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Optical doping of $Al_xGa_{1-x}N$ compounds by Ion Implantation of Tm ions

M. Fialho[1)], K. Lorenz[1),2)], S. Magalhães[1),3)], A. Redondo-Cubero[1)], J. Rodrigues[3)], N. F.Santos[3)], T. Monteiro[3)], E. Alves[1),2)]

1) IST/ITN, Instituto Superior Técnico, Universidade Técnica de Lisboa, EN10, 2696-953 Sacavém, Portugal,
2) Centro de Física Nuclear da Universidade de Lisboa, 1649-003 Lisboa, Portugal,
3) Departamento de Física e i3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Abstract. $Al_xGa_{1-x}N$ ($0<x\leq1$) samples grown by halide vapor phase epitaxy on (0001) sapphire were implanted with Tm ions to optimize the conditions to achieve maximum optical efficiency. The ions were implanted under random and channeled orientations with a fluence of $1x10^{15}$ cm^{-2}. The damage profile and the defects' nature were investigated by Rutherford Backscattering/Channeling Spectrometry and High Resolution X-ray Diffraction. The structural measurements show a higher resistance of the lattice to irradiation damage with the increase of the AlN content. Results of the angular scans measured along the <0001> axis for samples with AlN contents of 0.15 and 0.77 suggest a relation between the AlN content and Tm specific sites in the lattice. Rapid thermal annealing treatments under N_2 ambient were performed to remove damage and promote optical activation of rare earth intra-$4f^n$ transitions. After annealing the observed intraionic emissions of Tm^{3+} ions were characterized by photoluminescence.

Keywords: AlGaN, RBS/C, HRXRD, PL, Ion Implantation
PACS: 61.72.U-, 61.85.+p, 78.55.Cr, 71.20.Eh

INTRODUCTION

AlGaN compounds are wide band gap semiconductors with suitable properties for optoelectronic applications. Incorporation of Rare Earth (RE) elements extend the optical range to all the visible and infrared wavelength regions, since these elements exhibit sharp optical emission lines due to the intra-$4f^n$ shell transitions of the RE ion core. AlGaN with a large direct band gap ranging from 3.45 eV (GaN) to 6.20 eV (AlN) is expected to reduce the thermal quenching of RE ions light emission [1]. Furthermore, the AlN content increases the resistance of III-nitrides to irradiation damage, thus a low damage level is expected during RE doping by ion implantation [2].
Recent studies show a dependence of the blue emissions from Tm^{3+} on the AlN molar fraction of AlGaN [3-4]. Glinka *et al.* studied the defects in Tm-doped AlGaN hosts induced by Tm^{3+} and their role in the nonradiative de-excitation of the most efficient photoluminescence (PL) transition of Tm^{3+} [5]. RE implantation doping of semiconductors offers reproducibility, quantitative control and allows lateral patterning for selective area doping suitable for electroluminescent device application. However, there are few reports on this doping technique regarding AlGaN:Tm. The large sensitivity of the blue emission from Tm^{3+} on the AlN content of AlGaN indicates the possibility to optimize the RE excitation and emission properties through careful band gap engineering of the host [6].

In this work we study the structural properties of AlGaN implanted with Tm ions for channeled and random implantations. Preliminary studies of Tm localization were performed using the ion channeling technique. Optical properties are accessed using PL with excitation with 325 nm (~3.8 eV) wavelength photons corresponding to below band gap excitation for AlN and $Al_{0.77}Ga_{0.23}N$ and near band gap excitation for $Al_{0.15}Ga_{0.85}N$.

EXPERIMENTAL

$Al_xGa_{1-x}N$ samples (x=0.15,0.77,1) grown by halide vapor phase epitaxy on (0001) sapphire (purchased from TDI) were implanted with Tm ions with a fluence of $1x10^{15}$ cm^{-2} at room temperature (RT). The implantation energy was 300 keV with the beam either tilted (10º) or aligned (0º) with the c-axis. Rapid Thermal Annealing (RTA) treatments at 1200ºC during 120 s in N_2 ambient were used to reduce the implantation damage. Rutherford Backscattering Spectrometry/Channeling (RBS/C) studies were performed with a collimated 2 MeV He^+ beam produced by a Van de Graaff accelerator. Random

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spectra were fitted using the NDF code [7]. High Resolution X-Ray Diffraction (HRXRD) was performed using Cu $K_{\alpha 1}$ radiation on a high resolution diffractometer D8Discover system from Bruker-AXS using a Ge (220) monochromator and a scintillation detector. Optical characterization was performed by PL at 77 K with a 325 nm He–Cd laser line.

