DOPING OF GaN BY Mg DIFFUSION

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ABSTRACT

In this work, we report a study of GaN doping by Mg diffusion. GaN films were grown on sapphire or SiC substrates by MBE. The samples were characterized by Hall measurements and photoluminescence before and after the diffusion. The diffusion was performed in the following manner: Mg layer was deposited on the sample by thermal evaporation, followed by the deposition of a capping layer (metallic or SiO_2). Samples were subsequently annealed in N_2 flow at 850°C or 900°C for 6 hours. We show that Mg diffusion doping is feasible, and that the results are highly dependent on the capping layer. However, it should be pointed out that the obtained results for different samples with the same capping layer may show significant variations in spite of similar properties before the diffusion. This is most likely due to relationship between Mg doping and the presence of threading dislocations, which hinders the reproducibility of diffusion doping process.

1. INTRODUCTION

GaN is a wide band-gap semiconductor, which is of considerable interest for applications in optoelectronic devices operating in visible and UV spectral regions. While GaN based LEDs and laser diodes are already commercially available, there remain several unresolved issues concerning improving the material quality and increasing the level of p-type doping. Efficient p-type doping of wide band-gap semiconductors is in general a challenging task. Despite the achievements in realization of good quality p-type GaN, the activation efficiency of Mg atoms is still as low as few percent, so that typically for Mg incorporation of the order of 10^{19} cm^{-3}, the achieved hole concentration is of the order of 10^{17} cm^{-3}. p-type doping of GaN is typically performed during growth, while the reports on other doping techniques common in semiconductor processing such as ion implantation,[1-3] and diffusion[1,4-6] have been scarce.

Studies of thermal stability and redistribution of the implanted dopants in GaN revealed that implanted Mg does not show change in the concentration profile for annealing temperatures up to 900°C.[2,3] However, annealing in these studies was performed for 10 min. only, which is much shorter than the annealing time for diffusion doping. Rubin *et al.*[1] obtained p-type GaN with hole concentration of 2×10^{16} cm^{-3} and mobility 12 cm^2/Vs by diffusion for 80h in a sealed ampoule at atmospheric N_2 pressure and 800°C temperature. Pan and Chi[4] obtained p-type GaN with carrier concentration 3×10^{15} cm^{-3} and mobility 13 cm^2/Vs by diffusion for 1h at 1100°C in a sealed evacuated quartz tube. Yang *et al.*[5] reported p-type GaN obtained by diffusion in a sealed vacuumed quartz ampoule at 900°C, followed by 5 min. rapid thermal annealing (RTA) at 950°C. The carrier concentration obtained in their work was 1.8×10^{17} cm^{-3} and mobility was ~55 cm^2/Vs. Mobility as high as 90 cm^2/Vs was also obtained by changing the RTA temperature.[5] Chi *et al.*[6] obtained hole concentration of 3×10^{15} cm^{-3} and 2×10^{17} cm^{-3} and a mobility of 13 cm^2/Vs and 10 cm^2/Vs for samples diffused in evacuated quartz tube at 1100°C for 1h and 900°C for 2h, respectively. Large variations in the obtained carrier concentrations and mobility by diffusion doping can be observed among the results reported in the literature. This is most likely due to differences in sample properties before the diffusion, and differences in the diffusion process.

In this work, we investigated the feasibility of Mg diffusion doping in undoped, Si doped, and Mg doped GaN samples with different capping layers. The samples doped with Mg during MBE growth were considered since

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p-type doping is of most interest for improving the contacts to the p-type GaN. One of the common methods for achieving improved ohmic contact is to have highly doped p-type layer between p-type semiconductor and the metal contact.[7] Diffusion doping, with its inherent non-uniform concentration profile with the highest concentration near the surface, is very suitable for this purpose. We also investigated diffusion doping for converting undoped and Si doped n-type GaN into p-type. Diffusion in our work was performed under N_2 flow instead of evacuated quartz tube, and the diffusion source was 100 nm thick Mg film deposited by thermal evaporation. In order to prevent evaporation of Mg during diffusion, capping layer was deposited on top of Mg film. Different metal capping layers (Au, Al, Ag, Cu) were considered. In addition, SiO_2 was also investigated since this capping layer was successfully used to prevent outdiffusion of Mg during the annealing of p-type samples doped during MOCVD growth.[8] In the following section, experimental details are given. In section 3, obtained results are presented and discussed.

2. EXPERIMENTAL DETAILS

The GaN samples for Mg diffusion doping were grown by MBE. Si doped n-type samples were grown on c-plane sapphire substrates, while undoped and Mg-doped samples were grown on SiC. The diffusion was performed in the following manner: 100 nm thick Mg layer was deposited on the sample by thermal evaporation, followed by the deposition of a capping layer. The purpose of the capping layer is to prevent the evaporation of Mg during the diffusion process. Different capping layers (metals and SiO_2) were investigated. Samples were subsequently annealed in N_2 flow at 850°C or, for Au capping layer, at 900°C for 6 hours. After diffusion, capping layer was removed using HCl or HF. The samples were characterized by Hall measurements and photoluminescence. The type of the conductivity was also confirmed by hot point probe method.

