Optimization and Analysis of Magnesium Doping in MOCVD Grown p-GaN*

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Abstract: p-type conductivity and crystal quality of Mg-doped GaN grown by MOCVD have been improved through optimization of the magnesium flow rate. The hole concentration first increased and then decreased with the magnesium flow rate while the mobility decreased monotonously. The optimum sample reached a hole concentration of $4.1\times10^{17}cm^{-3}$ and a resistivity of $1\Omega\cdot cm$. Based on a self-compensation model involving the deep donor $M_{Ga}V_N$, we calculate the hole concentration as a function of magnesium doping concentration N_A, which indicates that the self-compensation coefficient increases with N_A; the hole concentration first increases with N_A and reaches a maximum at $N_A\approx4\times10^{19}$, then decreases rapidly as doping concentration increases. XRD also indicate that dislocation density decreased as magnesium flow rate decreased.

Key words: p-GaN; self-compensation; magnesium doping; MOCVD
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1　Introduction

Highly conductive p-type GaN layers are important for nitride-based devices such as light emitting diodes (LED's) and laser diodes. The achievement of p-type conductivity[1,2] in Mg-doped GaN marked the beginning of nitride-based devices[4]. However, p-type doping efficiencies have remained low, causing low conductivity and thus hampering the further development of GaN-based devices. One reason for the low doping efficiencies is the large Mg-acceptor ionization energy of about 150～250meV[3,4]. The hydrogen passivation of the Mg acceptors adds to the problem, although this passivation can be removed partially by thermal annealing[1] or low energy electron beam irradiation (LEEBI)[2]. In highly doped cases, self-compensation through formation of deep donors is thought to be the main restriction on the doping efficiency[5].

During the growth procedure, the doping efficiencies of Mg-doped GaN films are determined by many factors such as magnesium flow rate, the ratio between N and Ga (Ⅴ/Ⅲ), growth temperature, and the pressure in the reactor. Several groups have indicated that a proper magnesium flow rate is important for achieving high doping efficiencies[5,6], which can reach a balance between the doping concentration and the self-compensation effect. We grew a series of samples with magnesium flow rates from 0.1 to 1.4μmol/min. Hall and XRD measurements indicate that we have successfully achieved high hole conductivity (with both high hole concentration and hole mobility) and improved crystal quality through optimizing the magnesium flow rate.

2　Experiment

The samples studied were grown on 50mm *c*-plane sapphire substrates using a metal-organic chemical vapor deposition reactor. Trimethyl-gallium (TMGa), ammonia (NH_3), and biscyclopentadienyl-magnesium (Cp_2Mg) were used as precursors. Hydrogen (H_2) was used as the carrier gas of organometals. 1.5μm thick Mg-doped GaN films were grown on top of 2μm thick undoped GaN layers. The growth temperature of Mg-doped GaN films was kept at 1000℃. We grew six samples, each with different magnesium flow rates (from 0.1 to 1.4μmol/min), while keeping Ⅴ/Ⅲ constant and the growth pressure at 13.3kPa.

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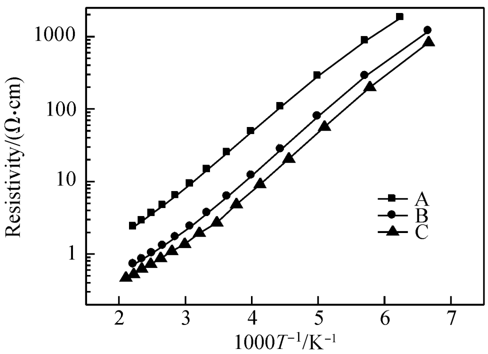

Fig.1 Measured resistivity as a function of temperature on the three Mg-doped GaN samples with different Mg flow rates

After growth, the samples were annealed at 800℃ in N_2 ambient for 20min to activate the Mg acceptor. Hall effect measurements were performed on the samples using lithographically defined van der Pauw structures to investigate the electrical properties. A Ni(20nm)/Au(20nm) bilayer was deposited on 5mm×5mm square samples by electron beam evaporation. Then the samples with electrodes were annealed in O_2 ambient for 5min to achieve ohmic contact. We also performed XRD measurements to characterize the crystal quality.

