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Optical and Electrical Properties of GaN:Mg Grown by MOCVD*

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Abstract: Mg-doped GaN layers prepared by metalorganic chemical vapor deposition were annealed at temperatures between 550 and 950℃. Room temperature (RT) Hall and photoluminescence (PL) spectroscopy measurements were performed on the as-grown and annealed samples. After annealing at 850℃, a high hole concentration of $8\times10^{17}cm^{-3}$ and a resistivity of 0.8Ω·cm are obtained. Two dominant defect-related PL emission bands in GaN:Mg are investigated; the blue band is centered at 2.8eV (BL) and the ultraviolet emission band is around 3.27eV (UVL). The relative intensity of BL to UVL increases after annealing at 550℃, but decreases when the annealing temperature is raised from 650 to 850℃, and finally increases sharply when the annealing temperature is raised to 950℃. The hole concentration increases with increased Mg doping, and decreases for higher Mg doping concentrations. These results indicate that the difficulties in achieving high hole concentration of $10^{18}cm^{-3}$ appear to be related not only to hydrogen passivation, but also to self-compensation.

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1　Introduction

Well controlled p-type doping is one of the foremost obstacles in the progress of device development of Ⅲ-nitrides for fabricating visible and ultraviolet light-emitting devices. Low energy electron-beam irradiation[1] or thermal annealing in N_2 atmosphere[2] is necessary to obtain significant hole concentrations for GaN grown by metal-organic chemical vapor deposition (MOCVD). Although the underlying mechanism for these activation processes is not yet fully understood, it is widely believed that hydrogen impurities created in the growth passivate Mg acceptors by forming Mg-H neutral complexes. Observation of a local vibrational mode (LVM) for the Mg-N-H complex by infrared (IR) absorption[3] and Raman scattering[4] in as-grown samples gives convincing evidence for this hypothesis. Therefore, a postgrowth treatment is required to activate the Mg acceptors through dissociation of Mg-H complexes.

However, there is strong evidence that p-type doping of GaN is a more complex process and Mg-H complexes may not be the only passivating centers[4,5]. Theoretical calculations predict that nitrogen vacancies are the dominant point defects in p-type GaN because of their low formation energy[6,7]. Moreover, due to the high Mg ionization energy, high doping concentrations in the $10^{19}cm^{-3}$ range are required to achieve hole concentrations in the low $10^{17}cm^{-3}$ range. Saarinen *et al*. applied positron annihilation spectroscopy (PAS) to identify Mg_{Ga}-V_N complexes as important compensating centers in Mg-doped GaN layers[5]. Despite that, we still lack an understanding of the defects responsible for determining the electrical and optical properties of Mg-doped GaN layers.

In this work, we perform Hall and photoluminescence (PL) spectroscopy measurements of Mg-doped GaN:Mg layers prepared by MOCVD. Two closely connected effects are observed. First, a RT PL band peaked around 2.8eV dominates the PL spectra. Second, the hole concentration as a function of Mg concentration reaches a maximum value. The stability of defects in heavily Mg-doped GaN layers is also investigated. The role that Fermi level plays on defect stability in p-type GaN:Mg layers is taken into account.

2　Experiment

p-type GaN:Mg layers were grown on sapphire substrate using a horizontal MOCVD reactor. Trimethyl-gallium (TMGa) and ammonia (NH_3) were used as Ga and N precursors, respectively, and bis-cyclopentadienyl magnesium (Cp_2Mg) as the p-type doping source. First, a 4μm semi-insulating GaN ($n<5\times10^{16}cm^{-3}$) layer was grown on sapphire followed by a 1.5μm GaN:Mg layer at 1040℃. The mole ratio of

