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Influence of the thermal annealing on hydrogen concentration in GaN layers – SIMS characterization

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The aim of this work was the investigation of the influence of different thermal annealing conditions on hydrogen concentration in GaN:Mg layers. The 0.5 μm GaN:Mg/0.5 μm GaN layers deposited on sapphire with LP MOVPE (low pressure metal organic vapour phase epitaxy) were examined. Samples were characterized with the use of SIMS (secondary ions mass spectroscopy) technique applying CAMECA IMS 6F system. Magnesium concentration in the samples determined with the use of SIMS measurement was 3×10^{19} and 5×10^{19} at/cm^3. The annealing was performed using RTA (rapid thermal annealing) technique and MOVPE reactor as a furnace. Samples were annealed in temperatures ranging from 750 to 950 °C with one, two or three thermal -steps of annealing.

1. Introduction

Magnesium is the most often used dopant in the production of p-type layers in GaN based optoelectronic devices. Due to the ionization energy reaching 200 eV, the doping concentration in the range of several 10^{19} cm^{-1} produces hole concentration only 10^{17}–10^{18} cm^{-1} at room temperature. Furthermore, the acceptors in as-grown MOVPE Mg doped GaN are passived with hydrogen. Activation of Mg acceptors is accompanied by cracking Mg-H complexes during the annealing of the samples at the temperature over 700 °C.

The behaviour of hydrogen in GaN layers has been earlier studied theoretically [1] and with the use of several different experimental methods [2], [3] and [4]. In this paper, we report the annealing effects on hydrogen in Mg doped GaN epilayers characterized by SIMS technique.

2. Experimental procedure

Mg doped GaN layers were grown in LP MOVPE reactor. Trimetylgallium (TMG), NH_3 (ammonia) and bis-cyclopentadienyl magnesium Cp_2Mg were used as precursors of Ga, N and Mg, respectively. Epilayers of 0.5 μm GaN:Mg on 0.5 μm undoped GaN were grown on sapphire with nucleation layers. Samples were annealed in the following conditions:

1) in RTA under atmospheric pressure
   - two and three thermal-step,
   - one thermal-step for 15 min,
2) in MOVPE reactor (as a furnace) 300 mbar absolute pressure with one thermal-step for 30 min.

All samples were annealed in N_2 flow (1 l/min) atmosphere at temperatures ranging from 700 to 950 °C. One sample was also annealed in O_2 flow (1 l/min) atmosphere. Concentrations of Mg, H and O were determined by SIMS technique using an ion microprobe CAMECA IMS 6F instrument. Cesium beam current was 60 nA. The size of the raster on the sample was about 125×125 μm. Secondary ions were collected from a central region of 30 μm diameter. For magnesium concentration $MgCs^+$ complex was measured and $GaCs^+$ taken as a reference. For H and O concentrations H^- and O^- ions were measured and GaN^- complex taken as a reference. The sensitivity of the SIMS measurement for Mg, H and O were 1×10^{16}, 9×10^{17} and 4×10^{18} cm^{-1}, respectively. Sensitivity levels were performed by measuring undoped GaN layers obtained with MOVPE technique. The values of sensitivity levels for H and O are probably determined by the impurities in GaN layers. The thickness of the layer was measured using an α-step profilometer.

