Influence of the AlN molar fraction on the structural and optical properties of praseodymium-doped AlGaN (0 ≤ x ≤ 1) alloys

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Abstract

The effects of the AlN molar fraction on structural and optical properties of praseodymium implanted AlGa1−xN (0 ≤ x ≤ 1) layers were investigated. Using photoluminescence and excitation luminescence techniques we are able to observe the intra-4f 2 → 3P1 transitions, this ion is seen as an attractive optical activator in several nitride hosts giving rise, for instance, to the 2S+1L manifold transitions, this ion is seen as an attractive optical activator in semiconductors. The trivalent praseodymium (Pr 3+) is among the system interesting to study the excitation mechanisms of RE in/praseodymium-doped AlGaN alloys covering AlN molar fractions from 0 to 1, scarce information is available for the behaviour of the praseodymium in the alloys.

Keywords:
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XRD
RBS/C
PL
PLE

1. Introduction

AlGaN alloys with different AlN molar fractions (0 ≤ x ≤ 1) have an enormous potential as active materials for the development of UV solid-state lightning and detectors [1–3]. With increasing bandgap energy, when compared with its counterpart binary GaN, the alloys are expected to be suitable hosts for the incorporation of several rare-earth ions, which give rise to luminescent transitions that cover ultraviolet, visible, and infrared spectral regions [4–11]. Besides the possibility to incorporate higher lying rare-earth levels into the band gap, the temperature quenching of luminescence is also expected to decrease for increasing host band gap [12]. Furthermore, tuning the band gap of the AlGaN alloy from 3.5 eV (GaN) to 6.2 eV (AlN) makes this system interesting to study the excitation mechanisms of RE in semiconductors [5]. The trivalent praseodymium (Pr3+) is among the rare-earth ions that offer a number of features in the mentioned spectral range. In particular, and due to the intra-4f2 transitions, this ion is seen as an attractive optical activator in several nitride hosts [13–17] giving rise, for instance, to the 2S+1L manifold transitions 3P1 → 3H3 and 3P0 → 3F2 in the green (526 nm) and red (652 nm) regions, respectively. While recent reports on the intrionic properties of Pr3+, Tb3+, and Eu3+ in AlGa1−xN alloys covering AlN molar fractions from x = 0 to 1 [4–11], scarce information is available for the behaviour of the praseodymium in the alloys.

In this work, we investigate the effects of disorder in the structural and luminescence features of the Pr3+ ion-implanted AlGa1−xN (0 ≤ x ≤ 1) samples.

2. Experimental

AlGaN layers (0 ≤ x ≤ 1) purchased from TDI Inc. were grown by halide vapour phase epitaxy (HVPE) on (0 0 0 1) sapphire substrates. On top of the GaN sample a ~10 nm thick AlN capping layer was grown in order to allow thermal annealing at temperatures above 1000 °C [18]. Samples were implanted with 150 keV Pr ions to a fluence of 2 × 1014 ion/cm2 and with an angle of 10° between the surface normal and the beam. Post-implant annealing was performed in a tube furnace in 1 bar N2 over-pressure for 20 min at 1100 °C in the case of GaN and at 1300 °C for AlGa1−xN (x > 0). During annealing the samples surface was protected by an unimplanted piece of AlN placed face to face with the samples, as a proximity cap, to inhibit the dissociation of the surface. Rutherford backscattering/channeelling (RBS/C) measurements were performed with a 1 mm diameter collimated beam of 2 MeV He+ ions. The backscattered particles were detected at 140° with respect to the incoming beam direction using a silicon surface barrier detector with a resolution of 13 keV.