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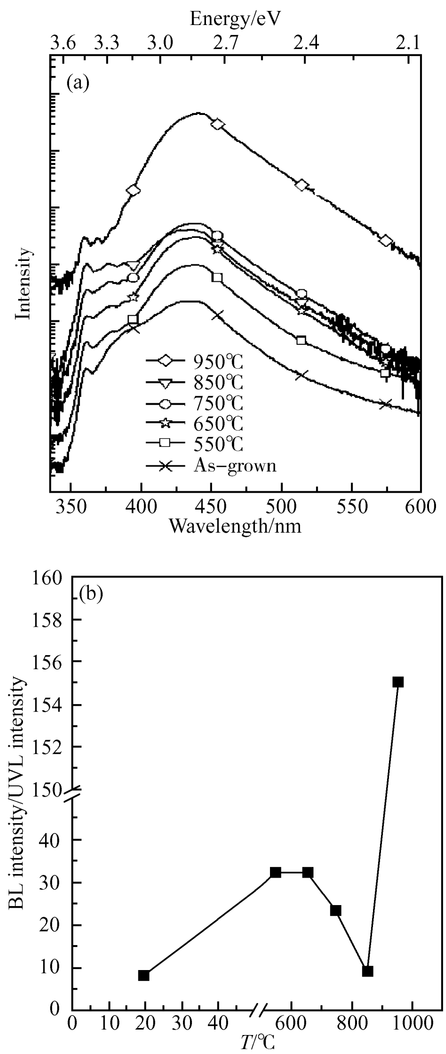

Fig.1 (a) PL spectra for GaN:Mg layer before and after annealing at different temperatures;(b) Relative intensity of BL to UVL as a function of annealing temperature

Cp_2Mg to TMGa ([Cp_2Mg]/[TMGa]) varied between 0.004 and 0.015. To achieve p-type characteristics in the GaN:Mg layer, rapid thermal annealing (RTA) was carried out under various conditions. A one-step RTA process was performed on the samples prepared with a [Cp_2Mg]/[TMGa] ratio of 0.0065 at temperatures of 550, 650, 750, 850, and 950℃ in N_2 atmosphere for 20min. The samples were studied by PL and RT Hall measurements in the as-grown condition and after each annealing step. Photoluminescence was excited with the 325nm line of a He-Cd laser (10mW).

3 Results and discussion

Figure 1 (a) shows the typical PL spectra at 295K of GaN:Mg layers before and after annealing at different temperatures. The peak centered at ~3.5eV corresponds to the band edge emission of the underlying GaN layer. An apparent intensity ultraviolet emission band around 3.2eV (UVL) is observed in the as-grown sample, which was previously attributed to donor-acceptor pair (DAP) emission involving a shallow donor of unknown origin and a Mg acceptor[8]. After annealing, the intensity of this DAP emission band is decreased by one order of magnitude and the peak position gradually shifts to 3.27eV (UVL). The shift in the peak position may be explained by the reduction of potential fluctuations[9] as a result of screening from the carriers. A third band with a peak around 2.8eV (BL) is observed and the intensity of this peak changes significantly after annealing. To clearly demonstrate the change of the intensity of the observed peaks, Figure 1 (b) shows the relative intensity of BL to UVL (BL intensity/UVL intensity) as a function of annealing temperature (T). BL intensity/UVL intensity increases after annealing at 550℃, but decreases when the annealing temperature is elevated from 650 to 850℃, and finally increases sharply when the annealing temperature is raised to 950℃.

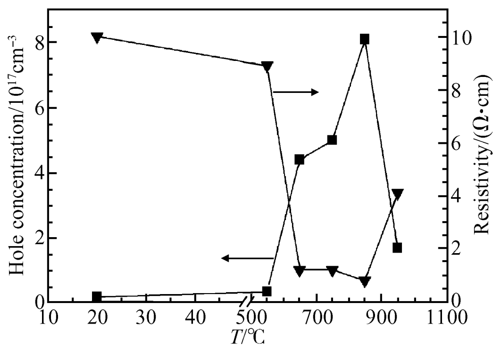

Fig.2 Hole concentration and resistivity in GaN:Mg layers as determined by Hall measurement versus the annealing temperature

The observed change in the PL spectra upon annealing can be attributed to changes in the defect concentrations. Prior to annealing, shallow donors are present in high concentrations, leading to UVL. Upon annealing at 550℃ in nitrogen, the shallow donors are eliminated and the intensity of UVL decreases sharply. Since the UVL is quenched by annealing at a relatively low temperature of 550℃, it must involve a donor that has a high diffusivity. One possibility is hydrogen, which has a high diffusivity in GaN and has been predicted to be a donor[10]. IR absorption[3] and Raman scattering data[4] show clear evidence that H-related complexes are present in as-grown GaN:Mg layers. The BL that becomes dominant upon annealing has been previously attributed to deep donor shallow acceptor (DDAP) emission, where, in this case, the donor is deep and the acceptor is shallow[9].