3 Results and discussion

Figure 1 shows the temperature dependent resistivity of the three GaN:Mg samples (labeled A, B, and C) with magnesium flow rates of 1.4, 0.48 and 0.28μmol/min. The three curves are almost parallel to each other in the measured temperature range. By fitting the curve of hole concentrations obtained by temperature dependent Hall measurement (not shown here), we determined the ionization energy of the Mg-acceptor is around 170meV, which is in the range of the reported scales and shows no notable difference for the three samples. As for the mobility, variable temperature Hall measurements show that it is $-3/2$ times exponentially dependent on temperature when $T > 200$K, which indicates that the crystal scatter is the main restriction on the hole mobility in this temperature range.

Figure 2 shows the RT hole concentration and mobility of the six samples measured from the Hall effect. The figure indicates that when the Cp_2Mg flow rate increases from 0.1 to 1.4μmol/min, the hole concentration first increases to a maximum of 4.1×10^{17} cm^{-3} at a Cp_2Mg flow rate of 0.14μmol/min and then decreases to 6.1×10^{16} cm^{-3}. Mobility decreases monotonously from 19.8 to 6.99$cm^2/(V\cdot s)$.

We assume that self-compensation by deep donors such as $M_{Ga}V_N$ complexes formed by nitrogen vacancy V_N and the substitutional magnesium acceptor Mg_{Ga} is responsible for the decreasing hole concentrations at higher Cp_2Mg flow rates. That a photoluminescence band near 2.8eV originated from deep donor-acceptor pair transitions indicates the existence of $M_{Ga}V_N$[5,7] and positron annihilation experiments prove a considerable open volume of $M_{Ga}V_N$ in heavily Mg-doped GaN[8]. Based on the self-compensation model given by Kaufmann *et al*., we calculated the self-compensation coefficient and hole concentration as a function of magnesium doping concentration.

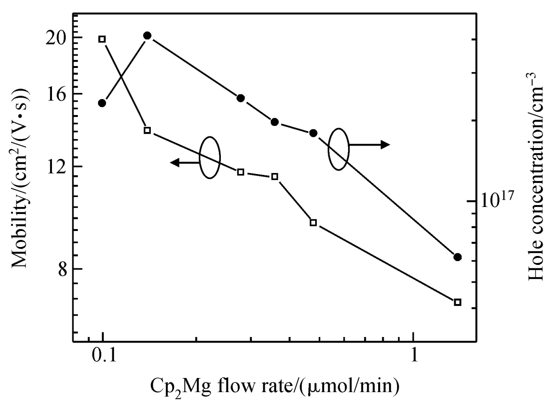

Fig.2 Measured hole concentration and mobility of the six samples with different Mg flow rates

Considering self-compensation by $M_{Ga}V_N$[9], hole concentration versus doping concentration can be obtained by the following equations:

$$p = -\frac{2cN_A + K}{2} + \sqrt{\frac{(2cN_A + K)^2}{4} + KN_A(1-3c)} \quad (1)$$

$$c = \frac{1}{3}\left(\frac{N_A}{N_{CC}}\right)^3 \times \left(\frac{1+\sqrt{1+\alpha N_{CC}/N_{val}}}{1+\sqrt{1+\alpha N_A/N_{val}}}\right)^3 \quad (2)$$

c is the self-compensation coefficient and defined as $c = N_D/N_A$, where N_D is the concentration of $M_{Ga}V_N$ and N_A the magnesium concentration. N_A of our samples is obtained by linear interposition of Tokunaga's results under the same growth condition[10]. $K = 1/\beta N_{val}\exp(-E_A/kT)$ and $\alpha = 4\beta\exp(E_A/kT)$, where β is the valence band degeneracy factor, N_{val} the temperature dependent vb density of states, and E_A the acceptor activation energy. N_{CC} is a fit parameter introduced to simplify the calculation, which equals the value of the doping concentration when complete compensation occurs.

Here we use $E_A = 170$meV, $\beta = 3.6$, and $N_{CC} = 5.1\times10^{20}$ cm^{-3}, which is obtained from fitting with six experimental points.