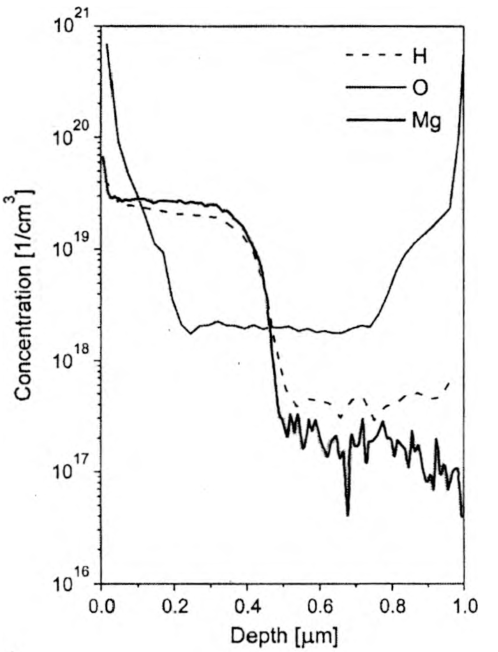
3. Discussion

There were two samples prepared for annealing, slightly differing in the concentration and the profile of magnesium. Two and three thermal-step annealing was applied for sample 1 and one thermal-step for sample 2. SIMS measurements of magnesium, hydrogen and oxygen in those as-grown GaN:Mg epilayers are shown in Figs. 1 and 2. The concentrations of Mg and H in the doped layer (3×10^{19} cm^{-3} in sample 1 and 5×10^{19} cm^{-3} in sample 2) are equal. Differences in oxygen concentration between as-grown sample 1 and 2 result from different vacuum conditions of SIMS apparatus. Figure 3 shows Mg, H and O concentration in the undoped GaN sample, which indicates sensitivity level of the SIMS measurement. The concentration of Mg about 10^{17} cm^{-3} in the undoped layer (Figs. 1 and 2) resulted from the memory effect in MOVPE reactor.

The two steps annealing process for Mg activation has been earlier studied. CHUNG *et al.* [4] reported an enhancement in the hole concentrations in the samples processed in that way. In our experiment we applied the following annealing conditions:

- 900 °C for 1 min and 750 °C for 15 min,
- 750 °C for 1 min and 900 °C for 15 min,
- 750 °C for 5 min, 800 °C for 10 min and 900 °C for 15 min.

SIMS measurement of the samples processed at such conditions shows the profile of hydrogen with concentration only one order of magnitude smaller than in



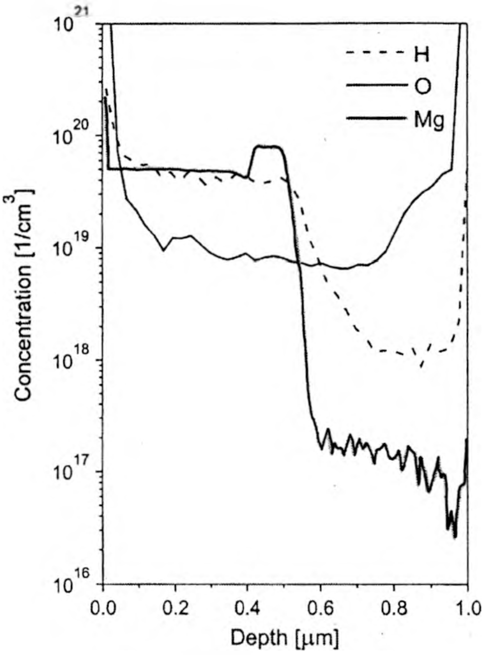


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Fig. 1. SIMS result of as-grown GaN:Mg layer – sample 1.
Fig. 2. SIMS result of as-grown GaN:Mg layer – sample 2.

