Mater. Res. Soc. Symp. Proc. Vol. 892 © 2006 Materials Research Society 0892-FF23-15.1

Influence of the Annealing Ambient on Structural and Optical Properties of Rare Earth Implanted GaN

K. Lorenz[1], E. Nogales[2], R. Nédélec[3], J. Penner[3], R. Vianden[3], E. Alves[1], R.W. Martin[2], K.P. O`Donnell[2]
[1]Instituto Tecnológico e Nuclear, EN10, 2686-953 Sacavém, Portugal
[2]Department of Physics, University of Strathclyde, Glasgow, G4 0NG, U.K.
[3]HISKP, University of Bonn, 53115 Bonn, Germany

ABSTRACT

GaN films were implanted with Er and Eu ions and rapid thermal annealing was performed at 1000, 1100 and 1200 ºC in vacuum, in flowing nitrogen gas or a mixture of NH_3 and N_2. Rutherford backscattering spectrometry in the channeling mode was used to study the evolution of damage introduction and recovery in the Ga sublattice and to monitor the rare earth profiles after annealing. The surface morphology of the samples was analyzed by scanning electron microscopy and the optical properties by room temperature cathodoluminescence (CL). Samples annealed in vacuum and N_2 already show the first signs of surface dissociation at 1000 ºC. At higher temperature, Ga droplets form at the surface. However, samples annealed in NH_3+N_2 exhibit a very good recovery of the lattice along with a smooth surface. These samples also show the strongest CL intensity for the rare earth related emissions in the green (for Er) and red (for Eu). After annealing at 1200 ºC in NH_3+N_2 the Eu implanted sample reveals the channeling qualities of an unimplanted sample and a strong increase of CL intensity is observed.

INTRODUCTION

Doping GaN with optically active rare earth (RE) elements allows the production of electroluminescent emitters that cover the entire visible spectral range [1]. Ion implantation is a powerful technique to introduce ions in a reproducible way with a defined concentration profile. However, for GaN this method still suffers from the incomplete annealing of the resultant lattice damage and the dissociation of the surface at high temperatures [2]. It was shown previously that the emission intensity of Eu-implanted GaN increases strongly with rising annealing temperature [3]. However, higher annealing temperatures require an increase of the partial nitrogen pressure to suppress the loss of N from the sample. To prevent surface dissociation, several approaches were reported in literature including the use of a proximity cap (i.e. a piece of unimplanted GaN placed face to face with the sample), the predeposition of a capping layer or the annealing in high N_2 overpressures [2-4]. The annealing atmosphere can influence the stability of the surface and thus the recovery of the crystal. Using a NH_3 containing atmosphere is closer to the growth conditions in the MOCVD reactor and can help to stabilize the surface. However, at the same time highly reactive hydrogen can damage the surface; etching effects were observed for heat treatment of GaN in NH_3 at temperatures above 800 ºC [5]. Emission properties can also be influenced by incorporated hydrogen. Lozykowski et al. [6] reported an improvement in luminescence intensity for Pr implanted GaN annealed at 1100 ºC in NH_3 as compared to samples annealed in N_2. In this work we study the structural and optical properties of Er and Eu implanted GaN after rapid thermal annealing in different atmospheres for annealing temperatures up to 1200 ºC.

EXPERIMENTAL DETAILS

GaN samples, grown by molecular organic chemical vapor deposition (MOCVD) on sapphire ubstrates, were implanted at room temperature with 300 keV Er and Eu ions to a fluence of 1×10^{15} at/cm^2 and 8×10^{14} at/cm^2, respectively.

After implantation the samples were annealed in a rapid thermal annealing apparatus for 120 s at emperatures in the range 1000 to 1200 ^{o}C, while placed between graphite strips in vacuum or in lowing gas: N_2 gas or in a mixture of NH_3+N_2 with a mixing ratio of 5:1. In all cases, a piece of unimplanted GaN was placed face to face with the samples as a proximity cap to further inhibit out-iffusion of nitrogen from the surface.

Rutherford backscattering / channeling (RBS/C) studies were performed with a 1 mm iameter collimated beam of 2 MeV He^+ ions. The backscattered particles were detected at 140^o nd close to 180^o with respect to the incoming beam direction, using silicon surface barrier detectors with energy resolutions of 13 and 16 keV, respectively.