3. RESULTS AND DISCUSSION

Table I summarizes all the results obtained in this study. Empty columns in the table indicate that the sample was too resistive to obtain reliable Hall measurement results. The type of the sample was determined by hot point probe method, which was successful regardless of the sample resistance. Surface carrier concentrations N_s are listed instead of volume concentration since the diffusion typically results in non-uniform concentration profile. Secondary Ion Mass Spectrometry (SIMS) measurements to investigate Mg diffusion were also carried out. The sample which showed the best result (17 pma) exhibited Mg diffusion depth up to 0.2 μm (into 0.5 μm GaN film). Other samples have shown smaller Mg diffusion depth. It can be observed that the samples M142 and M144, which were Mg doped but showing n-type before the diffusion, remained n-type after the diffusion with Al capping layer. These samples exhibited increased carrier concentration and mobility, which is most likely due to annealing effects. After removing the samples from the furnace, it was observed that metal film was absent. Therefore, it can be concluded that the annealing temperature is too high for Al as a capping layer, so that both Al and Mg film evaporated from the surface, resulting in no change in conductivity type of the sample. On the other hand, Au capping layer was stable at higher temperature (900°C). After the diffusion with Au capping layer, the originally undoped sample M125 showed p-type conductivity with high mobility and high surface hole concentration.

Ag and Cu capping layers were stable at annealing temperature of 850°C. The samples with these capping layers, which were n-type Si doped before the diffusion, showed p type conductivity but high resistance after the diffusion. Sample with Cu capping layer was more resistive. Furthermore, the surface of the samples showed metallic tint (gray for Ag and reddish for Cu), which could not be removed by cleaning in HCl and/or HF. High sheet resistance of the samples indicates that the metal is not located on the surface, but has probably diffused inside the sample. The samples showed strong band-edge emission at 3.48 eV before the diffusion. However, photoluminescence (PL) was entirely quenched after the diffusion. The role of Ag and Cu metal contamination in PL quenching cannot be entirely ruled out. However, it is clear that Ag and Cu are not suitable as capping layers for Mg diffusion doping of GaN.

SiO_2 was also used as a capping layer. The results obtained for two samples, which were n-type before the diffusion, are listed in Table I. It can be observed that for one sample p-type conductivity was achieved, while the other sample remained n-type after the diffusion. Kuroda *et al.*[9] found that the Mg diffusion from p-type into n-type region in GaN pn junctions is closely related to the presence of dislocations. Since the dislocation density may vary from one sample to another, as well as over the different areas of the same wafer if there is temperature non-uniformity during growth, it is difficult to achieve good reproducibility of the diffusion doping results. Further work is needed in order to improve the diffusion doping process. This will include optimization of the

capping material (Au, SiO_2, or their combination, and possibly Si_3N_4 though this material would be difficult to remove after the diffusion), diffusion temperature, and diffusion time. Furthermore, annealing in nitrogen overpressure should be considered to prevent nitrogen outdiffusion. Increase in number of nitrogen vacancies caused by nitrogen outdiffusion is a recognized problem in annealing p-type GaN.[10]

Table I Summary of sample properties before and after the diffusion, and diffusion conditions.

Sample	Properties before diff. N_s (cm^{-2}), μ (cm^2/V-s), type	Capping layer	Annealing temp. (°C)	N_s (cm^{-2})	μ (cm^2/V-s)	type
M125	1.43×10^{14}, 234, n	Au	900	1.84×10^{14}	142.0	p-type
M144	8.89×10^{11}, 82.3, n	Al	850	1.97×10^{12}	144.0	n-type
M142	1.30×10^{13}, 24.0, n	Al	850	1.56×10^{13}	41.2	n-type
17pma	4.30×10^{13}, 104.0, n	SiO_2	850	8.19×10^{14}	10.6	p-type
18am	5.49×10^{13}, 242.0, n	Cu	850	--	--	p-type
18pm	5.70×10^{13}, 247.0, n	Ag	850	--	--	p-type
17pmb	2.22×10^{14}, 49.5, n	SiO_2	850	8.50×10^{13}	123.0	n-type

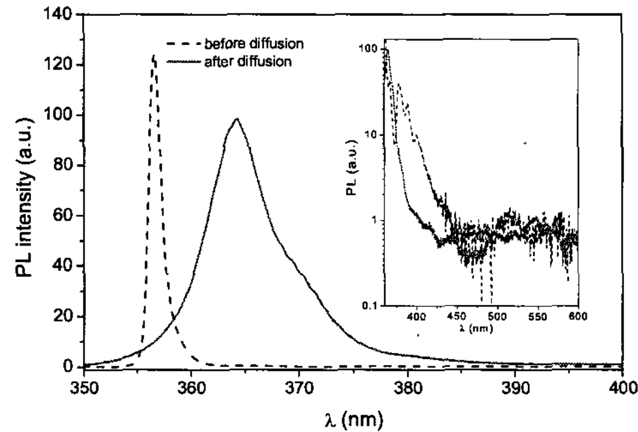

Fig. 1 The room temperature photoluminescence of the sample 17pma before (dashed line) and after (solid line) Mg diffusion. The inset shows the logarithmic scale plot.

