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Influence of carrier gas H_2 flow rate on quality of p-type GaN epilayer grown and annealed at lower temperatures*

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In this work, we study the influence of carrier gas H_2 flow rate on the quality of p-type GaN grown and annealed at lower temperatures. It is found that the concentration of H atoms in Mg-doped GaN epilayer can effectively decrease with appropriately reducing the carrier gas H_2 flow rate, and a high-quality p-type GaN layer could be obtained at a comparatively low annealing temperature by reducing the carrier gas H_2 flow rate. Meanwhile, it is found that the intensity and wavelength of DAP peak are changed as the annealing temperature varies, which shows that the thermal annealing has a remarkable effect not only on the activation of acceptors but also on the compensation donors.

Keywords: p-type GaN, thermal annealing, H atom state

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1. Introduction

In recent years, gallium nitride (GaN) and its ternary alloys have attracted a great deal of attention thanks to their material properties, which are advantageous for applications in light emitters and detectors devices.[1–5] Nevertheless, the quality of p-type GaN sometimes still acts as a bottleneck that limits the performance of these devices.[6] Up to now, Mg, as a singly useful element, has been used to dope p-type GaN. The Mg atoms doped in the GaN layer are often passivated by H atoms through forming a neutral Mg–H complex because the H atoms are contained in the growth environment for metal organic chemical vapor deposition (MOCVD) system.[7,8] This issue was first treated by Amano *et al.* through the low-energy electron beam irradiation.[9] Unfortunately, this method has a fatal defect in that it only can activate several hundred nanometer-thick materials. Subsequently, thermal annealing reported by Nakamura *et al.* is successful to solve this Mg passivated problem.[7] Nevertheless, some recent studies found that the high growth temperature and annealing temperature for p-type GaN will lead to In-segregation in InGaN quantum wells (QWs) of the active region for laser diode (LD) or light emitting diode (LED).[10–13] Therefore, relatively low growth and annealing temperatures are needed to avoid reducing the device performance. However, it is often difficult to achieve high quality p-type GaN at lower growth temperature as the crystalline quality degenerates with the decreasing of growth temperature. The degeneration of crystalline quality means that the density of defects will be largely increased and deteriorate the quality of p-type GaN. At the same time, previous studies have proven that the efficiency of H atoms diffusing out of GaN layer will decrease with f annealing temperature lowering,[14] which will affect the efficiency of Mg acceptor activation. Therefore, to achieve a high-quality p-type GaN with a comparatively low growth and annealing temperature, some other growth conditions must be changed accordingly. In this paper, the influence of carrier gas H_2 flow rate on the quality of lower-temperature-grown and-annealed p-type GaN is studied.

2. Experiment

A series of 1-μm thickness Mg-doped GaN films was grown on a 2-μm-thick unintentionally doped GaN layer in an MOCVD system. Trimethylgallium (TMG), ammonia (NH_3), and Bis-cyclopentadienyl magnesium (Cp_2Mg) were used as

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precursors for Ga, N, and Mg, respectively. The H_2 was taken as the carrier gas to transport all precursors into the MOCVD reactor. The detailed parameters for p-type layer growth are shown in Table 1. As shown in Table 1, two samples A and B had the same growth temperature (GT), Cp_2Mg flux, V/III ratio, and growth pressure (GP). The only difference between these two samples was the carrier gas H_2 flux, which was 14.7 L/min and 8.7 L/min for sample A and sample B, respectively, and extra N_2 was used to ensure that their total fluxes were the same. Two samples were cut into many pieces and then annealed at temperatures ranging from 500 °C to 850 °C in an N_2 ambient environment to activate the Mg acceptor. The annealing time was fixed to 20 min. After thermally annealing the sample, its carriers' concentration and resistivity were measured by van der Pauw (Hall) measurement, and room temperature photoluminescence (PL) spectrum was measured by a 325-nm excitation line of a He–Cd laser. The Mg and C concentration of annealed p-type GaN films were measured by secondary ion mass spectroscopy (SIMS).

Table 1. Growth and annealing condition for p-type GaN samples.