The surface morphology was studied with a Cameca SX100 electron probe microanalyser EPMA), modified to allow also the measurement of room temperature cathodoluminescence CL) or with a field emission gun scanning electron microscope (FEGSEM).

RESULTS

Figure 1 presents secondary electron images obtained in the EPMA for Er implanted samples nnealed at 1000 ºC and 1100 ºC in NH_3+N_2, vacuum, and N_2, as indicated. After annealing at 1000 ºC in N_2 or in vacuum the surface already shows localized defects with a lateral size around 1 micrometer. For the higher annealing temperature the surface of those samples is strongly damaged and Ga droplets form. In contrast to this, very good results are achieved when using a NH_3+N_2 annealing atmosphere: the surface remains smooth also for annealing at 1100 ºC.

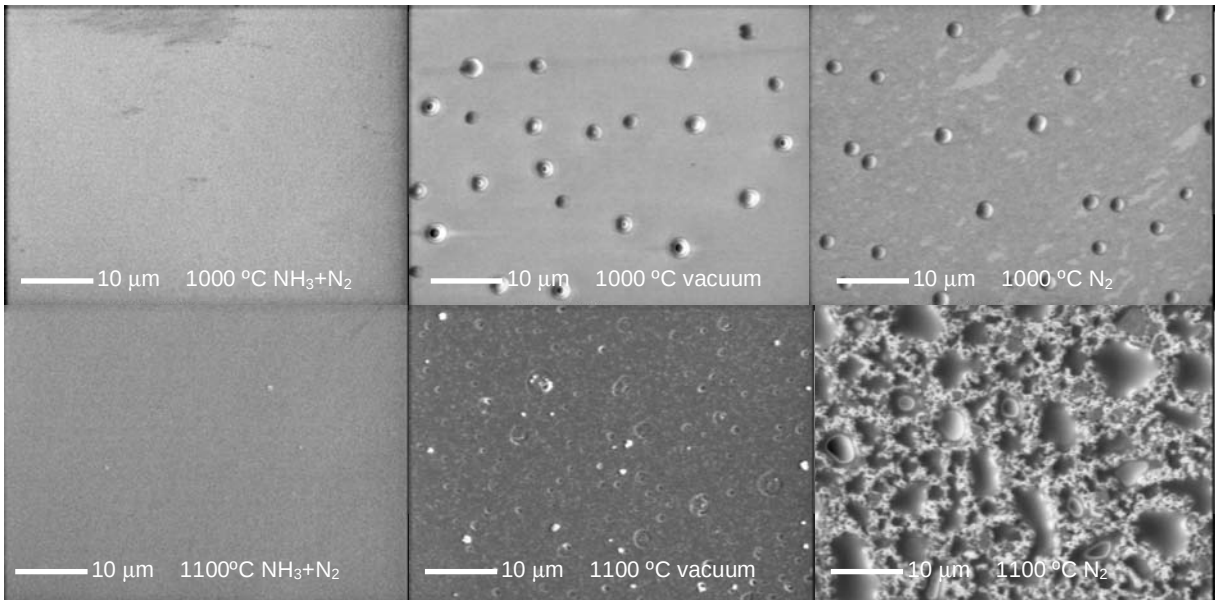

Figure 1. Secondary electron images obtained in the EPMA for Er implanted samples annealed t 1000 ºC and 1100 ºC in N_2+NH_3, vacuum, and N_2.