Figure 2 shows the hole concentration and resistivity in GaN:Mg layers annealed at different temper-

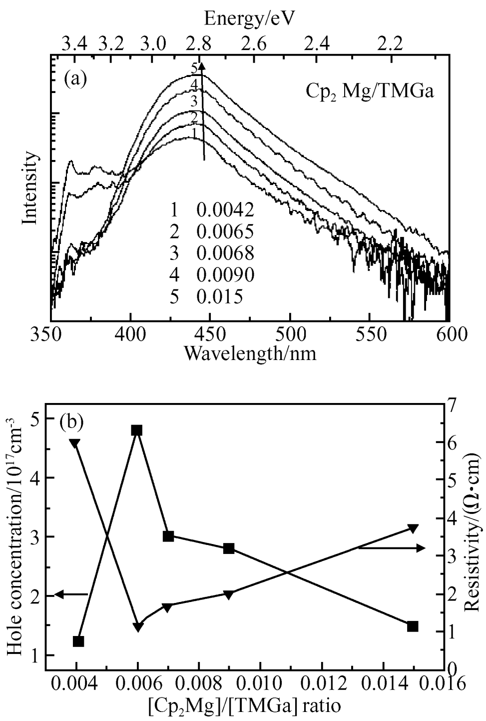

Fig. 3　Dependence of the intensity of the PL bands (a), and the hole concentration of GaN:Mg layers on [Cp_2Mg]/[TMGa] ratio (b)

atures. The layers show poor p-type conductivity before annealing. Thermal annealing from 550 to 950℃ for 20min has no obvious effect on our GaN:Mg layers with high crystal quality, as demonstrated by X-ray diffraction.

After annealing at 550℃, the hole concentration and the resistivity change little. As the annealing temperature increases from 550 to 850℃, the hole concentration continuously increases from $10^{16}cm^{-3}$ to $8\times10^{17}cm^{-3}$ and the resistivity decreases from 9 to 0.8Ω·cm. However, the hole concentration drops dramatically after the annealing temperature is raised to 950℃, and the resistivity increases to 4Ω·cm.

Figure 3(a) shows the dependence of the intensity of the PL bands, and Figure 3(b) shows the hole concentration of GaN: Mg layers on the [Cp_2Mg]/[TMGa] ratio. The p-type GaN:Mg layers under investigation were annealed at 750℃ for 20 min. The increment of the [Cp_2Mg]/ [TMGa] ratio corresponds to the increase in Mg doping concentration[11].

The data in Fig.3 (b) show that initially the hole concentration increases as Mg doping increases, but decreases later for higher Mg doping concentrations. The resistivity shows the opposite trend. The difficulties in achieving high hole concentration above $8\times10^{17}cm^{-3}$ and low resistivity below 0.8Ω·cm appear to be primarily related to self-compensation of Mg[12]. As indicated in Fig. 3 (a), for moderately Mg-doped p-type GaN, the UVL is seen as a weak peak,

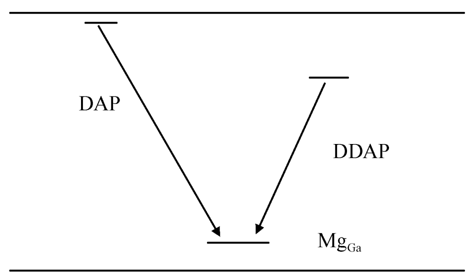

Fig. 4　Schematic energy band diagram to illustrate the peaks observed in Mg-doped GaN　D indicates the donor state, and DD indicates the deep donor state.

compared to the BL. For heavily Mg-doped GaN, however, the UVL quenches, and the BL dominants the spectra. It seems that the intensity of the BL, is not directly related to the p-type conduction mechanism[13], but increases as the Mg doping concentration increases. This band has therefore been assigned to the recombination involving isolated Mg acceptors and deep donors presumably induced by self-compensation. A candidate for the deep donor is Mg_{Ga} associated with a nitrogen vacancy (V_N), which is the only native defect with a relevant concentration in p-GaN[7], and has the opposite charge of Mg_{Ga}. Thus, neutral Mg_{Ga}-V_N complexes are expected to form. At a growth temperature around 1000℃ the constituents are oppositely charged and V_N is mobile.