Sample	Growth temperature/°C	Growth pressure/mbar	H_2 flow rate/(L/min)	Cp_2Mg flux/sccm	t_{annl}/min
A	930	150	14.7	135	20
B	930	150	8.7	135	20

3. Results and discussion

Figures 1(a) and 1(b) show the Hall measurement results after thermally annealing the samples with the annealing temperature changing from 500 °C to 850 °C. By comparing the results, we can find that two samples have the same changing tendency with the increase of annealing temperature, we here the resistivity and carrier concentration of both samples change monotonically with annealing temperature. On the whole, the quality of p-type GaN layer is improved with the increase of annealing temperature; *i.e.*, the resistivity decreases and the carrier concentration increases. A further analysis reveals that the p-type performance of sample B is far superior to that of sample A when a comparatively low annealing temperature is used. However, this difference disappears quickly when the annealing temperature increases, and the Hall measurement results for the two samples are almost the same when the annealing temperature reaches to 850 °C. For p-type GaN, in a device structure sample, even though a high temperature heat treatment is good for the p type contact layer, some other parts may deteriorate in the device. For example, there may happen an unwanted decomposition of InGaN in the InGaN/GaN multiple quantum well sample at high temperature.[10–13] Therefore, a relatively low annealing temperature may still be a good choice for achieving the p-type GaN. In this respect, as clearly shown in Fig. 1, the p-type properties of sample B are much better than those of sample A. It is shown that when the annealing temperature is between 550 °C and 750 °C, both carrier concentration and Hall mobility of sample B are better than those of sample A.

To obtain more information about these two samples, we have shown the Mg concentration profile obtained through SIMS measurement in Fig. 2. Figure 2 shows that the carriers' density are 1.0×10^{19} cm^{-3} and 6.0×10^{18} cm^{-3} for sample A and sample B, respectively, and that the Mg doping concentration in p-type GaN layer decreases with carrier gas H_2 flux decreasing. At the same time, from Fig. 2 we can also see a small difference in thickness of GaN:Mg epilayer between two samples, which implies that the growth rate for p-type GaN epilayer increases slightly with H_2 flow rate decreasing on condition that the growth times for two samples are set to be the same (3000 s).

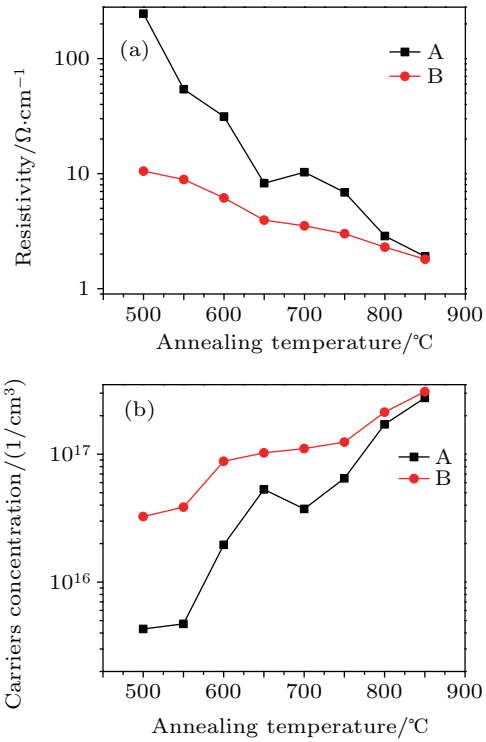


Fig. 1. (color online) Annealing-temperature-dependent (a) resistivity and (b) concentration of carriers for sample A (square) and sample B (circle). The lines connecting data points are used only as a guide of eye.

It is noticed that even the total Mg doping concentration in sample B is lower than that in sample A. In addition, the the p-type properties of sample B are much better than those of sample A at a comparatively low annealing temperature. To understand the Hall measurement results for these two samples annealed at different temperatures, we measure the H concen-

tration profiles for these two samples after being annealed at different temperatures. Figure 3 shows the H concentration profiles for these two samples after being annealed at 550 °C, 650 °C, 750 °C, and 850 °C. It is obvious that the H atoms' concentration in annealed sample B is lower than that in annealed sample A for any annealing temperature, which may be the main reason for the far better p-type quality for sample B than that for sample A when annealed at a comparatively low annealing temperature, although the Mg doping concentration in sample B is a little lower than that in sample A. Meanwhile, we find that the H concentration for two samples almost keep the same when annealed at relatively low temperatures of 550 °C, 650 °C, and 750 °C.

