Optical and structural properties of an Eu implanted GaN quantum dots/AlN superlattice

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Abstract

GaN/AlN structures made of GaN quantum dots (QDs) separated by AlN spacer layers, were doped with Europium by ion implantation. Rutherford Backscattering/Channelling measurements showed that Eu is incorporated mainly on near-substitutional cation sites within the superlattice region. Only slight deterioration of the crystal quality and no intermixing of the different layers are observed after implantation and annealing. After thermal annealing, photoluminescence associated with Eu$^{3+}$ ions was observed. From its behaviour under different photon energy excitation and sample temperature we concluded that the Eu-related emitting centres are located inside the GaN QDs or dispersed in the GaN and AlN buffer or spacer layers. The 624 nm PL line, associated with Eu-doped GaN QDs, shows very low thermal quenching, suggesting recombination of confined carriers through rare-earth ion excitation.

Keywords: GaN, quantum dots, ion implantation, rare earths, RBS, PL, PLE
1. Introduction

Rare earth doped wide band gap semiconductors have been widely studied in the last decade due to their potentialities for light-emitting diodes. The rare-earth doping option of group III nitrides (Gallium nitride (GaN), aluminium nitride (AlN), indium nitride (InN) and their alloys) is particularly attractive resulting in blue, green and red light emission\textsuperscript{1-3}. Eu\textsuperscript{3+}, one of the most studied lanthanide ions in GaN, gives rise to red luminescence which is of particular importance due to the strong loss of efficiency of conventional GaN-based LEDs in this spectral region\textsuperscript{4}. Different Eu-related optical centres were identified in GaN due to their characteristic $^2S+1L_J$ manifold transitions $^5D_0\rightarrow^7F_J$\textsuperscript{5-8}, one of them showing laser action upon optical pumping\textsuperscript{9}. However, a restriction to the use of rare-earth ions is their relatively low luminescence efficiency, which is partly due to the low concentration of rare-earth ions combined with nonradiative carrier recombination. Recently, a remarkable enhancement of Eu\textsuperscript{3+} luminescence efficiency was reported for Stranski-Krastanov MBE grown GaN quantum dots (QDs) on AlN templates using an in-situ doping methodology\textsuperscript{10}. Using EXAFS measurements these authors have proven that Eu is located inside the GaN QDs rather than on the AlN layers. The dominant intra-atomic $4f^6$ transition of Eu\textsuperscript{3+} in the GaN QDs was found to be shifted to lower energies when compared with the observed emission in GaN:Eu layers suggesting that Eu\textsuperscript{3+} in GaN QDs have a specific signature\textsuperscript{10}. The rare earth doping of QDs offers a possible way to enhance luminescence efficiency in the visible range due to the strong confinement of carriers in QDs. In this work stacks of GaN QDs separated by AlN spacer layers were implanted with Eu\textsuperscript{3+} ions. The incorporation and optical activation of Eu\textsuperscript{3+} into the GaN QDs is discussed.
2. Experimental

Ten periods of self assembled GaN quantum dots separated by 8.8nm thick AlN spacer layers were grown by molecular beam epitaxy (MBE). The growth was performed on a c-plane sapphire substrate. A GaN buffer layer was grown followed by an AlN buffer layer; the QDs were formed by depositing nine monolayers of GaN.

7x10^{14} \text{at/cm}^2 Eu ions were implanted along the surface normal, with an energy of 120keV. The Eu-profile was measured by Rutherford Backscattering showing a distribution reaching ~120nm deep into the sample with the maximum Eu concentration at a depth of ~50nm. Post-implant thermal annealing to remove implantation damage and optically activate RE ions was performed for 20 min at 1000ºC in a tube furnace under 3.8 bar N\textsubscript{2} pressure and placing a thick GaN film on sapphire face to face to the sample as a proximity cap.

Rutherford Backscattering/Channelling (RBS/C) measurements were performed with a beam of 2 MeV He\textsuperscript{+} ions. The backscattered particles were detected at 140º or 160º with respect to the incoming beam direction using a silicon surface barrier detector with a resolution of 13 keV.

X-ray diffraction reciprocal space maps (XRD RSM) around the (105) reciprocal lattice point were acquired with a high resolution diffractometer equipped with a Göbel mirror, a 2-bounce Ge(444) monochromator and a position sensitive detector using Cu K\textsubscript{α1} radiation.

Steady state photoluminescence (PL) was measured using a Spex 1704 monochromator (1m, 1200 mm\textsuperscript{-1}) fitted with a cooled Hamamatsu R928 photomultiplier. The samples were mounted in the cold finger of a closed cycle helium cryostat allowing the sample temperature to be controlled in the range from 14 K up to room temperature (RT). A cw He-Cd laser (325 nm line) or an 1000W Xe lamp coupled to a monochromator were
used as photon excitation source. Photoluminescence excitation (PLE) measurements were recorded on a modular double grating spectrofluorimeter (Jobin Yvon Fluorolog-3) 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. To investigate the lattice vibrational properties, room temperature Raman spectra were acquired under UV (325 nm) and visible (514.5 nm) excitation and analysed in backscattering geometry using a Horiba (Jobin-Yvon HR 800) micro-Raman spectrometer with 2400 grooves/mm and a Jobin-Yvon T6400 micro-Raman system equipped with a double monochromator.