STRUCTURAL CHARACTERIZATION

Figure 1 shows random and <0001> aligned RBS/C spectra for the $Al_xGa_{1-x}N$ sample with x=0.15. Comparison with the aligned spectrum of the as-grown sample shows a significant increase of the backscattering yield after implantation.

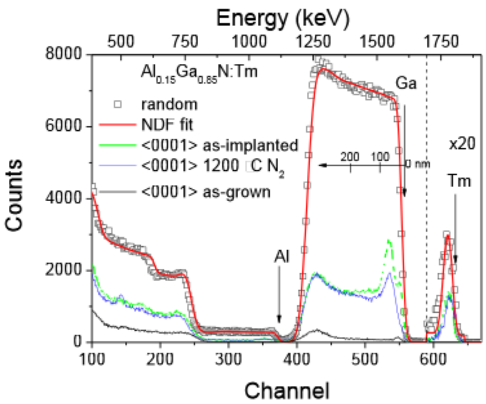

Figure 1. Random and <0001> aligned RBS spectra for $Al_{0.15}Ga_{0.85}N$ sample implanted with $1x10^{15}$ cm^{-2}.

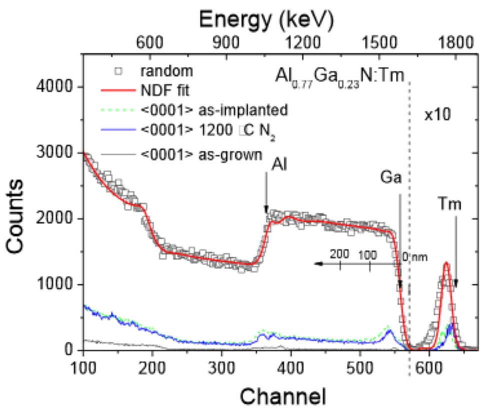

Figure 2. Random and <0001> aligned RBS spectra for $Al_{0.77}Ga_{0.23}N$ sample implanted with $1x10^{15}$ cm^{-2}.

The implantation damage is mostly concentrated close to the impurity distribution depth. Figure 2 shows the RBS/C results for x=0.77. The lower backscattering yield along the aligned direction clearly shows that the crystal resistance to implantation damage increases with increasing AlN content. The minimum yield (c_{min}) for Ga in the implanted region of the as-implanted samples is 0.320±0.001 for x=0.15 and 0.147±0.001 for x=0.77 compared to a minimum yield around 0.020±0.001 of the as-grown samples. Kucheyev *et al.* explained this effect on the basis of the large Al-N energy bond, as compared to the energy of Ga-N bond [8].

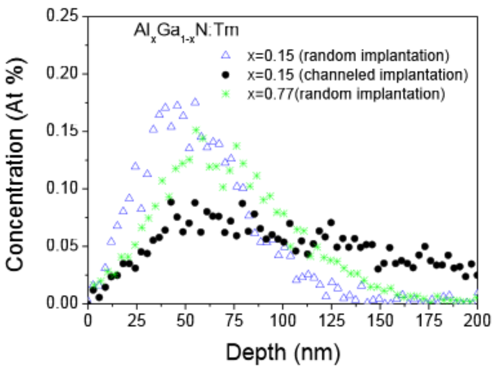

Figure 3. Depth profile of Tm ions in two different implantation geometries with a fluence of $1x10^{15}$ cm^{-2}.

The maximum concentration of the randomly implanted ions occurs at a projected range value of 48 nm for x=0.15 and 65 nm for x=0.77, respectively. The implanted profiles are represented in Figure 3 where the profile of the sample implanted along the <0001> direction is also shown. The influence of the Ga/Al ratio on the stopping of the implanted ions is well reproduced by TRIM (2008) [9] simulations where projected range (r_p) values of 53 nm for x=0.15 and 65 nm for x=0.77, were calculated. For the aligned implantation we achieved a very broad profile extending to deeper regions as expected due to the strong channeling effect along the c-axis.