Generally, we hold the view that the thermal annealing is a process of Mg activation, in which the Mg–H complexes are depassivated and H atoms are released away from the material. Some researches suggested that the temperature dependence of quality for p-type GaN in the annealing experiment comes from the different escape efficiencies of H atoms away from the epilayer.[14] Nevertheless, in our experiment we can find that the p-type quality has a big improvement with annealing temperature increasing from 550 °C to 750 °C while the net H concentration in either A or B almost keeps uninfluenced by the annealing temperature. The carriers' concentration for sample A and sample B are 6.0×10^{16} cm^{-3} and 9.0×10^{16} cm^{-3} respectively when the annealing temperature increases from 550 °C to 750 °C. Obviously, the p-type quality improvement in our experiment cannot be explained by the model of escaping H atoms from the p-GaN epilayer.[14] The H atom in GaN material can exist in different states such as negative ion (H^-), positive ion (H^+), or neutral charge states (H^0, H_2). In p-type GaN most of H atoms are H^+ ions before annealing the sample as H^+ has the lowest energy state, and the H^+ ion always forms a neutral complex with Mg acceptor in GaN and passivate it.[15–17] It is reported that a thermal annealing can make H atoms change into various states, and the concentration for each state is determined by the thermal equilibrium and affected by annealing temperature.[18] The improvement of p-type quality means that the H^+ concentration in p-type layer decreases with annealing temperature increasing in our experiment. With the increase of annealing temperature, more and more Mg acceptors are activated by thermal annealing. It is worth noting that for all states of the H atom, only H_2 can diffuse out to escape from the material. Consequently, our experimental results can be explained by the fact that at the relatively low annealing temperature between 550 °C–750 °C, even though the H atom state changes with the increase of annealing temperature, the H atoms' concentration in p-type GaN layer keeps unchanged as the H_2 formation efficiency is still quite low. This result is consistent with the theoretical calculation made by Myers *et al.* which shows that H_2 forms only when the H atoms' concentration begins to exceed uncompensated Mg concentration.[19] When the annealing temperature continually increases to 850 °C, the H_2 formation efficiency is improved, which causes the H atoms' concentration to decrease significantly, and this improves the p-type quality. From this analysis, we can conclude that the H atom's concentration in the p-type GaN layer can be effectively reduced by appropriately reducing the flux of carrier gas H_2, which is helpful in achieving better quality with a comparatively low annealing temperature. At the same time, we find that the Hall measurement result can be improved while the H atoms' concentration in the material is almost the same after being annealed at a comparatively low temperature, which can happen due to the fact that at this annealing temperature, the state of H atom changes but the probability of forming H_2 molecules is still low.

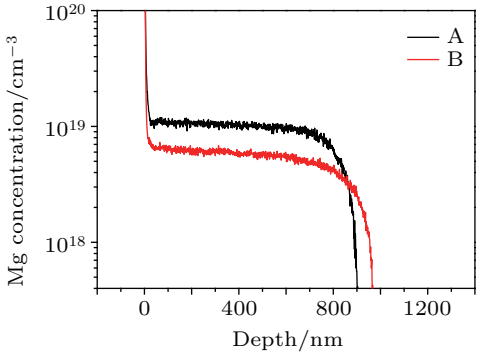


Fig. 2. (color online) Plots of Mg concentration for samples A (black) and B (red) grown with two different H_2 carrier gas fluxes, respectively. GaN:Mg epilayer of sample B is thicker than that of sample A.

We also measure the room-temperature PL spectra for these samples as shown in Fig. 4. From PL spectra, we can find that there are mainly two types of luminescence peaks for samples after being annealed at different temperatures. The first type of peak around 361 nm belongs to GaN band-to-band emission peak, which represents the high quality of p-type GaN that is not doped ultra-heavily. The second type of peak is in a wide range of blue luminescence located in a range of 390 nm–450 nm, which is due mainly to the transition from compensation donors to Mg acceptor energy level (DAP).[20–22] From Fig. 4 we can find that the intensity and central wavelength of DAP peak for both samples change with the increase of annealing temperature(there exist two overlapped curves in Fig. 4(b), but it cannot affect the overall trend of peak value changing with temperature). All of our samples are measured under the same test condition, so the peak intensity and wavelength of DAP peak can partly reflect the energy level state in the material. Generally, the energy level of the Mg acceptor is stable in the p-type GaN material; however, previous researches have proven that there are several different kinds of compensation donors and they have different energy levels in GaN material.[23–25] So the central wavelength

of the DAP peak changing with the increase of annealing temperature should originate from the movement of the energy levels of dominating compensation donors, which means that at different annealing temperatures the dominant compensation donors are different in GaN layer, so we can conclude that besides activating Mg acceptor from Mg–H complex, the annealing process has an annealing effect on the compensation donors. Meanwhile, the intensity of the DAP peak is proportional to the concentration of neutral DAP, and the neutral DAP equal to the compensation donors' concentration in the p-type GaN, so the intensity of DAP peak is related to the compensation donors. The DAP peak intensity changing with annealing temperature should be caused by the number of compensation donors changing in the annealing process. It is found from Fig. 4 that the tendencies of PL intensity changing with annealing temperature for samples A and B are similar: they increase to their own maximum value and then decrease as annealing temperature continually increases. Though the specific mechanism for this change tendency is hard to understand, we can get to know that annealing process has an effect on compensation donors. In the annealing process, the H atom can change into various states and in these states of the H atom the H^- can combine and change the donors' state.[18] The effect of annealing on the compensation donors also relates to the H state changing in the annealing process, but more work needs to be done to confirm this point.