X-ray diffraction (XRD) reciprocal space maps (RSM) were acquired using monochromated CuKα radiation on a high-resolution diffractometer D8Discover system from Bruker-AXS using an asymmetric 2-bounce Ge(2 2 0) monochromator and a scintillation detector.
Steady-state photoluminescence (PL) was excited either by the 325 nm line of a cw He–Cd laser or by a 1000 W Xe lamp coupled to a monochromator. The samples were mounted in the cold finger of a closed cycle helium cryostat and the sample temperature could be controlled in the range from 14 K up to room temperature (RT). PL was measured using a Spex 1704 monochromator (1 m, 1200 mm−1) fitted with a cooled Hamamatsu R928 photomultiplier. Photoluminescence excitation (PLE) measurements were recorded at RT on a modular double grating spectrofluorimeter (Fluorolog-3, Jobin Yvon-Spex) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. The spectra were corrected for the wavelength-dependent response of the optical system and the spectral distribution of the lamp using a photodiode reference detector.

3. Results and discussion

The RT PLE spectra of the studied AlxGa1−xN alloys monitored on the highest intensity line of the 3P0−3F2 transition of the Pr3+ ion are shown in Fig. 1. The expected bandgap change with increasing AlN molar fraction is clearly observed. From the PLE spectra an estimate of the composition (indicated in Fig. 1b) was calculated using the dependence of the alloys bandgap

\[ E_g(x) = E_g(GaN)(1-x) + E_g(AlN)x - bx(1-x), \]

with \( E_g(GaN) = 3.4 \text{ eV} \), \( E_g(AlN) = 6.1 \text{ eV} \), and a bowing parameter \( b = 0.86 \) or 1 eV [2,3]. The derived values for the composition agree well with RBS measurements.

Even at RT the Pr3+ doped layers exhibit characteristic luminescent features of the trivalent rare-earth ion such as the green 3P1−3H5 and red 3P0−3H6. Inside the AlN wide bandgap semiconductor the Pr3+ energy levels corresponds to the multiplet manifolds \((2S+1LJ)^{(2S+1LJ)}\) 1S0, 3P2, 3P1, 3P0, 1I6, 3P2, 3F4, 3F3, 3F2, 3H6, 3H5, and 3H4 [19]. However, from the RT PLE spectra monitored in the highest PL intensity lines of the Pr3+ ion, we are not able to observe any intra-configurational absorption (4f−4f) that populates the radiative emitting levels. For samples with AlN mole fraction lower than 36% the atomic-like 4f2 energy levels are populated via bandgap excitation and eventually band-tail defect states observed in the RT PLE spectra. For higher contents an additional violet absorption band, indicated by an arrow in Fig. 1a, can also contribute to the excitation. This band, that blue shifts with increasing Al contents, is also observed when the emission is monitored on the unstructured blue/green PL defect bands. Impurity active centres associated with native defects such as \((V_{III})^3\) and \((V_{III-complex})^2\) have been recently reported in AlxGa1−xN alloys [20] and its peak position is known to suffer a blue shift with increasing AlN molar fraction.

Cooling down the samples increases the line intensity and resolves the rare-earth PL features. The 14 K PL spectra of the red (≈652 nm) 3P0−3F2 transition in selected doped alloys are shown in Fig. 2. Increasing AlN molar fraction promotes an energy shift of the main peaks, which is accompanied by an increase of the full-width at half-maximum (FWHM) up to an AlN molar fraction of \( x \approx 0.7 \). A similar trend was recently reported for other intra-4f transitions (e.g. Eu3+, Tb3+, Er3+) [4–6,9,21] as well as for the

**Fig. 1.** (a) RT PLE spectra monitored on the highest intensity PL line transition of the Pr3+ ion. The spectra are normalized to the maximum intensity value at the band edge. (b) Bandgap energy as a function of AlN molar fraction. The dot lines are theoretical calculations (see text) and the full squares are the values estimated from the PLE spectra. (c) and (d) RT PL and PLE spectra for two selected doped samples. The PL spectra (solid line on the right side) were measured using (c) 325 nm or (d) 280 nm excitation light. PLE spectra were monitored in the 3P0−3F2 transition (dotted line) or on the broad band (full line on the left side).
excitonic emission in undoped Al$_x$Ga$_{1-x}$N alloys [22–25]. The enlargement of excitonic FWHM and increasing exciton localization energy for the undoped alloys was explained in terms of the potential fluctuations caused by disorder [22–25] that are also likely to be the cause of the increase of the FWHM of the rare-earth emission lines. All these results strongly suggest that the quality of the ternary alloys depends on the AlN molar fraction. The disorder-related effects have a maximum when $x/0.7$.

