CHARACTERIZATION OF Be-IMPLANTED GaN ANNEALED AT HIGH TEMPERATURES

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ABSTRACT

Single crystalline (0001) gallium nitride layers were implanted with beryllium and subsequently annealed within the range of 300-1100 ^{o}C for 10-60 minutes under a flux of atomic nitrogen obtained using a rf plasma source. The nitrogen flux protected the GaN surface from decomposition in vacuum at high temperatures. SIMS measurements revealed that no long range diffusion of the implanted Be occurred at 900 or 1100 ^{o}C. XRD spectra showed defect-related peaks in the as-implanted samples; these peaks disappeared upon annealing at 900 ^{o}C and higher for 10 minutes. Photoluminescence (PL) measurements showed one new line at 3.35 eV which provided strong evidence for the presence of optically active Be acceptors.

INTRODUCTION

Doping of semiconductors by ion implantation offers advantages in comparison to doping during film growth. (i) The concentration as well as the lateral and depth distributions of the dopants are precisely controllable, and (ii) almost all elements can be implanted with sufficiently high purity. However, this process is compromised by the radiation damage which has to be removed via annealing treatments. In the case of gallium nitride (GaN), this essential annealing procedure for dopant activation is very difficult due to the decomposition of the GaN surface for temperatures above 900 °C [1-3]. Annealing temperatures (T_A) of around 1300 °C for >5 minutes are necessary for GaN to fulfil the rule of thumb claiming that implanted semiconductors should be annealed up to 2/3 of the melting point for satisfying electrical activation [3-5].

At this writing, three special annealing procedures for temperatures above 900 °C have been investigated with limited success: (i) Rapid thermal annealing (RTA). During this process GaN is heated up to high temperatures and cooled down within a few seconds. Decomposition is a time dependent diffusion process, and in this small time frame significant decomposition of the implanted layer starts only for temperatures over 1150 °C [6,7]. (ii) N_2-overpressure. Annealing under N_2-overpressure in the kbar range opposes the surface decomposition, but only a slightly higher temperature limit of 1250 °C can be realized due to the exponential rise of the N vapor pressure as a function of temperature [8]. (iii) Polycrystalline AlN cap. An AlN layer, sputter deposited after the implantation, on top of the GaN layer was used to protect decomposition during annealing. Depending on the crystalline quality of the AlN annealing temperatures of 1300 °C for 30 sec. and good results were reached but only for some selected samples [5,9].

In this article we introduce a new annealing technique which allows the annealing of GaN at a temperature of 1100 °C for at least 1 hour. We have applied this technique to Beryllium implanted GaN, because achievement and control of substantial activation of p-type dopants in GaN remains a critical issue vis a` vis improved performance of devices fabricated in this material. The most commonly used p-type dopant is magnesium (Mg) which substitutes on Ga sites and has an ionization energy of ~ 0.25 eV. One-to-two orders of magnitude higher atomic concentration of Mg must be incorporated into GaN to achieve the desired hole concentration at

https://doi.org/10.1557/S1092578300002465 Published online by Cambridge University Press

room temperature [10]. This incorporation reduces the hole mobility due to the enhanced carrier-impurity scattering processes [11]. Beryllium (Be) is a more promising candidate for p-type doping given its measured lower ionization energy of ~ 0.15 eV [12,13].

EXPERIMENTAL

One-to-two μm thick epitaxial, monocrystalline and undoped GaN films were grown on on-axis n-type, Si-face α(6H)-SiC(0001) substrates at 1000 °C and 45 Torr using a vertical, cold-wall, RF inductively heated MOVPE deposition system [11]. A 0.1 μm high-temperature monocrystalline (1100 °C) AlN-buffer layer was deposited prior to the GaN growth. Deposition was performed using triethylaluminum (TEA) and triethylgallium (TEG) in combination with 1.5 SLM of ammonia (NH_3) and 3 SLM of H_2 diluent.