The results are shown in Fig.3. The self-compensation coefficient increases monotonously with magnesium concentration; the hole concentration first increases proportionally with increasing N_A, reaches a

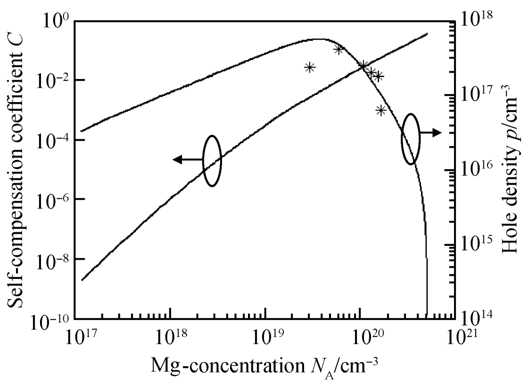

Fig. 3　Calculated hole concentration and self-compensation coefficient as a function of doping concentration

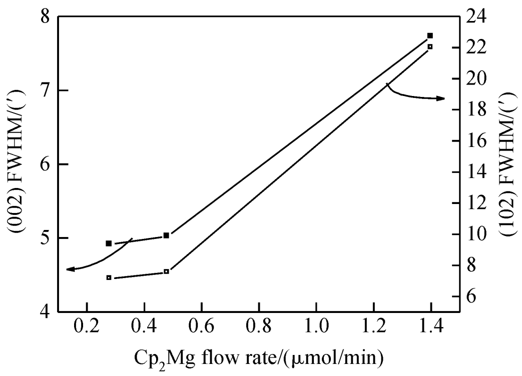

Fig. 4　Cp_2Mg flow rate dependence of FWHM of (002) and (102) faces of the GaN films

maximum at $N_A \approx 4\times10^{19}$, and then decreases rapidly as magnesium concentration increases. The influence of self-compensation is negligible at low or moderate doping levels, i.e., lower than $10^{19}cm^{-3}$, but becomes increasingly significant when N_A becomes comparable with N_{CC}.

In Fig. 3, the curve of the hole concentration can be divided into two regions: the left region before the turning point and the right region after it. From calculation we found the left region to be much less sensitive to N_{CC} than the right. Therefore, even though there are few experimental points in the left region, the curve is relatively valid for the whole region. The Mg concentrations were estimated from the Mg flow rate, which may lead to some errors in our results. However, the shape of the curve in Fig. 3 will not change too much in this case, which also reflects the tendency of the Mg doping at p-GaN influenced by formation of $M_{Ga}V_N$ complexes.

Figure 4 shows full width at half maximum (FWHM) of $\omega/2\theta$ X-ray diffraction curves of the three samples. The FWHMs of the (002) and (102) faces decrease quickly when the Mg flow rate decreases from 1.4 to 0.48μmol/min, and then decrease slowly as the Mg flow decreases to 0.28μmol/min, which indicates lower dislocation densities and improved crystal quality with lower doping levels. The results also indicate when the Mg flow rate is below 0.48μmol/min, the influence of the Mg doping level on the crystal quality becomes less important. Better crystal quality can also be reflected from better hole mobility, as shown in Fig. 2.

4　Conclusion

We have obtained relatively high hole conductivity and crystal quality by optimizing the magnesium flow rate during growth of p-type GaN by MOCVD. The resistivity of the optimized sample reached 1Ω · cm and the hole concentration reached $4.1\times10^{17}cm^{-3}$. XRD results showed that the crystal quality improved as the magnesium flow rate (doping level) decreased. Self-compensation by $M_{Ga}V_N$ complexes may be responsible for the low hole concentrations in heavily doped cases. The results of calculation indicate that at lower doping levels, the self-compensation coefficient is negligible and the hole concentration increases proportionally with doping concentration. The self-compensation coefficient becomes increasingly significant in high doping levels and leads to the hole concentration decreasing rapidly with increasing doping concentration.

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MOCVD 生长的 p 型 GaN 薄膜中 Mg 掺杂的优化与分析*

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摘要： 通过优化 Mg 流量增强了 MOCVD 生长的 GaN 薄膜的 p 型电导并改善了晶体质量. Hall 测量结果表明空穴浓度首先随着 Mg 流量的升高而升高，达到极大值后开始降低；迁移率始终随 Mg 流量的升高而降低. 最优的样品在室温下空穴浓度达到 4.1×10^{17} cm^{-3}，电阻率降至 1Ω·cm. 考虑施主型缺陷 $M_{Ga}V_N$ 的自补偿作用，计算了空穴浓度随掺杂浓度变化的曲线关系. 计算结果表明自补偿系数随掺杂浓度的增大而增大；空穴浓度首先随掺杂浓度的增大而增加，在受主浓度为 $N_A\approx4\times10^{19}$ 左右时达到极大值，之后随着掺杂浓度的增大而迅速降低. XRD 数据表明在实验范围内晶体缺陷密度随着掺杂浓度的降低而降低.

关键词： p 型 GaN；自补偿；掺杂浓度；MOCVD

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