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Effect of growth conditions on electrical properties of Mg-doped p-GaN

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Abstract

In this work the effect of carrier gas and post-growth activation conditions on the electrical properties of Mg-doped p-GaN single layers grown in a vertical flow close-coupled showerhead MOCVD system is investigated. The results of Hall effect measurements show that although the optimal Mg precursor flow rate depends on the growth atmosphere and is smaller when N_2 is used as a carrier gas, similar electrical properties could be realized with both H_2 and N_2 carrier gases. The results of SIMS analysis demonstrate that while Mg incorporation is higher for N_2 carrier gas, the efficiency of Mg activation is higher when H_2 is used as carrier gas. We have also observed that the structural quality of N_2 grown layers is substantially lower compared to the H_2 case.
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1. Introduction

The activation of Mg acceptors in GaN layers is one of the key steps in manufacturing group III nitride based optoelectronic devices. As-grown Mg-doped GaN layers are typically highly resistive and do not have p-type conduction. Some kind of post-activation such as low-energy electron beam irradiation (LEEBI) [1] or thermal annealing [2] is needed to activate the Mg acceptors. The main reason for Mg passivation is considered to be hydrogen in the growth chamber [3,4]. Reduction of the amount of hydrogen in the growth process should be an efficient way to achieve better electrical properties in p-GaN layers. Sugiura et al. [5] have reported as grown p-type GaN using nitrogen as the carrier gas. However, in some other publications (see, e.g., Nakamura et al. [3]), it is stated that hydrogen produced as the result of dissociation of ammonia effectively passivates the already activated p-GaN. Park et al. [6] confirmed Nakamura's results by experiments, where dimethylhydrazine was used as a source

for nitrogen and as-grown p-type GaN was obtained. However, the role of the carrier gas in electrical passivation of Mg acceptors is not completely understood. Recently there have also been many studies in which different thermal annealing ambients have been studied in order to obtain more effective Mg activation. Thermal activation in oxygen ambient has given very promising results compared to the traditional nitrogen annealing [7–10]. Higher hole concentrations have been obtained in oxygen ambient at lower temperatures. These results have been explained with the formation of H_2O in oxygen ambient at low temperatures [9].

In this study the effect of carrier gas and post-activation annealing conditions on the electrical properties of MOCVD-grown Mg-doped p-GaN were examined. Mg molar flow rate to the growth chamber was optimized for both H_2 and N_2 carrier gases. In addition, the effects of post-activation atmosphere and temperature were investigated. The purpose of this study was to optimize p-GaN growth and annealing conditions for device applications and examine how the electrical properties of the p-GaN layers depend on the amount of magnesium in the growth atmosphere.

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2. Experimental procedure

Samples used in this study were all grown in a vertical flow 3 × 2 in close-coupled showerhead (CCS) MOCVD reactor at the growth pressure of 100 Torr. Ammonia was used as the nitrogen precursor and trimethylgallium (TMGa) and bis-cyclopentadienyl magnesium (Cp$_2$Mg) were used as precursors for gallium and magnesium, respectively. Two-inch c-plane sapphires were used as substrates. A low-temperature nucleation layer and 2-µm-thick undoped GaN layer were first grown in a H$_2$ atmosphere. The Mg-doped p-GaN film was grown on top of this buffer layer (see Fig. 1). Mg flow rate was varied with both carrier gases, all other growth parameters were kept constant during the study. The growth of p-GaN was carried out at 1000 °C with a V/III ratio of 1100, which are typical growth conditions for p-GaN cap in InGaN based LED structures. Higher growth temperature was not used in this study, because high temperature p-GaN growth might affect the InGaN quantum well structures during LED fabrication. Carrier gas flow rate was 9000 sccm with both carrier gases. Mg flow rate was varied in the range of 275–400 sccm in hydrogen and 100–300 sccm in nitrogen atmosphere. After the growth, the samples were cooled down in a mixture of carrier gas and NH$_3$.

Thermal activation experiments were performed in both, nitrogen and oxygen atmospheres. The annealing temperature was varied to obtain the optimal annealing conditions for the samples grown in different conditions. In some publications, optimal annealing temperature in nitrogen ambient has been as high as 900 °C [11]. Annealing in such a high temperature would definitely affect the MQW structures during LED fabrication, and that is why the annealing temperature was limited to less than 800 °C in nitrogen and 700 °C in oxygen ambient. Annealing time was 30 min in both ambients.

The Van der Pauw method was used in room temperature Hall effect measurements. Indium solder was used to fabricate ohmic contacts for the electrical measurements. Secondary ion mass spectrometry (SIMS) measurements were performed in order to get a knowledge of Mg concentrations in samples grown under different conditions.

3. Results

All of the as-grown samples fabricated in this study were highly resistive and did not show any p-type conduction. There was no difference between the carrier gases and the amount of magnesium in the reactor did not have any effect either. Acceptor activation was not obtained during the cooling in N$_2$ and NH$_3$ ambient after the N$_2$ atmosphere growth process. This clearly indicates that the hydrogen released during ammonia dissipation can have a significant role in Mg passivation. This is in contradiction with the results from some other studies in which as-grown p-type GaN has been obtained by H$_2$ free growth with ammonia as the N precursor [5].