3. Results and discussion

The (105) XRD RSM of the as-grown sample showed that the GaN and AlN buffer layers are mostly relaxed and the multilayer period thickness was determined to be 9.5 nm (Figure1). Fits to the random RBS spectra performed with the NDF code\(^1\) indicated that the second buffer layer as well as the spacer layers in the multilayer structure are not pure AlN but contain about 10 to 15% of GaN. For RBS measurements in grazing incidence geometry it is possible to resolve the first GaN QD planes. The determined period thickness of ~9(1) nm is in good agreement with the average value measured by XRD. The total thickness of the 10 period superlattice measured by RBS was ~98(5) nm and the one of the AlGaN buffer layer ~360(5) nm which means that approximately 85% of the Eu ions were incorporated into the region of the superlattice while the remaining fraction was stopped within the AlGaN buffer layer. It cannot be excluded that a very
small fraction of Eu ions can be channelled across the 360 nm thick AlGaN buffer layer and are stopped only in the GaN buffer layer.

Figure 2 presents random and <0001> aligned RBS/C spectra taken after implantation and annealing. Implantation and annealing does not cause any significant changes in the RBS spectra and no Eu diffusion was observed. The inset in Figure 2 shows spectra taken in grazing incidence geometry (θ=84º) before and after the implantation where the first GaN QD planes are resolved. No signs of intermixing of the layers were found. However, the implantation does affect the crystalline quality of the samples. As a measure for crystal quality the RBS/C minimum yield (yield in the aligned spectrum divided by the random yield) in a depth window comprising the Ga-signal from the superlattice region was determined. It increased from 11% for the virgin sample to 35% after the implantation and decreased to 17% after annealing showing that probably higher annealing temperatures are necessary in order to completely remove implantation damage. Recent annealing studies on unimplanted GaN QD/AlN multilayers showed that the superlattice is maintained for annealing temperatures as high as 1200ºC\textsuperscript{12}. Note that thick GaN films under similar annealing conditions start to dissociate already at around 1000ºC while AlN is thermally more stable and acts as a protective cap. This is a promising result since a strong increase of Eu emission in thick GaN capped by AlN was observed when the annealing temperature was increased from 1000ºC to 1300ºC\textsuperscript{13}.

Full angular scans across the <0001> and <-2113> axes were performed. The <0001> Ga-scans from the superlattice region for the virgin and the implanted/annealed sample (Figure 3) reveal, besides the increased minimum yield, a narrowing of the Ga-scan from the GaN QDs. The Al-scan cannot be assessed due to the overlap with the Ga-signal from the GaN buffer layer. Nevertheless, Monte Carlo simulations show that the scans for Al and Ga in a GaN/AlN superlattice have the same width when the windows
comprise several bi-layers. The scan for Eu is significantly narrower than those for the matrix atoms showing that Eu is displaced from the substitutional site. The N-site can be excluded from measurements across the < -2113 > axis (not shown) which allows the distinction between the cation and anion sites. In both thick AlN and GaN films, implanted Eu was found to be incorporated into lattice sites which are slightly displaced from the substitutional cation site. However, only in AlN a strong displacement normal to the c-axis was found which is in agreement with the assumption that the majority of the Eu ions are stopped within the relatively thick AlN spacer layers and only a small fraction within the QDs. The volume fraction of GaN QDs within the superlattice region was estimated from RBS to be in the order of ~5-10%.

Figure 4 shows Raman spectra for excitation at 325 and 514.5 nm. The positions for phonon lines in unstrained GaN and AlN are marked. In the present case, lines are slightly shifted from these positions due to strain in the superlattice. The 653 cm⁻¹ peak corresponds to E₂ phonons of AlN layers under tensile strain and the 601 cm⁻¹ is assigned to E₂ phonons from GaN QDs. The B and C modes are enhanced under the resonant excitation conditions.

Figure 5 shows the low temperature PL spectra after implantation and annealing obtained with two different excitation wavelengths below the AlN band gap. Besides the usual transitions from GaN buffer layers a blue band is observed which has been assigned to large GaN QDs. The emission in the red is dominated by the intra-4f⁶ transitions of the Eu³⁺ ions.

The energy position and the width of Eu-related transitions vary significantly with the composition in AlₓGa₁₋ₓN hosts, as is shown in Figure 6. The ⁵D₀ → ⁷F₂ transition shifts to low energies when we consider a sequence of host matrixes, going from GaN to AlN.
In the alloys this shift is accompanied by a broadening of the emission lines, which merge in a more or less unstructured band, as also observed for other rare earth ions. Depending on the energy of the exciting photons, in the GaN QD/AlN sample different red Eu-related emission is observed (Figure 7). When the sample is excited with 325 nm light a series of narrow lines extending from 620 nm to 626 nm is detected, while an unstructured broad line, centred at 624 nm, was measured for excitation at 380 nm. We interpret these results as a manifestation of Eu emitting centres associated to different environments and excitation paths. The positions of the narrow lines are in accordance with the lines found in thick Eu-doped GaN and AlN films (see Figure 6) and are attributed to Eu dispersed in the GaN buffer or wetting layers and AlN buffer or spacer layers, while the broad 624 nm line is believed to arise from Eu located inside the GaN QDs. This last result is in accordance with previous observation of in-situ doped GaN:Eu QD samples.