Concerning the population mechanisms that give rise to the Pr$^{3+}$ emissions, we can assume that the main excitation paths to the $4f^2$ radiative recombination levels are via host sensitization and/or inter-configurational $4f^n$-$4f^{n-5}$d absorption, as observed in other wide bandgap materials [26]. However, from this preliminary optical analysis we cannot rule out a population channel via defect states. In particular, from the RT PLE spectra shown in Fig. 1, it is clear that the host sensitization occurs and also a below bandgap absorption band is involved on the $4f^2$ excitation. Different broad emission bands are observed in the PL spectra of selected doped alloys, taken at 14 K, with different excitation wavelengths, as shown in Fig. 3. Further complementary measurements are needed in order to understand the rare-earth excitation mechanisms.

RBS characterization of the as-implanted samples show that the damage introduced by the implantation is highest for the GaN sample and drops for Al-containing alloys similar to previous measurements on Eu-implanted AlGaN [27]. Fig. 4 shows RBS/C spectra from selected alloys. The decrease of Pr-backscattering yield in the $<0001>$ aligned spectra in all samples furthermore indicates that directly after the implantation the majority of Pr ions is found on substitutional cation sites as reported previously for Pr-implanted GaN [16]. However, note that measuring only along the $<0001>$ direction we cannot exclude a displacement of Pr along this axis. While the annealing of GaN and AlN after RE implantation was studied before and optimized parameter were used in this work [18,28], little structural information is available on RE implantation and thermal annealing of AlGaN. Fig. 5 shows the (105) RSM of the sample Al$_{0.77}$Ga$_{0.23}$N:Pr before and after annealing at 1300°C. The intense reflection of the Al$_{0.77}$Ga$_{0.23}$N substrate is seen. In the as-implanted sample the reflection expands to lower values of $Q_c$ showing that the $c$-axis in the implanted layer is expanding due to the introduced implantation damage, while the $a$ lattice parameter remains unchanged. A similar expansion of the $c$-parameter after RE implantation is also typical for implantation into GaN [29]. After annealing at 1300°C, the expansion of the lattice is reversed due to the removal of implantation damage, however, the intensity of the Al$_{0.77}$Ga$_{0.23}$N reflection is decreasing indicating some deterioration of the crystalline quality of the sample. RBS spectra on the same sample (not shown) also show a slight loss of
Ga from the surface, some diffusion of Pr towards the surface and an increase of de-channelling in the aligned spectrum possibly due to extended defects or the formation of different phase inclusions during annealing.

4. Conclusion

Al$_x$Ga$_{1-x}$N (0 $\leq$ x $\leq$ 1) alloys intentionally doped with Pr$^{3+}$ by ion implantation followed by thermal annealing were analysed by optical and structural techniques. PL and PLE data allow the identification of the intra-4f$^2$ transitions of the Pr$^{3+}$ ion in all the studied samples. The high-resolved spectra in the region of the red $^3P_0 \rightarrow ^1F_2$ transition show an enlargement of the line widths with the AlN molar fractions, up to x = 0.7. This behaviour was also reported for the excitonic recombination in the alloys, and for 4f$^2$-related transitions in Al$_x$Ga$_{1-x}$N samples doped with other rare-earth ions. This general trend suggests that the alloy disorder increases with Al content, reaching a maximum at x = 0.7. Pr$^{3+}$ ions are excited via host sensitization and via below band gap absorption. Our preliminary structural results show that annealing conditions have to be optimized for the different AlGaN compositions to avoid deterioration of crystal quality or diffusion of the implanted ions. Nevertheless, the fact that similar results were found for several rare-earth ions, different AlGaN starting materials and different implantation and annealing conditions hints to underlying common physical principle.

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