From the Hall effect measurement results in Figs. 2 and 3, it is easy to see that under the above described growth
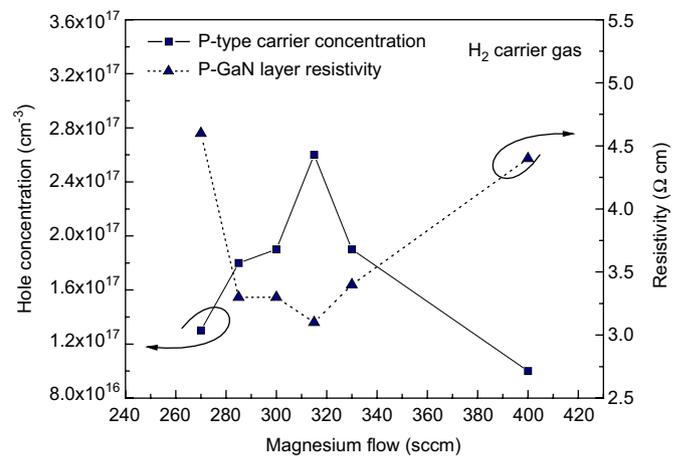
Fig. 2. Carrier concentration and resistivity of 1-µm-thick p-GaN layers with different Mg precursor flows. Hydrogen was used as the carrier gas during growth. All samples were annealed in an O$_2$ atmosphere at 600 °C for 30 min.
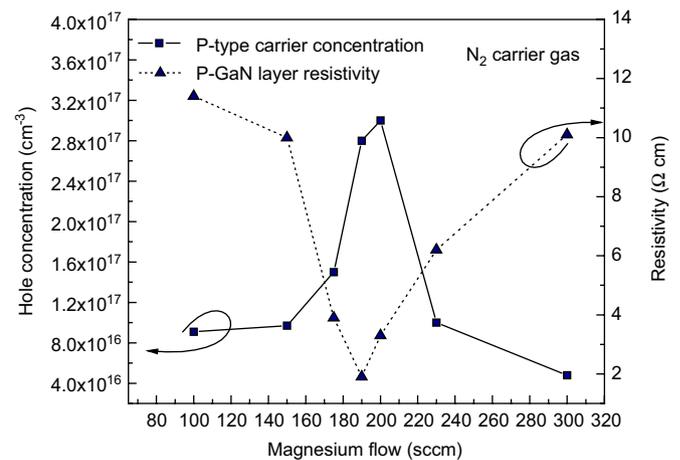
Fig. 3. Carrier concentration and resistivity of 1-µm-thick p-GaN layers with different Mg precursor flows. Nitrogen was used as a carrier gas during growth. All samples were annealed in an O$_2$ atmosphere at 600 °C for 30 min.

Fig. 1. Schematic structure of the samples. The GaN nucleation layer and the undoped GaN layer were grown in a hydrogen atmosphere.

conditions there is a well defined Mg flow rate in both carrier gases, at which the optimal electrical properties (hole concentration and resistivity) are obtained. Similar thermal activation conditions were used for all of the samples in this experiment. Annealing was performed in oxygen ambient at $600\,°C$ for $30\,min$. These conditions were found to be optimal for all the samples in this series of experiments. The results clearly show that the optimal Mg flow rate differs a lot depending on a carrier gas and is much smaller when N_2 is used as the carrier. The reason for decreasing p-type carrier concentration after a certain amount of incorporated Mg is the increase of Mg-related defects introduced at high Mg doping. The increase in lattice distortion due to the large difference in the atomic size between Ga and Mg deteriorates the crystal quality, which prevents Mg from acting as an electrically active acceptor. Formation of Mg complexes with increasing Mg doping can also prevent an increase in the amount of electrically active Mg [11,12].

To study the efficiency of Mg incorporation depending on the carrier gas, SIMS measurements were performed on sample A, grown at a Cp_2Mg flow rate of $300\,sccm$ and H_2 used as a carrier gas, and on sample B, grown at a Cp_2Mg flow rate of $190\,sccm$ and N_2 used as a carrier gas. As shown in Figs. 2 and 3, these samples exhibited the highest hole concentration for each type of growth conditions. The concentration of Mg atoms as determined by SIMS was 3×10^{19} atoms/cm^3 for sample A and 7.5×10^{19} atoms/cm^3 for sample B. Although the amount of Mg atoms incorporated into the solid phase is more than two times larger for N_2 carrier gas, the concentration of holes after the activation annealing is nearly the same for both samples, which means that the proportion of the electrically active Mg atoms is substantially larger in case H_2 is used as a carrier gas and more Mg atoms stay as defects when N_2 carrier gas is used. The reason for these phenomena might be the inherently lower crystalline quality of GaN typically obtained when growing in a N_2 rich ambient; however, more studies on this subject are required. In any case, it is preferable to get a high hole concentration at the lowest possible concentration of Mg atoms, because a substantial increase in the amount of Mg atoms leads to additional deterioration of crystalline quality.