Beryllium was twice implanted at 100 keV and 200 keV to create a broad depth distribution of this element. The dose ratio between the two implantation energies was 2/3 to adjust the maximum impurity concentration of both implantations. TRIM simulations gave a mean ion range of 276 nm (FWHM = 175 nm) and 472 nm (FWHM = 1060 nm), respectively, for the two energies [14]. The total implantation dose ranged between 10^{13} cm^{-2} and $2.5x10^{14}$ cm^{-2}.

All implanted samples were first sequentially annealed in a tube furnace under vacuum at 300, 600 and 900 °C for 10 minutes. The samples were transferred into a MBE chamber for annealing at higher temperatures. Heating of the samples was performed under a flux of atomic nitrogen obtained using a rf plasma source (300 W, Model RF 4.5, SVT Associates). The atomic nitrogen flux protected the GaN surface at 1100 °C for at least 1 hour using a distance between sample and rf source of around 40 cm.

Secondary ion mass spectroscopy (SIMS) was performed by the Analytical Instrumentation Facility at NC State University using a Cameca IMS-6f. Samples were analyzed with a 200 nA, 10 keV O^- primary beam. Two dimensional ω-2θ X-ray diffraction (XRD) pattern were measured using a Philips X'Pert-MRD system with a resolution of 0.001°. Photoluminescence measurements (PL) were performed after each annealing step at 14 K by exciting the GaN samples with a He-Cd laser (3.81 eV). Hall measurements were done after the deposition of Ni(50 nm)-Au(100nm) contacts.

RESULTS AND DISCUSSION

Figure 1 shows SIMS-profiles of implanted Be with a dose of 10^{13} cm^{-2} before and after annealing at 900 °C and 1100 °C for 15 minutes. Both implantation profiles of the 100 keV and 200 keV implantation are clearly visible and in good agreement with TRIM calculations [14]. Within the experimental resolution, no long range diffusion was observed after annealing. This observation is in agreement with Ref. [15], where also no redistribution was observed up to 800 °C. This excellent thermal stability of Be in GaN indicates a strong bonding of Be in the lattice. Therefore, diffusion of Be into GaN from an external source is not practical and ion

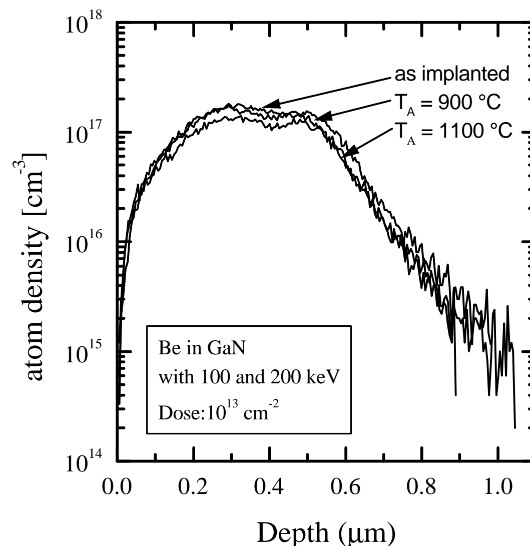

Figure 1: SIMS profiles of Be implanted in GaN, unannealed and annealed to 900 °C and 1100 °C for 15 minutes.