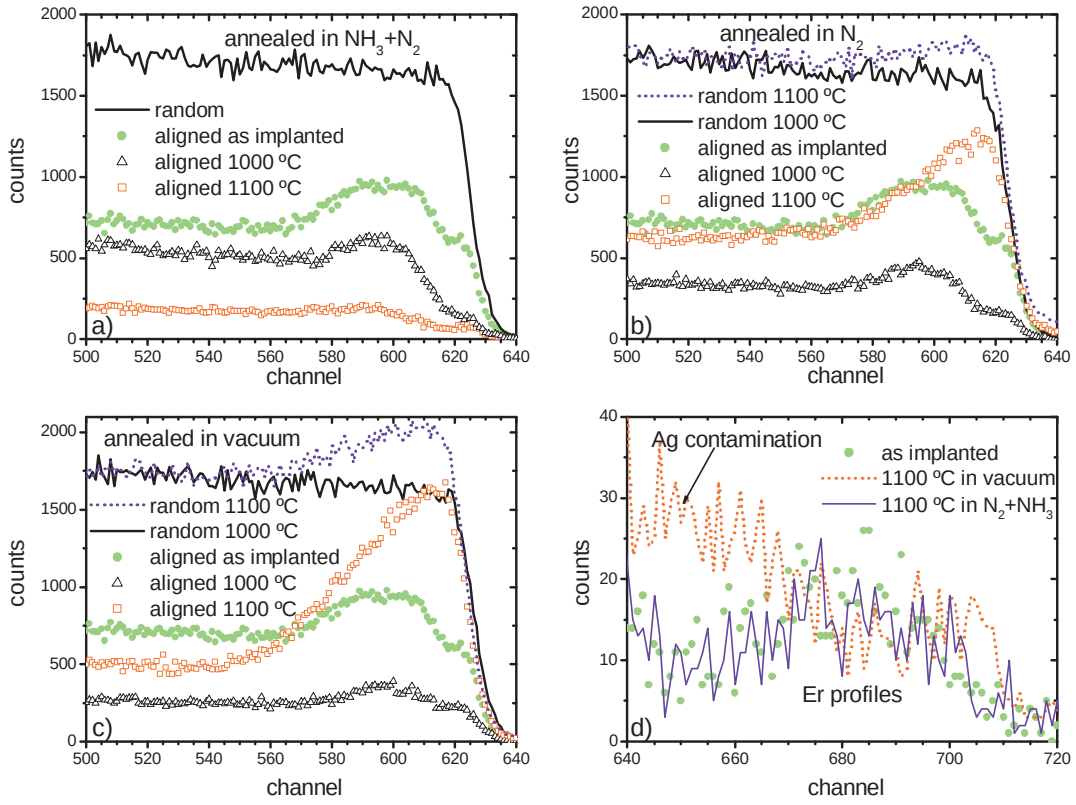

Figure 2. RBS/C random and <0001> aligned spectra of the Ga signal for Er-implanted GaN samples before and after annealing at 1000 and 1100 ºC in (a) NH_3+N_2, (b) N_2 and (c) vacuum; (d) RBS/C random spectra showing the Er profiles before annealing and after annealing at 1100 ºC and the contamination with Ag of the samples annealed in N_2 and vacuum.

Figures 2 a)-c) show the Ga signal of the RBS/C random and <0001> aligned spectra before and after annealing at 1000 and 1100 ºC in NH_3+N_2, N_2 and vacuum. Annealing at 1000 ºC reduces the lattice damage in a similar way for all annealing atmospheres. The small defects seen in SEM do not affect the RBS/C spectra showing that those defects are superficial. The Er profiles do not change after 1000 ºC annealing. Increasing the annealing temperature to 1100 ºC does only for annealing in NH_3+N_2 atmosphere result in any further reduction of the lattice damage (Fig. 2a). In both N_2 and vacuum, the backscattering yield of the aligned spectra increases strongly within a layer as thick as the implanted region, showing that severe damage reaches deep into the sample. The Er profile after annealing at 1100 ºC in NH_3+N_2, does not show any changes while in the two other cases a shift of the Er profile to the surface is noticed. Also in those two samples a contamination of the sample by Ag is observed (Fig. 2d). The origin of this contamination is the silver paint used to mount the samples during SEM and CL measurements. While for stochiometric GaN this paint is easily removed from the surface with acetone, the Ag ions diffuse deep into samples which have formed Ga droplets at the surface. The increase of the random yield at the Ga edge is due to both, the additional counts due to the Ag atoms as well as a relative increase of Ga atoms when N diffuses out of the crystal and Ga droplets are formed.