Photoluminescence measurements before and after the diffusion were performed. Fig. 1 shows the PL result for the sample 17pma. It can be observed that, after the diffusion, band edge emission is shifted and it becomes significantly broader. Both before and after the diffusion, emission spectrum is completely dominated by the near-band-edge emission, while yellow band emission is very weak. Weak blue band peak at 2.8 eV (443 nm) can be observed after the diffusion, while the peaks at 3.28 eV (378 nm, most likely corresponding to donor-acceptor pair emission in Si doped samples, located around 3.3 eV[11]), 3.19 eV (389 nm) and 3.09 eV (401 nm) disappear. It should be pointed out that the PL spectrum of Mg doped GaN is dependent on the Mg concentration.[11,12] However, significant differences exist between PL spectra of the samples doped during growth and the samples doped by diffusion.[6] While the diffusion doped samples with low carrier concentration (~10^{15} cm^{-3}) show blue band emission[4,6] similar to that of the samples doped during growth, samples doped by diffusion with high carrier concentration (~10^{17} cm^{-3}) have PL emission similar to that of undoped GaN.[6] Chi *et al.*[6] obtained only near-band-edge and yellow emission at room temperature from the diffused sample with p-type conductivity and carrier concentration of 2×10^{17} cm^{-3} while blue band was completely absent. Absence of the blue band in samples having high hole concentrations is in agreement with the result obtained in this work.

Fig. 2 shows low temperature PL spectrum of the diffused sample 17pma. Existence of the two peaks at 378 nm and 390 nm is in excellent agreement with previously reported low temperature (10K) PL results for diffused samples with carrier concentration ~10^{17} cm^{-3} showing peaks at 379 nm, 390 nm, and 401 nm. The difference between our result and the result of Yang *et al.*[5] is that the second phonon replica at 401 nm in our work is not clearly distinguished (only a weak shoulder is visible in our result), and that the yellow band emission is

negligible in our work while their result shows yellow band which is weaker than the emissions above 3 eV. Absence of any peaks around 2.8 eV in low temperature PL spectra can be observed both in our results and the results of Yang *et al.*[5] It should also be pointed out that there are results for Mg doping during MBE growth which also show no blue (2.8 eV) band emission[13] in spite of hole density of 4×10^{17} cm^{-3}. 10K PL spectrum in Ref.[13] shows band edge peak at 3.46 eV (358 nm), and peaks at 3.27 eV (379 nm), 3.18 eV (390 nm), and 3.09 eV (401 nm) with no blue and no yellow band emission, which is in very good agreement with our results for diffusion doped samples.

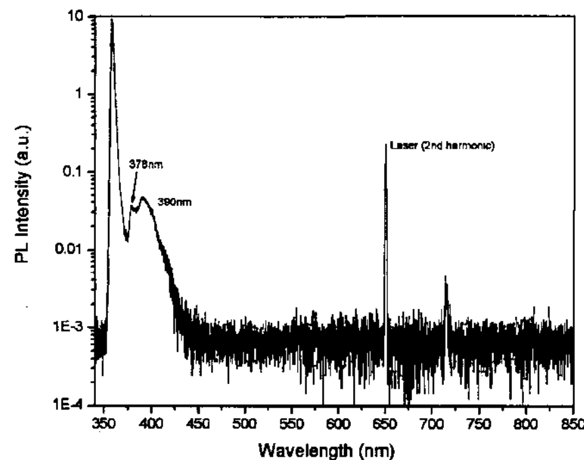

Fig. 2 Low temperature (9.2K) photoluminescence of the sample 17pma after diffusion doping.

4. CONCLUSION

We have shown that Mg diffusion doping is feasible, and that the results are highly dependent on the capping layer. However, it should be pointed out that the obtained results for different samples with the same capping layer show significant variations in spite of similar properties before the diffusion. This is not surprising, since Mg diffusion may be related to the presence of threading dislocations. Relationship between diffusion and dislocations makes it difficult to achieve high reproducibility of the diffusion doping process, though it may be possible to achieve improvements with further optimization of the procedure, i.e. capping layer, diffusion temperature, and diffusion time.

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