After thermal annealing at 550～850℃ the Mg_{Ga}-V_N complexes dissociate and V_N migrates to the surface. As a result, the hole concentration increases, while the intensity of BL decreases, as shown in Figs. 1 and 2. The Mg_{Ga}-V_N complexes are observed in as-grown MOCVD GaN: Mg, but not in the material grown by MBE[5]. The relevant difference is related to the presence of hydrogen in the growth environment. The as-grown MOCVD GaN: Mg commonly shows poor p-type conductivity because Mg acceptors are passivated by hydrogen. A postgrowth thermal anneal is required to activate the Mg acceptors and obtain significant hole concentration, as illustrated in Fig. 2. Hydrogen is absent in the MBE growth and the as-grown material already possesses well p-type conductivity. These results suggest that the Mg_{Ga}-V_N complexes are stable at the growth temperature around 1000℃ only if the Fermi level is close to the midgap; otherwise the complexes dissociate. Thereby, as shown in Figs. 1 and 2, when the annealing temperature is raised from 850 to 950℃, large amounts of V_N are expected to form. As a consequence, the net hole concentration drops, and the Fermi level moves away from the maximum of the valence band, which results in the formation of Mg_{Ga}-V_N complexes again. Based on the analysis above, the dramatic increase in the intensity of BL in Fig.1 is understandable.

In summary, Figure 4 shows a schematic energy band diagram to illustrate the DAP peak (UVL) and DDAP peak (BL) observed in Mg-doped GaN layers. The shallow donor responsible for UVL is attributed to hydrogen, whereas the deep donor defect responsible for BL is attributed to nitrogen vacancy complexes associated with Mg acceptors.

4 Conclusion

After annealing at 850℃, a high hole concentration of $8\times10^{17}cm^{-3}$ of and a resistivity of 0.8Ω·cm are obtained. PL and Hall results on Mg-doped GaN layers indicate that the difficulties in achieving higher hole concentration appear to be related to self-compensation and hydrogen passivation. The observed dependence of the relative intensity of BL to UVL on annealing temperatures can be explained in terms of hydrogen donors. Upon annealing, the hydrogen related DAP defects dissociate and the associated luminescence band quenches, whereas Mg acceptors are activated and hole concentration increases. There is evidence that deep donors, which are assigned to Mg_{Ga}-V_N complexes, are formed as the Mg doping concentration increases. The Fermi level position may be a critical factor in the stabilization of Mg_{Ga}-V_N complexes. When the Fermi level position is near the maximum of the valence band, resulting from high hole concentration, Mg_{Ga}-V_N complexes are not stable, and dissociate after annealing between 550 and 850℃.

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MOCVD 生长的 GaN:Mg 外延膜的光电性质*

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摘要：用 MOCVD 技术生长 GaN:Mg 外延膜，在 550 ～ 950℃温度范围内，对样品进行热退火，并进行室温 Hall、光致发光谱(PL)测试. Hall 测试结果表明，850℃退火后空穴浓度达到 $8\times10^{17}cm^{-3}$ 以上，电阻率降到 0.8Ω·cm 以下. 室温 PL 谱有两个缺陷相关发光峰，位于 2.8eV 的蓝光峰(BL)以及 3.27eV 附近的紫外峰(UVL). 蓝光峰对紫外峰的相对强度(BL/UVL)在 550℃退火后升高，之后随着退火温度的升高(650～850℃)而下降，继续提高退火温度至 950℃，BL/UVL 急剧上升. 空穴浓度先随着 Mg 掺杂浓度的增加而升高；但继续增加 Mg 掺杂浓度，空穴浓度反而下降. 这些结果表明要实现空穴浓度达 $10^{18}cm^{-3}$，不仅要考虑 H 的钝化作用，还要考虑 Mg 受主的自补偿效应.

关键词：霍尔效应；光致发光；p 型 GaN

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