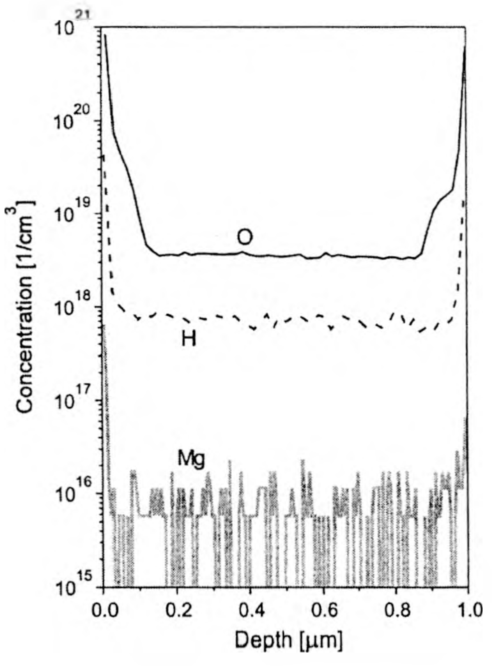
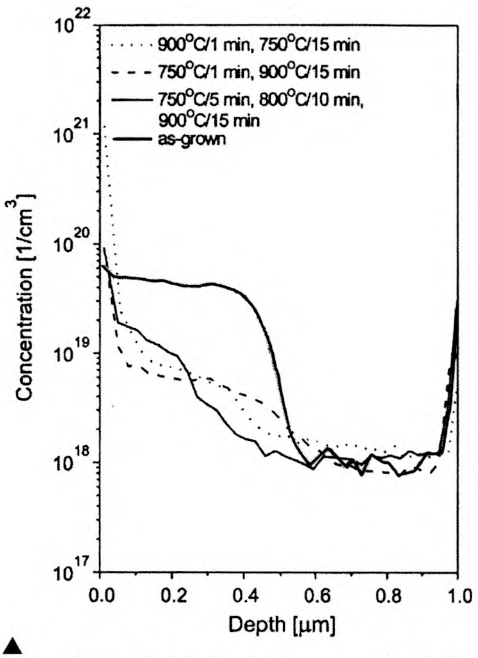


Fig. 3. SIMS result of undoped GaN layer.



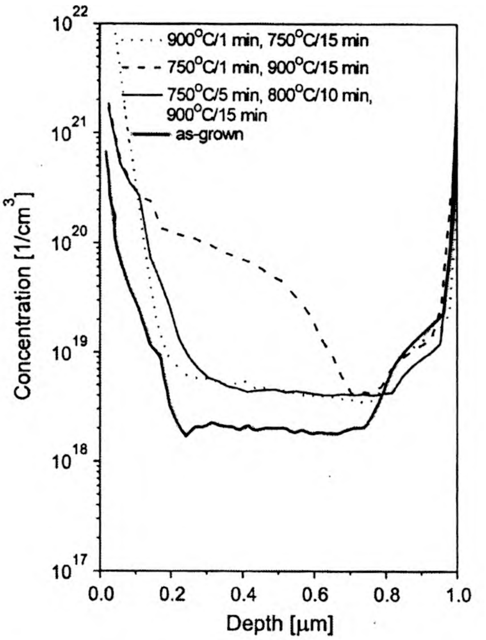


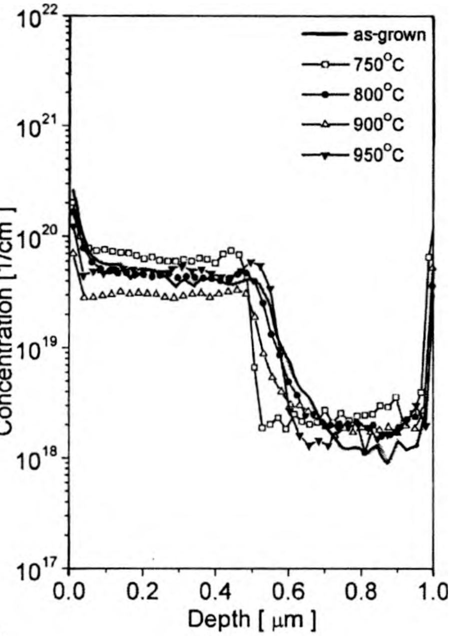
Fig. 4. Hydrogen concentration in sample 1 after two and three thermal-step RTA annealing in N_2 flow – SIMS results.

Fig. 5. Oxygen concentration in sample 1 after two or three thermal-step RTA annealing in N_2 flow – SIMS results.

the as-grown sample (Fig. 4). Two thermal-step annealed samples have lower gradient of hydrogen concentration across the magnesium doped layer than the sample annealed with three thermal-steps. SIMS measurement of so processed sample shows also the increased concentration of oxygen in some places, even two orders of magnitude higher than in the as-grown sample (Fig. 5).