In the other part of the study we examined the dependence of the electrical properties of p-GaN on different thermal annealing conditions. Fig. 4 shows the resistivities of samples grown in hydrogen with different acceptor activation conditions. Samples were grown with optimal Mg molar flow rates. There is a clear temperature limit at $550\,°C$, above which resistivity stays almost constant in both annealing ambients. Similar results for high temperature annealing have also been obtained in another study [10]. Contrary to other published results [10,11], where temperatures as high as $600–700\,°C$ were needed to effectively activate p-GaN in a nitrogen ambient, the electrical properties of H_2 grown p-GaN
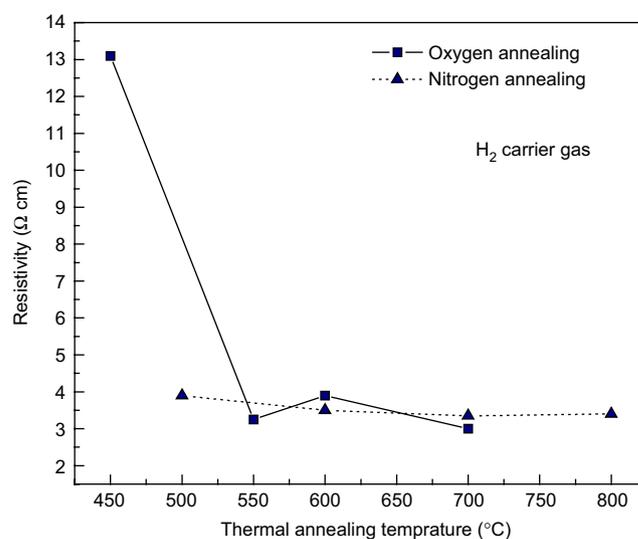
Fig. 4. Resistivity of 1-μm-thick p-GaN layers after oxygen and nitrogen thermal activations at different temperatures. Annealing time was $30\,min$. Hydrogen was used as carrier gas and Mg flow was $285\,sccm$ during the growth.
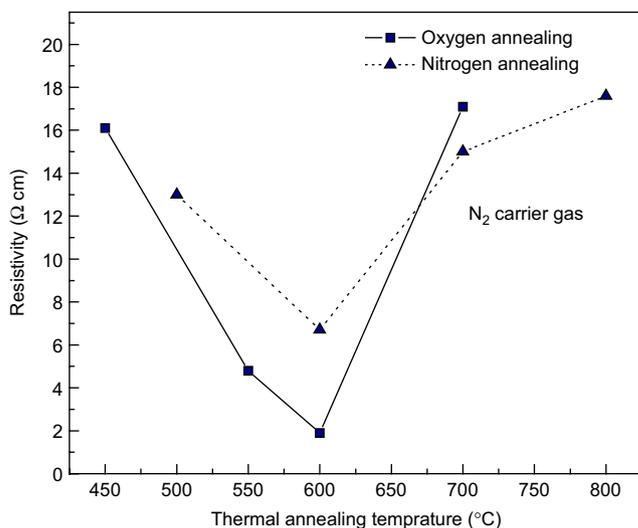
Fig. 5. Resistivity of 1-μm-thick p-GaN layers after oxygen and nitrogen thermal activations at different temperatures. Annealing time was $30\,min$. Nitrogen was used as carrier gas and Mg flow was $190\,sccm$ during the growth.

layers in our study did not exhibit any dependence on the annealing ambient.

Fig. 5 shows the corresponding results for samples grown in nitrogen. From the data we can conclude that there seems to be a certain temperature range near $600\,°C$, where a resistivity minimum is achieved in both annealing ambients. However, annealing in oxygen is more efficient for Mg activation in the case of p-GaN grown in nitrogen. Based on these results, we can conclude that optimal annealing conditions and details of the activation mechanism both depend on the growth ambient and, as a result, on the crystalline properties of the Mg-doped GaN. Further studies of microscopic structural properties of Mg doped

GaN grown in various growth ambients are required to give an interpretation of the observed phenomena.

4. Conclusion

In summary, low resistivity p-type Mg-doped GaN has been obtained by MOCVD growth with H_2 and N_2 as carrier gases. As-grown p-type conductivity was not obtained with either of the growth ambients. The optimal Mg flow rate showed a strong dependence on the carrier gas and was smaller in N_2 ambient than in H_2. The results of SIMS analysis demonstrate that Mg incorporation is higher for N_2 carrier gas, although a substantially smaller part of the incorporated acceptors becomes electrically active in this case, compared to H_2 grown layers, thus increasing the amount of Mg atoms, which stay as defects further deteriorating the crystalline quality of the layers. We have also demonstrated that the activation annealing ambient does not affect the electrical properties of H_2 grown p-GaN in a wide range of annealing temperatures, which makes the activation process more stable and flexible. In contrast to that, smaller resistivity and higher hole concentration were obtained when annealing N_2 grown p-GaN in oxygen compared to nitrogen with a clear resistivity minimum at an annealing temperature of $600\,^\circ C$. We believe that the observed phenomena are related to different crystalline properties of Mg-doped GaN grown under different growth ambients. Further studies are required to understand the fundamental reasons behind the observed phenomena.

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