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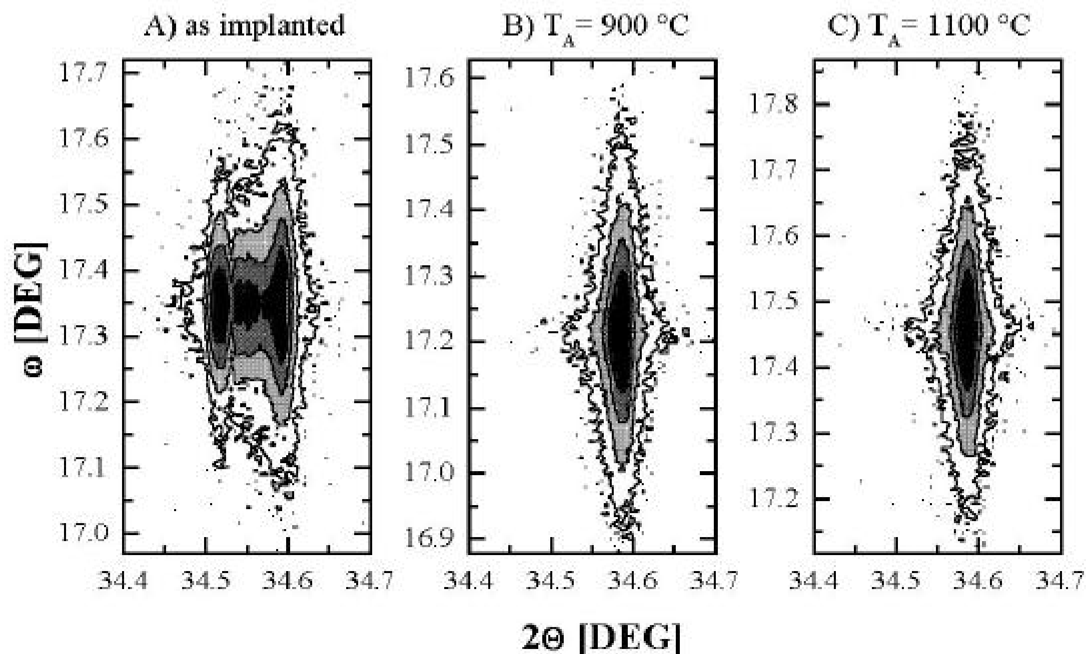

Figure 2: XRD 2-axis ω-2θ map of the (0002) GaN peak (A) dirctly after Be implantation with a dose of $2.5x10^{14}$ cm^{-2} and after subsequent annealing to a temperature of 900 °C (B) and 1100 °C (C) for 10 minutes. (Note: contour plots have log-scale).

implantation or epitaxial growth are the only possibilities to introduce Be into GaN.

Figure 2A displays a two dimensional ω-2θ X-ray diffraction (XRD) pattern of the GaN (0002) peak of a Be-implanted sample with a dose of $2.5x10^{14}$ cm^{-2}. Note: A vertical section of figure 2 is a rocking curve. No significant broadening of the rocking curve was observed compared to the non-implanted situation, but one remarkable characteristic is that a few new peaks appeared at the left side of the (0002) peak after the implantation process. The intensity of these peaks increased at the expense of the main (0002) peak with growing implantation dose. This effect has already been observed [16] and can easily be attributed to an expansion of the GaN crystal lattice by interstitials created during the implantation process. This strong defect related peaks disappeared already upon annealing at 900 ^oC for 10 minutes (Figure 2B) resulting into a spectrum which is comparable to the non-implanted spectrum. Consequently, no improvement was observed for a higher annealing temperature of 1100 °C (Figure 2C). We can conclude that in the view of XRD the GaN lattice is already fully recovered after annealing at a temperature of 900 °C.

The low temperature PL spectra of a Be-implanted GaN sample with a dose of $5x10^{13}$ cm^{-2} are summarized in Fig. 3. No PL lines were observed directly after ion implantation for this dose, but they were observed in the case of lower implantation doses. After annealing to a temperature of 900 °C for 15 minutes PL lines have been detected. However, the intensity of the band edge luminescence is several orders of magnitude lower in comparison to as-grown, unimplanted GaN samples. The weak luminescence line at 3.467 eV (commonly labeled as I_2) in Fig. 3 originates from recombinations of free excitons and/or excitons bound to shallow donors. The LO-phonon replicas for this line could not be observed in the implanted samples due to its low intensity; however, their positions at 3.384 eV and 3.292 eV were determined from the as-grown, unimplanted GaN grown on the same SiC-wafer. This results in a phonon energy of about 85 ± 5 meV for our samples, which is in agreement with values in the literature [17]. The second

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luminescence peak at 3.444 eV is most likely related to defects created during the implantation procedure, as this line also was observed with varying intensities after implantation of Li, Si, Ge, In and Er [18]. We believe that this line is produced by nitrogen vacancies due to donor-band (eD) transitions, because it appears also in unimplanted GaN samples depending on the growth conditions.

