 16 keV, respectively, located in the standard IBM geometry. PL measurements were carried out at room temperature with a 325 nm cw He–Cd laser and the excitation power density was typically less than 0.6 W cm$^{-2}$. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm$^{-1}$) equipped with a cooled Hamamatsu R928 photomultiplier.

3. Results and discussion

The RBS/C random and aligned spectra for the binaries AlN and GaN (Fig. 1(a)) and the ternary AlGaN samples (Fig. 1(b)) show the damage in the Al (in the case of AlN) and Ga (in the case of AlGaN and GaN) sublattice after implantation. The aligned spectra of unimplanted (virgin) samples are shown for comparison. Before implantation all samples show good crystalline quality with minimum yields of $\chi_{\text{min}} \sim 2\%$. Uniquely for sample A$_{0.6}$Ga$_{0.4}$N it is slightly higher ($\chi_{\text{min}} = 6\%$).

The Eu profiles as measured by RBS show the maximum of $\sim 0.13$ at-% at a depth of $\sim 45$ nm for all samples and a tail reaching as deep as $\sim 120$ nm for low Al contents and slightly deeper for A$_{0.74}$Ga$_{0.26}$N and AlN (Fig. 2). No shift of the maximum was observed for the different materials despite the significant difference in density between the binaries GaN and AlN (SRIM2003 [8] simulations yield a range of 55 nm for GaN and 77 nm for AlN). In contrast, similar implantations in AlN for which the Eu beam is impinging on the sample along the $c$-axis yield an ion range of 120 nm, evidencing strong ion channelling effects in this material [9].

Theory predicts isolated RE ions to be incorporated on substitutional cation sites in GaN and AlN [10,11]. However, experimental lattice site location studies of implanted RE ions in most cases show a slight displacement from the substitutional site [12]. In particular Eu was found displaced from the Ga and Al site in GaN and AlN, respectively [9,13]. The interaction with defects and/or clustering of RE are likely reasons for the displacement. Angular channelling scans (not shown) confirm that also in AlGaN implanted Eu is incorporated slightly displaced from the substitutional cation site.

The fraction $f_s$ of Eu ions on this near-substitutional site can be estimated by $f_s = (1 - \chi_{\text{min}}) / (1 - \chi_{\text{min}}^{\text{Ga/Al}})$. The near-substitutional fraction $f_s$ and the values for the minimum yields for Eu and Ga (Al for AlN) are shown in Fig. 3. The highest and lowest values for $\chi_{\text{min}}$ (Ga/Al) are observed for GaN and AlN, respectively, showing the strong resistance of the AlN lattice to radiation damage. The AlGaN samples show significantly lower $\chi_{\text{min}}$ (Ga) than GaN, however, no consistent trend of damage suppression with higher Al content is observed in contrast to implantation.
studies performed on AlGaN grown by MOCVD [5]. The near-substitutional fraction is lowest in Al$_{0.6}$Ga$_{0.4}$N which might be due to the slightly worse crystalline quality of the as grown material. For the other samples $f_s$ decreases with increasing Al content, possibly due to the oversize of the Eu ions which is more significant when substituting for the Al than for the Ga atom. It must be noted that $f_s$ as defined above is a relative value dependent on the damage level and does not necessarily reflect the absolute number of Eu ions in an undisturbed environment.

Fig. 4 shows the room temperature PL spectra obtained with 325 nm ($\sim$3.8 eV) He–Cd excitation for the Eu implanted and annealed Al$_{1-x}$Ga$_x$N ($x = 0, 0.3, 0.6$ and $0.74$) layers. The band gap for the AlGaN layers was estimated using $E_g(Al$_{1-x}$Ga$_x$N) = $E_g(AlN) + x(E_g(GaN))$ - $E_g$ = $E_g$ = $E_g(GaN)$ (1 - $x$) - $b \cdot x(1 - x)$. Assuming a bowing parameter of $b = 1$ the derived values for $E_g$ are $4.03$ eV, $4.84$ eV and $5.28$ eV for $x = 0.3, 0.6$ and $0.74$, respectively. However, we must note that the published values for the bowing parameter in Al$_{1-x}$Ga$_x$N vary significantly and our derived values are just rough estimates [14]. According to these estimates excitation with the He–Cd laser is performed above the band gap in the case of GaN and below the band gap for all the other samples. Below band gap excitation of RE ions is possible either by direct resonant excitation of the RE levels or by absorption through broad bands e.g. due to defects and subsequent energy transfer to the RE ion. Broad absorption bands below the band gap were for example reported for RE doped AlN [15]. The spectra in Fig. 4 are dominated by the strong Eu related emission line around 622/623 nm due to the $5D_0 \rightarrow 7F_2$ transition. Broad emission bands at shorter wavelengths are probably due to native defects or defects which were created during the implantation/annealing process. All spectra were taken under the same excitation conditions and the intensity was maximized for the line of the $5D_0 \rightarrow 7F_2$ transition. We observe a strong increase of PL intensity when the Al content is increased from 0 to 30%, however, for higher Al contents the intensity of the $\sim 622$ nm emission drops steeply. It is difficult to correlate the PL trend with structural properties. However, it is worth to note that the sample showing the highest PL intensity has a low defect density combined with a high fraction of Eu ions on near-substitutional sites. Possibly, temperature quenching due to defect related non-radiative recombination paths is reduced in this sample. However, a detailed optical analysis is necessary to understand the excitation processes occurring in PL measurements.

4. Conclusions

Al$_{1-x}$Ga$_x$N samples with $0 \leq x \leq 1$ were implanted with $8 \times 10^{14}$ at/cm$^2$ Eu ions at 300 keV. The implantation damage decreases considerably for all samples containing Al with best results for AlN, showing the strong radiation
hardness of this material. PL spectra after annealing at 1100 °C show Eu related luminescence lines in the red spectral region for all samples. The PL intensity increases strongly when the Al content is increased from 0 to 30%. High luminescence intensity at room temperature, low implantation damage and high stability during annealing at high temperatures makes AlGaN with AlN contents around 30% a promising material to replace GaN in RE based luminescent devices.

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