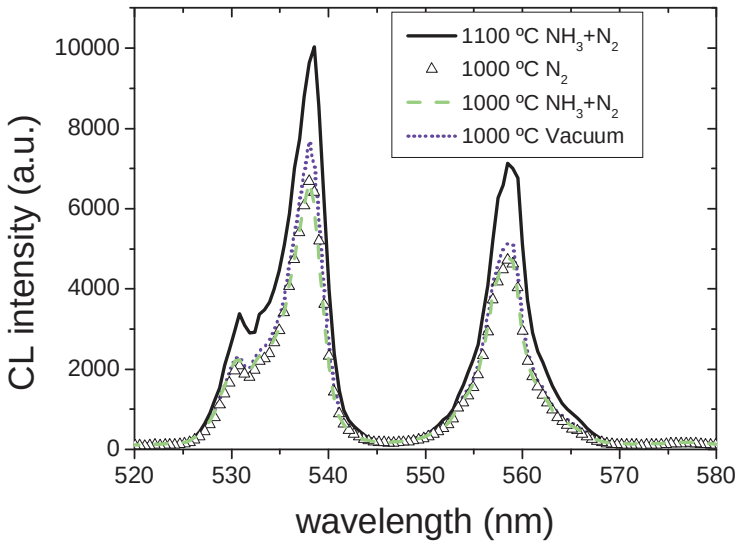

Figure 3. RT CL spectra of Er-implanted GaN annealed at 1000 ºC in three different atmospheres and annealed at 1100 ºC in NH_3+N_2 taken with an electron beam of 5 kV and 40 nA.

The structural properties are reflected in the optical characteristics of the samples. All samples show the typical green emission lines arising from the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ intra-4f shell transition of trivalent Er^{3+} ions. However, for the highly damaged samples, annealed at 1100 ºC in N_2 or vacuum, the CL intensity is very weak. Fig. 3 compares the RT CL spectra of the samples annealed at 1000 ºC with the one annealed at 1100 ºC in NH_3+N_2. The latter, being the sample with the best structural properties, clearly shows the highest CL intensity; the integrated CL being 50 % higher than that of the sample annealed at 1000 ºC.

Figure 4 shows the SEM images of the Eu implanted and NH_3+N_2 annealed samples taken in the FEGSEM. Although the surface looks damaged after annealing at 1200 ºC there are also large regions of the sample with a smooth surface and only localized defects (Fig. 4b).

The surface damage seen with SEM does not feature the RBS/C spectra showing that the damaged surface layer is very thin.

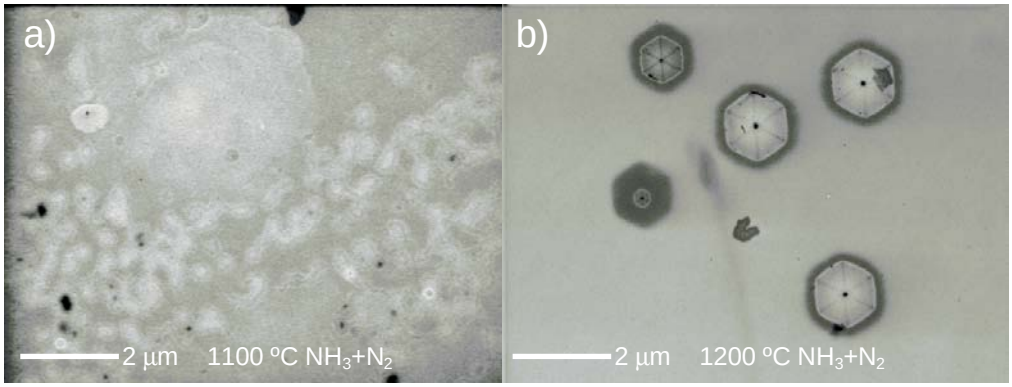

Figure 4. FEGSEM images of Eu-implanted GaN annealed at 1100 ºC and 1200 ºC in NH_3+N_2.

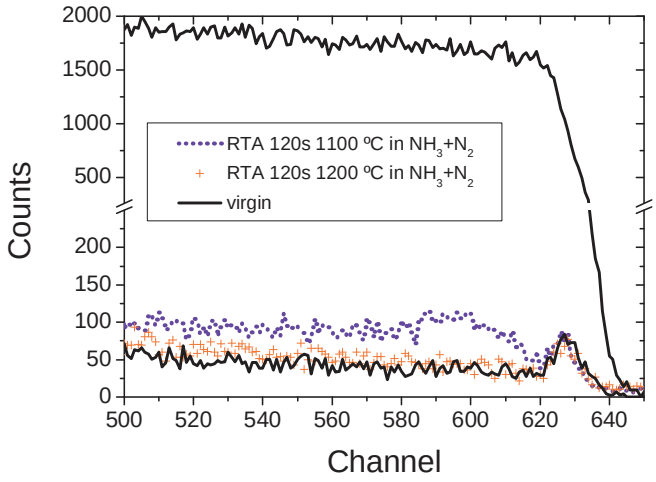

Figure 5. RBS/C random and <0001> aligned spectra of the Ga signal for Eu-implanted GaN samples after annealing at 1100 and 1200 ºC in NH_3+N_2. The aligned spectrum of a virgin sample is also shown.