One Be related transition with low intensity was observed at 3.35 eV. The intensity of this line varied as a function of the lateral quality of the GaN sample. We attribute this line to band-acceptor (eA) recombinations. For this case, the ionization energy of Be acceptors was calculated to be 150 ± 10 meV [12]. Dewsnip and co-workers [13] also observed a new line in GaN samples doped with Be during growth at 3.376 eV. However, they calculated the ionization energy to be 90-100 meV due to the assumption that this line is a donor-to-acceptor transition. Temperature dependent PL measurements showed different intensity behaviors of the lines at 3.444 eV and 3.35 eV; therefore, we can exclude that the line at 3.35 eV is a phonon replica of the 3.444 eV line. Furthermore, we never observed the line at 3.35 eV after implantation of Li, Si, Ge, In and Er into GaN even when the line at 3.444 eV was present [18]. These observations prove that the line at 3.35 eV is only related to the implanted Be acceptors.

Figure 3 also shows the recorded PL spectra for the same Be implanted GaN sample as a function of annealing temperature. Conflicting with the XRD-results, the implanted material was only partly recovered in view of PL at an annealing temperature of 900 °C, which is in agreement with Ref. [19]. After annealing to 1100 °C for 15 minutes a strong recovery of the PL lines occurred and was further improved after the 1 hour anneal. The intensity of the I_2-line grew more than two orders of magnitude and reached about 80 % of the intensity of the pre-implanted samples. However, the defect-related line at 3.444 eV is still visible and the Be-related line did not grow after the 1100 °C, 1 hour anneal. We can conclude that in view of the PL the implanted GaN is almost recovered after the 1100 °C, 1 hour annealing step, but point defects (invisible to XRD) are still present and may create Be-defect complexes, which are responsible for the low optical activation of Be acceptors.