Different hydrogen profiles were observed in samples annealed in a furnace (MOVPE reactor), Fig. 6. In this case the profiles were temperature independent. Small differences in concentrations are caused by the inaccuracy of SIMS scaling. The absence of the hydrogen out-diffusion from GaN:Mg layer is probably the result of the presence of the rest pressure of hydrogen or MOVPE precursors containing hydrogen in MOVPE reactor. The lack of diffusion into the undoped GaN layer indicates < 10^{-16} cm^2/s diffusion coefficient for H in GaN at 950 °C. Annealing in MOVPE reactor does not introduce oxygen into GaN layer.

The highest hydrogen out-diffusion from magnesium doped GaN layer was achieved with 15 min N_2 flow RTA annealing (Fig. 8). At the temperatures of 750 and 800 °C the hydrogen concentration decreases more than one order of magnitude. At 900 °C the hydrogen out-diffuses to concentration as low as in the undoped layer. In every sample annealed below 950 °C the oxygen concentration is approximately equal to the one in the undoped sample (Fig. 9). However, the concentration of oxygen



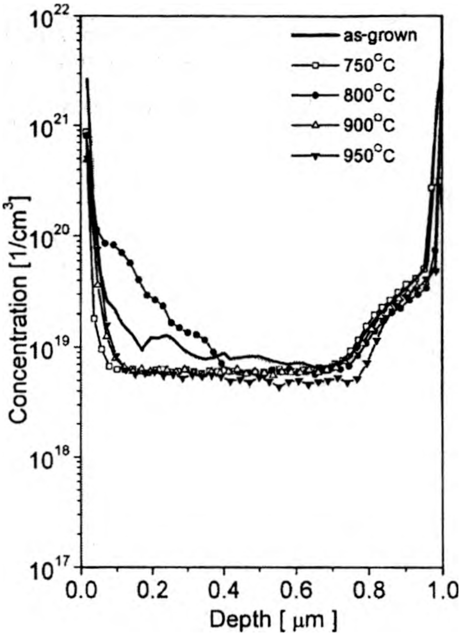


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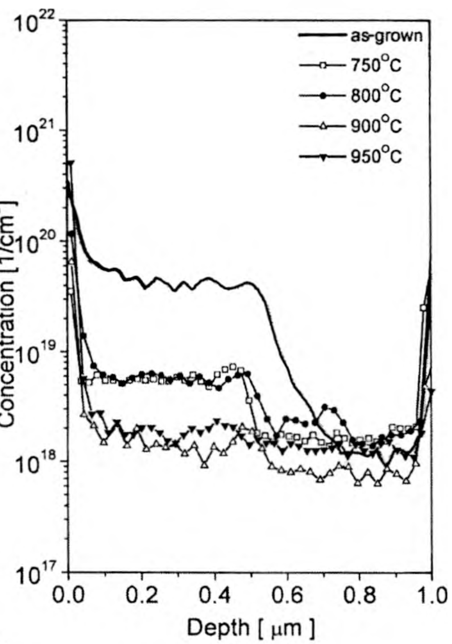
Fig. 6. Hydrogen concentration in sample 2 after 15 min furnace annealing in N_2 flow – SIMS results.
Fig. 7. Oxygen concentration in sample 2 after 15 min furnace annealing in N_2 flow – SIMS results.