RBS/C spectra (Fig. 5) reveal a very good recovery of the lattice in the entire implanted region: annealing at 1200 ºC produces an aligned spectrum similar to that of a virgin sample. No signs of loss of GaN or a shift of the Eu profile were observed.

In a previous study Eu was implanted under the same conditions through an epitaxial AlN-layer that was grown on top of the GaN; due to the presence of the cap, post-implant annealing could be performed up to 1300 ºC in N_2 without dissociation of the sample [3]. However, even for this temperature the implantation damage could not be fully removed. To our knowledge, Zolper et al [4] have published the only study in which the channeling quality of GaN was completely restored after implantation and annealing. In this work the annealing was performed at 1500 ºC in a N_2 overpressure of 15 kbar.

The RT CL spectra of the Eu doped samples after annealing at 1100 and 1200 ºC in NH_3+N_2 are shown in Fig. 6. The integrated intensity of the red luminescence arising from the $^5D_0 \rightarrow {}^7F_2$ intra-4f shell transition increases by a factor of 3 for the sample annealed at higher temperature.

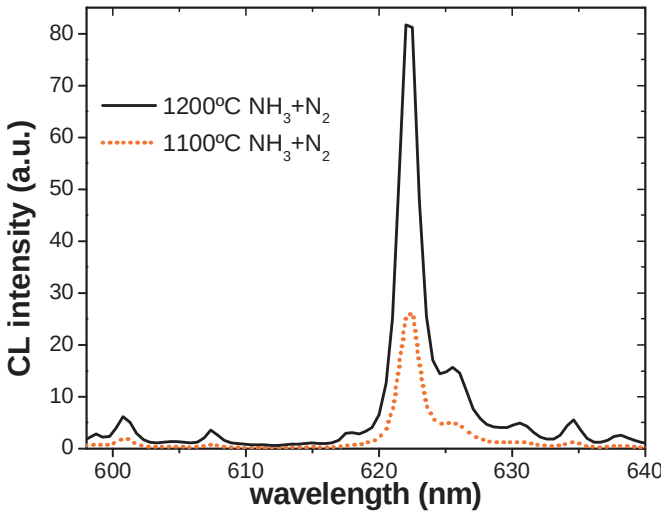

Figure 6. RT CL spectra of Eu-implanted GaN annealed at 1100 and 1200 ºC in NH_3+N_2 taken with an electron beam of 3 kV and 10 nA.

A similar increase of the CL intensity in this temperature range was also observed for samples capped with an epitaxial AlN layer showing that the damage at the surface seen by SEM does not harm the optical properties of the sample.

Our results suggest, that besides the annealing temperature the processes at the GaN surface play an important role in implantation damage annealing. Annealing in a NH_3+N_2 atmosphere was shown to be beneficial to stabilize the GaN surface. Possibly, the formation of reactive nitrogen species such as N or NH plays an important role during annealing. At 1200 ºC the dissociation of N_2 in the presence of Ga atoms was shown to be negligible [7]. Under equilibrium conditions NH_3 dissociates to form N_2 and H_2. However, catalytic processes at the sample surface influence the dissociation of ammonia and promote the formation of reactive N; at lower temperature the GaN growth by reactive molecular beam epitaxy (RMBE) is based on this process [8].

CONCLUSIONS

The structural and optical properties of Er and Eu implanted GaN samples were studied after rapid thermal annealing in different atmospheres. Samples annealed in N_2 and vacuum already show surface damage after annealing at 1000 ºC and are completely destroyed by annealing at 1100 ºC. Annealing in NH_3+N_2 atmosphere stabilizes the GaN surface which stays smooth up to higher temperatures and only shows very superficial damage for 1200 ºC, the highest annealing temperature studied. After annealing at 1200 ºC in NH_3+N_2 the channeling quality of the virgin GaN crystal was restored and the luminescence intensity improved significantly.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Dr. O. Briot (Univ. Montpellier II, France) for the supply of GaN material. The work was partially funded through the European Research Training Network RENiBEl (HPRN-CT-2001-00297) and the bilateral collaboration program by DAAD (Germany) / GRICES (Portugal).

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