The RTA treatment promotes some recovery of the implantation damage as observed from the decrease of the surface peak as well as the damage peak close to the end of range of the implanted ions, Figure 1 and Figure 2.

The effect of the implantation damage on the lattice distortion was assessed by HRXRD. The reciprocal space maps (RSM) around the (10-15) reciprocal lattice point for samples with x=0.15 and x=0.77 are shown in Figures 4 and 5, respectively.

After implantation, a shoulder is visible at lower Q_z values corresponding to an expansion of the c-lattice parameter due to implantation damage.

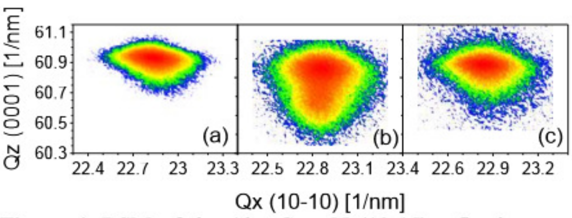

Figure 4. RSM of the $Al_{0.15}Ga_{0.85}N$ (10-15) reflection: as-grown (a), after 300 keV Tm random implantation at a fluence of $1x10^{15}$ cm^{-2} (b) and annealed at 1200 ºC during 120 s in N_2 ambient (c).

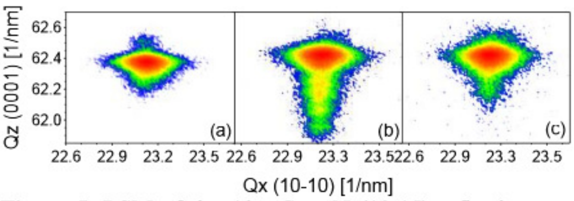

Figure 5. RSM of the $Al_{0.77}Ga_{0.23}N$ (10-15) reflection: as-grown (a), after 300 keV Tm random implantation at a fluence of $1x10^{15}$ cm^{-2} (b) and annealed at 1200 ºC during 120 s in N_2 ambient (c).

The c-lattice parameter variation is ~0.01 Å for $Al_{0.15}Ga_{0.85}N$. In the case of the sample with x=0.77 results show more than one shoulder. This could be explained by the formation of defect regions producing different lattice expansions or it may be a consequence of diffraction and interference. The well-defined diffraction peak from the implanted region could be understood as a consequence of the expansion of c-lattice parameter within a defined layer and interference between this shallow low-damage layer and deeper layers may give rise to additional peaks in the XRD curve as previously reported for implantation in silicon [10]. Multiple peaks in XRD curves after RE implantation have also been observed in GaN and were associated with distinct damage profiles at different depths by comparison with transmission electron microscopy [11]. To better understand the present results it is necessary to study more AlGaN samples with different compositions and with a wide range of implantation fluences and study the defect distribution with transmission electron microscopy. After annealing at 1200 ºC, the expansion of the lattice is reversed due to partial removal of implantation damage, as shown in Figure 4 (c) and Figure 5 (c). A similar behavior was obtained for the other samples.

The fraction f_s of Tm ions in the near substitutional site of Ga/Al can be estimated by $f_s = (1-c_{(Tm)min})/(1-c_{(Ga)min})$. For the sample with x=0.77 the fraction f_s is 88% after implantation and slightly decreases to 86% after annealing. For the sample with less AlN content, the fraction fs changes from 92% to 83% for the annealed sample.

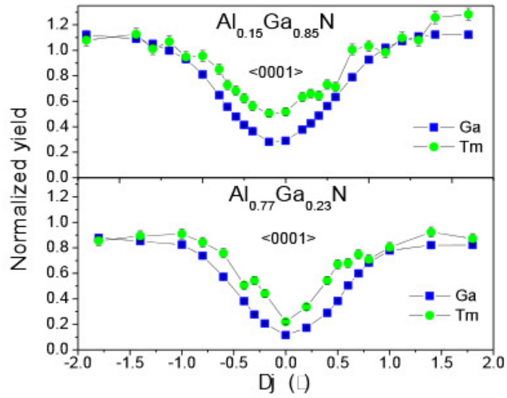

Figure 6. Experimental angular scans taken across the <0001> axis, using depth widows for Ga and Tm comprising the whole implanted area for as-annealed samples with $1x10^{15}$ cm^{-2}.