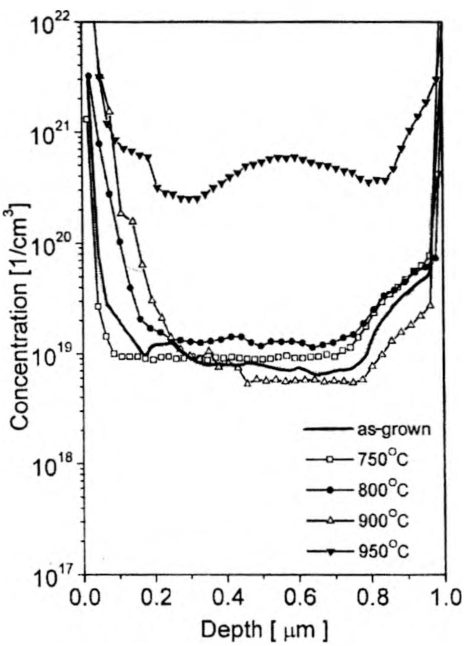


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Fig. 8. Hydrogen concentration in sample 2 after 15 min RTA annealing in N_2 flow – SIMS results.
Fig. 9. Oxygen concentration in sample 2 after 15 min RTA annealing in N_2 flow – SIMS results.

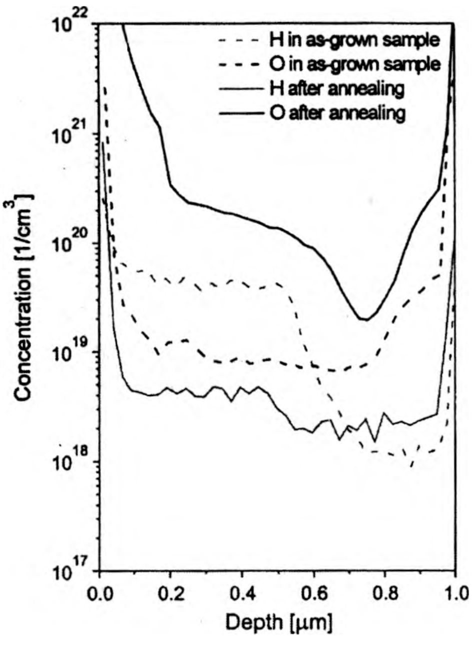

Fig. 10. O and H concentrations in sample 2 after 15 min RTA annealing in O_2 flow – SIMS results.

in the sample annealed at 950 °C is almost two orders of magnitude higher. The SIMS performed at various points on the sample showed different oxygen concentrations. The indicates the non-uniform oxygen diffusion into GaN layer. SIMS measurement shows also that there is an increase in the thickness of oxide layer on the surface after RTA annealing.

One sample was annealed also in O_2 flow atmosphere at 775 °C. The results of SIMS measurements of this sample are shown in Fig. 10. Annealing in O_2 atmosphere results in the same hydrogen out-diffusion as annealing in N_2 atmosphere, but it introduces much more oxygen into GaN layer.

4. Conclusions

The behaviour of hydrogen in magnesium doped MOVPE GaN layer, annealed in different conditions, was investigated. The profile and concentration of O and H were obtained using SIMS technique. The highest hydrogen out-diffusion was achieved after 15 min N_2 flow RTA annealing at temperature exceeding 900 °C. The concentration of hydrogen decreased almost two orders of magnitude reaching the sensitivity level of SIMS measurement.

References

[1] MYERS S.M., WRIGHT A.F., PETERSEN G.A., SEAGER C.H., CRAWFORD M.H., WAMPLER W.R., HAN J., MRS Internet J. Nitride Semicond. Res. **5S1** (2000), W9.4.

[2] PEARTON S.J., CHO H., REN F., CHYI J.-I., HAN J., WILSON R.G., MRS Internet J. Nitride Semicond. Res. **5S1** (2000), W10.6.

[3] MYERS S.M., HEADLEY T.J., HILLS C.R., HAN J, PETERSEN G.A., SEAGER C.H., WAMPLER W.R., MRS Internet J. Nitride Semicond. Res. **4S1** (1999), G5.8.

[4] CHUNG H.Y.A.,PELZMANN A., DRECHSLER M., SCHERER M., SCHWEGLER V., SEYBOTH M., KIRCHNER C., KAMP M., J. Cryst. Growth **230** (2001), 549.

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