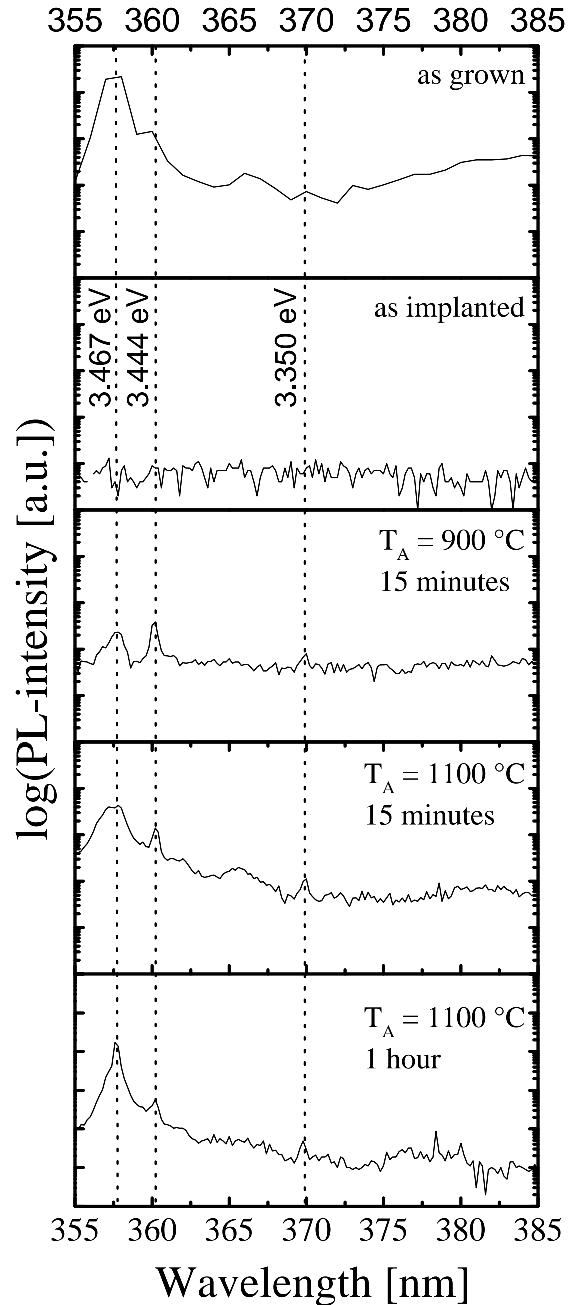

Figure 3: Photoluminescence spectra measured at 14 K of GaN. Spectra were recorded in the situations: as-grown, as-implanted with Be, and after annealing to several temperatures for different times. The implantation energies were 100 keV and 200 keV and the total implantation dose $5x10^{13}$ cm^{-2}.

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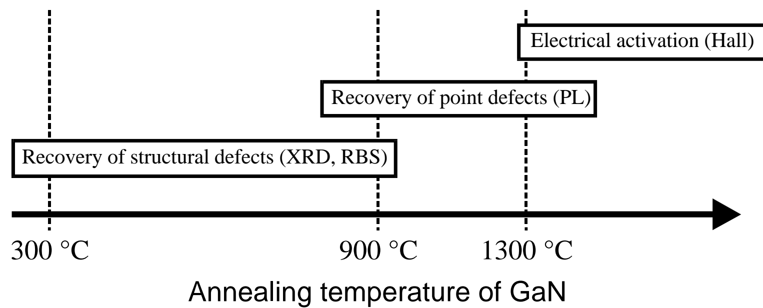

Figure 4: Fundamental recovery processes in ion implanted GaN and their detection methods as a function of annealing temperature (15 minutes).

Hall effect measurements were carried out after annealing to 1100 °C (1 hour) and deposition of Ni-Au contacts. All samples were too resistive for the determination of carrier concentrations or mobilities due to the remaining defects, which are creating compensating deep levels in the band gap.

CONCLUSIONS

We have summarized in Figure 4 the fundamental recovery processes in ion implanted GaN as a function of annealing temperature. The crystal structure of GaN is very resistant to ion bombardment due to the high ionicity of the Ga-N bond. This results in very high doses for amorphization [16]. However, structural defects can be readily created with medium implantation doses (10^{14}-10^{15} cm^{-2}), which can be detected by XRD or RBS-channeling [20]. These defects (mainly interstitials) lead to a lattice expansion which can be removed/recombined upon annealing to 900 °C. The recovery of point defects, visible by PL, starts around 800 °C and is not completed at a temperature of 1100 °C. Around 80 % of the free exciton line is recovered at this point. Based on primary observations on Mg-implanted GaN [21], we predict that after annealing to 1300 °C the GaN crystal is completely recovered and macroscopic electrical activation of the implanted impurities takes place.

We introduced in this article a new annealing procedure under a flux of atomic nitrogen obtained using a rf plasma source. In contrast to the N_2-overpressure technique [8] where the loss of nitrogen is prevented by the hydrostatic pressure, the atomic nitrogen flux protects the GaN surface by an exchange of nitrogen between solid and gas phase. An increase of the flux density by reducing the distance or increasing the power should result in the possibility to anneal GaN even to higher temperature as 1100 °C.

ACKNOWLEDGMENTS

The authors would like to thank D.P. Griffis and G.M. Guryanov for doing the SIMS measurements and Cree Research, Inc. for supplying the SiC substrates for this research. The implantations were conducted by ImplantSciences, Wakefield, MA (USA). This work was supported by the ONR under Contract N00014-92-J-1477 (M. Yoder, technical monitor). C.R. is grateful for funding by the DFG (Ro 1198/2-1). R. Davis was supported in part by the Kobe Steel, Ltd. Professorship.

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