Figure 6 shows the angular scans along the <0001> axes of the annealed samples. For both samples, the narrowing of the bottom of the Tm dip suggests the presence of a small fraction of Tm ions displaced from substitutional sites of Ga/Al. This feature is more pronounced for the sample with x=0.77 where the FWHM of the RE angular scan is smaller than the Ga angular scan. This fact agrees with the results obtained in previous work done with Pr ions[12]. Nevertheless, angular scans across <0001> axis are not enough to determine the precise location of Tm ions. Such study requires the analysis of angular scans across oblique <-2113> and <10-11> axes and further FLUX [13] simulations of the three axes. However, such kind of analysis is out of the scope of this manuscript and will be published elsewhere.

OPTICAL CHARACTERIZATION

PL measurements at 77 K were performed for all samples after implantation and after annealing. The as-implanted samples did not show any optical activity related with the Tm ions. In contrast, we measured a pure AlN compound which revealed intraionic emission of Tm^{3+} in the near infrared (NIR) spectral region after implantation. After annealing at 1200 ºC all samples exhibit the NIR luminescence, Figure 7. The blue emission due to the transition between the $^1G_4 \rightarrow ^3H_6$ multiplets of Tm^{3+} was only observed for pure AlN, Figure 8. The inset shows a high-resolution spectrum taken in the NIR spectral region where we can identify two transitions at ~795 nm and ~810 nm. As reported previously for other RE ions [14], the emission lines in the binary AlN are much sharper than

in the AlGaN samples since the RE are sensitive to compounds disorder in the ternaries.

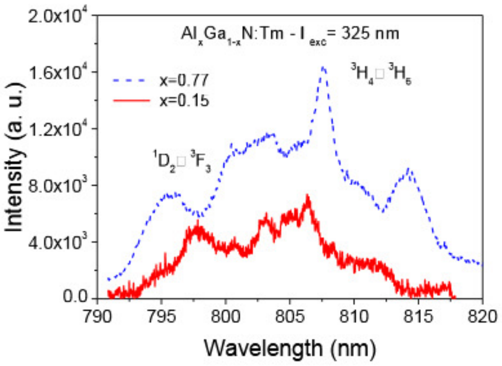

Figure 7. PL spectra of Tm-implanted $Al_xGa_{1-x}N$ samples after RTA at 1200 ºC in N_2 ambient for a fluence of $1x10^{15}$ cm^{-2}.

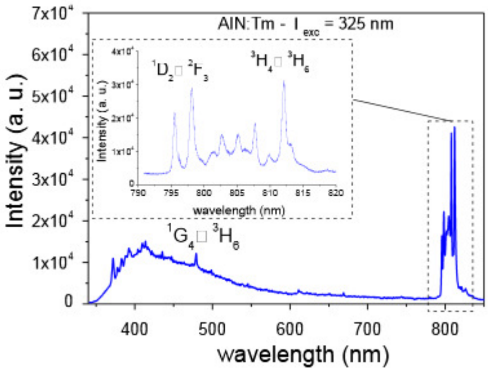

Figure 8. PL spectrum of a Tm-implanted AlN sample after RTA at 1200 ºC in N_2 ambient for a fluence of $1x10^{15}$ cm^{-2}.

CONCLUSIONS

AlGaN compounds doped with Tm^{3+} by ion implantation followed by RTA were studied by structural and optical techniques. RBS/C results showed that the increase of AlN molar fraction improves the lattice resistance to irradiation damage. HRXRD results show c-lattice parameter expansion due to implantation damage. The sample with x=0.77 shows multiple peaks in XRD curves which may be related to the formation of different defect regions. Annealing treatments at 1200 ºC partially recovers the crystal lattice. Channeling spectrometry measurements show the narrowing of Tm dips compared with Ga dips, this is more pronounced for the sample with x=0.77. The result suggests the presence of a small fraction of Tm ions displaced from substitutional sites of Ga/Al. After annealing the ions optical activation was observed as identified by the typical NIR emission of the Tm^{3+} ions. Additionally, blue luminescence was seen to occur for the AlN sample.

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