Photoluminescence excitation experiments show that Eu located in GaN QDs is preferentially excited with 380 nm light (Figure 7). To further confirm that the 624 nm emission is a signature of Eu located inside the QDs, PL measurements were carried out as a function of the temperature (Figure 8). Using 325 nm excitation a decrease of the integrated PL intensity by ~30% is observed between 14 K and 290 K. This quenching is usually observed in Eu doped GaN, AlN or Al_{x}Ga_{1-x}N alloys, and is likely due to an increase of nonradiative carrier recombination with increasing temperature and a decrease of carrier-mediated energy transfer between the matrix and the Eu ions. Using 380 nm excitation light very low thermal quenching of the PL was observed. This extraordinary result reinforces our assumption that the PL line at 624 nm is due to Eu located inside GaN QDs. More effective carrier trapping by Eu ions in GaN QDs than in GaN layers, combined with a lower number of nonradiative recombination centres in
the almost defect free QDs can explain the invariance of luminescence intensity with temperature.

**Conclusions**

GaN/AlN structures made of GaN QDs separated by AlN spacer layers, were doped with Europium by ion implantation. After thermal annealing to remove implantation damage and optically activate the Eu ions, Rutherford Backscattering Spectrometry and Ion Channelling measurements revealed no significant intermixing of the layers and a good recovery of the lattice after thermal annealing. The majority of the Eu ions are located on near-substitutional Ga- or Al-sites. Most ions are stopped within the relatively thick AlN spacer layers and only a small fraction within the QDs. After annealing, photoluminescence associated with Eu ions has been measured and the samples exhibit dominant intra-4f⁶ transitions (⁵D₀→⁷F₂) of Eu³⁺ in the red spectral region. From the observed fingerprint lines, different Eu-related emitting centres were identified and assigned to Eu located within the buffers and spacer layers and Eu incorporated inside the QDs. A broad line at 624 nm was identified as a typical signature of Eu³⁺ inside of the QDs, corroborating previous observations in in-situ doped samples⁹⁰. PL measurements with different excitation wavelengths indicate that the Eu³⁺ luminescence inside the QDs is preferentially excited at 380 nm. With this excitation conditions almost no thermal quenching of the intraionic recombination was observed showing that a higher efficiency can be reached when compared to the intraionic Eu³⁺ recombination in GaN, AlN and alloys. In conclusion it has been demonstrated that Eu doping of GaN QDs can be achieved by ion implantation. The strong carrier confinement in the QDs enable efficient emission from the Eu-ions even at room temperature.
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References


Figure captions

Fig. 1 - (105) asymmetric XRD RSM. The GaN layer is represented by the bottom peak and the top peak represents the AlN layer. The low intense peaks are due to the superlattice structure.

Fig. 2 - Random and <0001> aligned RBS spectra after implantation of $7 \times 10^{14}$ at/cm$^2$ Eu ions and annealing at 1000ºC. The inset shows spectra taken in grazing incidence geometry (84º tilt) where the first GaN QD planes can be resolved.

Fig. 3 - Full angular scans across the <0001> axis using depth windows comprising the Ga-signal of the superlattice region for the as-grown and implanted/annealed sample as well as the Eu-scan after annealing.

Fig. 4 - Raman spectra measured in backscattering configuration with different excitation energies.

Fig. 5 - PL spectra measured at 14 K excited with photons of different energy.

Fig. 6 - 14 K PL corresponding to the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ in different nitride based hosts.

Fig. 7 - 14 K PL and PLE spectra (monitored on the red Eu-related $^5D_0 \rightarrow ^7F_2$ transitions) for the doped GaN/AlN QD sample.

Fig. 8 - $^5D_0 \rightarrow ^7F_2$ PL as a function of temperature for two different excitation wavelengths.
Fig. 1

$Q_{z<001>}$ (Å$^{-1}$) vs. $Q_{x<100>}$ (Å$^{-1}$)
Fig. 2

N643 dots annealed

Counts

energy (keV)

GaN

Al$_{0.9}$Ga$_{0.1}$N

QD

Eu

x20

random

aligned

as implanted

virgin

θ=84°
Fig. 3

Normalized Yield vs. angle (deg) for implanted Eu, GaN QD as grown, and GaN QD after Eu implantation.
Fig. 4
Fig. 7
Fig. 8

\[ \lambda_{\text{exc}} = 325 \text{ nm}; \text{ GaN/AlN QD} \]

PL intensity (a.u.)

\[ \lambda_{\text{exc}} = 380 \text{ nm}; \text{ GaN/AlN QD} \]

PL intensity (a.u.)

Wavelength (nm)