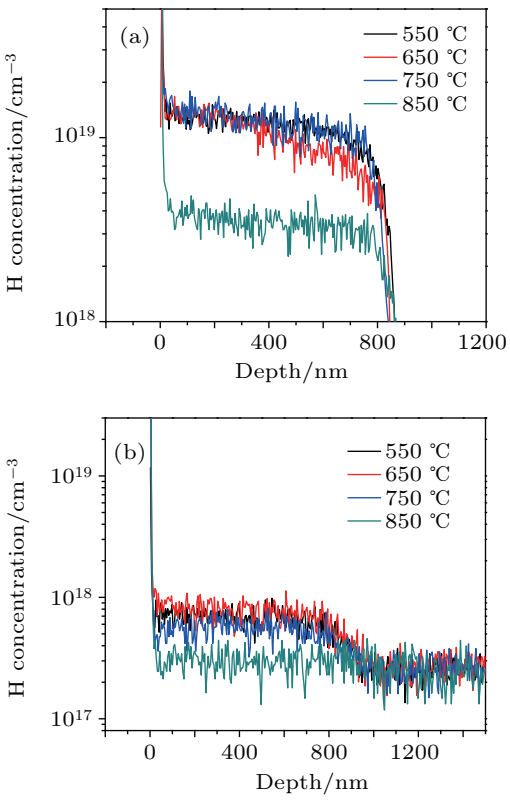


Fig. 3. (color online) Plots of H atoms' concentration versus depth for samples A (a) and B (b) after being annealed in a temperature range from 550 °C to 850 °C.

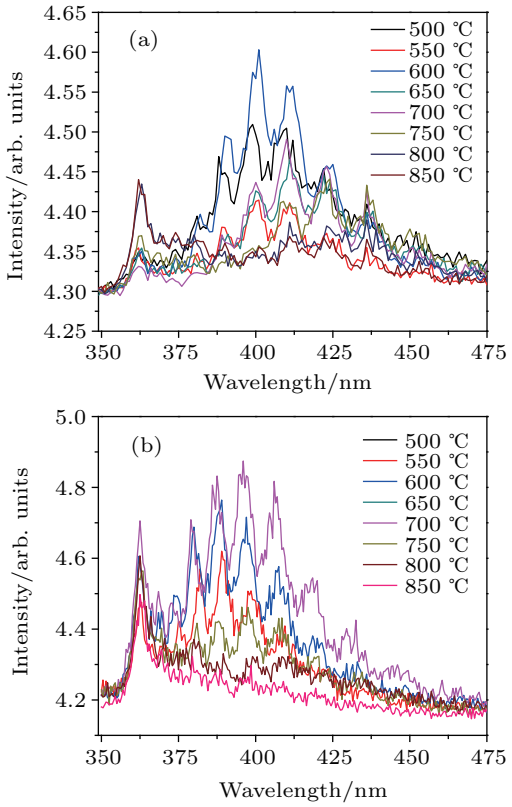


Fig. 4. (color online) annealing-temperature-dependent PL spectra excited by a 325-nm line of He–Cd laser for (a) sample A and (b) sample B.

4. Conclusions

In this work, we investigated the effect of carrier gas H_2 flux on the quality of lower temperature growth and annealed p-type GaN through Hall measurement, SIMS and room temperature PL. We find that the H atoms' concentration in Mg-doped p-type GaN layer epilayers can effectively decrease as the flow rate of carrier gas H_2 is appropriately reduced In addition, a high-quality p-type GaN can be obtained at a comparatively low annealing temperature. Meanwhile, we find that when annealing the sample at a temperature in a range of 550 °C–750 °C, the Hall measurement result can be improved while the H atoms' concentration in the layer is almost the same after being annealed in the temperature range. This can happen because in this annealing temperature range, the state of H atom changes but the probability of forming H_2 molecules is still low. Finally, we find that the thermal annealing has a remarkable effect, not only on the activation of acceptors but also on the concentration of compensation donors.

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