



Self-compensation in Mg doped p-type GaN grown by MOCVD

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Abstract

The hole concentration and the Mg related photoluminescence bands in MOCVD-grown GaN:Mg have been investigated as a function of Mg-concentration. The hole density was found to reach a maximum for an Mg-content near $3 \times 10^{19} \text{ cm}^{-3}$. When increasing the Mg-concentration beyond this value the hole density drops rapidly. The analysis of the PL spectra reveals that near the maximum of the hole concentration, the dominant radiative recombination mechanism changes from a free-to-bound to a donor–acceptor (D–A) pair transition. These results strongly indicate that self-compensation effects limit the hole density in GaN:Mg samples. Based on theoretical predictions and experience with acceptor doped II–VI compounds, it is suggested that the deep donor D_d involved in self-compensation is a nearest-neighbor associate of a Mg_{Ga} acceptor with a nitrogen vacancy V_{N} . © 1998 Elsevier Science B.V. All rights reserved.

PACS: 81.15.Gh; 72.80.Ey; 78.30.Fs

Keywords: GaN:Mg; Self-compensation; MOCVD

1. Introduction

Up to now Mg is the only acceptor in GaN that reproducibly generates useful p-conductivity. Due to the high Mg ionization energy of about 200 meV, doping concentrations of the order of several 10^{19} cm^{-3} are required to achieve hole

densities in the 10^{17} cm^{-3} range at room temperature (RT). Furthermore, there is convincing evidence that the magnesium acceptor is hydrogen passivated in the as-grown MOCVD material [1]. However, there are also indications that at these high Mg doping levels hydrogen passivation is not the only problem limiting p-conduction [2]. It is shown in this paper that for Mg-concentrations of $(2\text{--}3) \times 10^{19} \text{ cm}^{-3}$ two closely connected effects occur. At first, the hole density as a function of Mg-concentration reaches a maximum value. Second,

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an RT photoluminescence (PL) band, peaked around 2.8 eV, emerges. Clear evidence for the distant donor–acceptor (D–A) pair character of the 2.8 eV band is presented. The acceptor A is assigned to isolated Mg_{Ga} while the deep donor D_{a} (binding energy $E_{\text{D}} = 430$ meV) is suggested to be a nearest-neighbor associate of an Mg_{Ga} acceptor with a nitrogen vacancy, formed by self-compensation. The latter suggestion is in line with the predictions of theory [3] and is supported by experience from the wide band gap II–VI semiconductors [4].

2. Experimental details

A large number of Mg-doped wurtzite GaN layers were grown on 2" *c*-plane sapphire substrates using an AIXTRON 200/HT horizontal-flow MOCVD reactor. Prior to the growth of the 1–2 μm thick GaN : Mg layers, a 30 nm low-temperature GaN nucleation layer and a 1–2 μm thick insulating GaN buffer layer have been deposited. The growth temperature for the nucleation layer varied between 530 and 580°C whereas the GaN buffer layer and the GaN : Mg layers were deposited between 1000 and 1030°C. The Mg-concentrations as determined by secondary ion mass spectroscopy (SIMS) range from 4×10^{17} to $1 \times 10^{20} \text{ cm}^{-3}$. Hall effect measurements with evaporated Ni,Au contacts and PL at RT were used to characterize the thermally annealed (650°C, N_2 , 30 min) films. Photoluminescence was excited with the 325 nm line of an He–Cd laser (45 mW) and detected with a near UV enhanced, LN_2 cooled silicon CCD detector array.

3. Results and discussions

In Fig. 1 the hole densities of p-type GaN : Mg layers measured by Hall effect after thermal activation of the acceptors are plotted versus the Mg-concentration as determined by SIMS. The data show that initially the hole density increases with increasing Mg-content. A maximum of about $9 \times 10^{17} \text{ cm}^{-3}$ is reached for an Mg-content around $3 \times 10^{19} \text{ cm}^{-3}$. For higher Mg-concentrations the

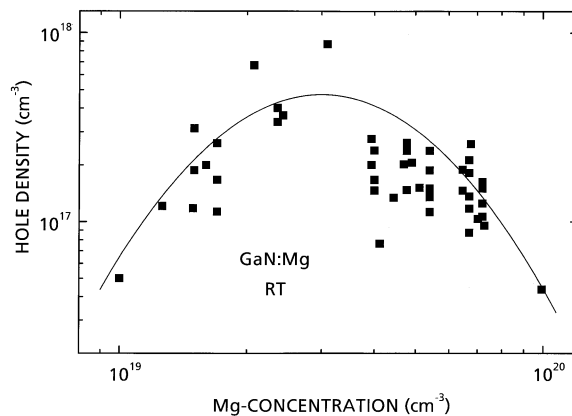


Fig. 1. Hole density in GaN : Mg films as determined by Hall effect versus the Mg concentration of the films as measured by SIMS. The full line is a guide to the eye.

hole density decreases again. This finding is in line with previous observations where GaN : Mg layers with the highest Mg-doping levels remain highly resistive even after LEEBI or thermal annealing treatment [2,5]. We would like to mention that our as-grown Mg-doped GaN samples with Mg-content below $2 \times 10^{19} \text{ cm}^{-3}$ show p-conduction already *without* post-growth treatment whereas the samples with higher Mg-content are highly resistive as-grown and reveal p-conduction only after post-growth thermal annealing. The saturation, and eventual decrease, of the hole concentration with increasing Mg-content is accompanied by a change in the RT–PL spectrum. Up to an Mg-concentration of about $2 \times 10^{19} \text{ cm}^{-3}$ the Mg related 3.2 eV band dominates, see the upper traces in Fig. 2. In addition, there is a relatively sharp line near 3.4 eV, assigned to the free exciton recombination. In the Mg concentration range $(2\text{--}3) \times 10^{19} \text{ cm}^{-3}$ a sudden change from the 3.2 to the 2.8 eV band occurs. At even higher concentrations this band dominates the spectrum while the 3.2 eV band and the 3.4 eV line become completely quenched as can be seen in the lower traces of Fig. 2. No change in spectral shape as compared to the lowest trace in Fig. 2 is observed for Mg levels above $5 \times 10^{19} \text{ cm}^{-3}$. The switching from the 3.2 to the 2.8 eV band has been consistently observed for several doping series. Detailed investigations have proven that the 2.8 eV band is not a shifted 3.2 eV band [6].

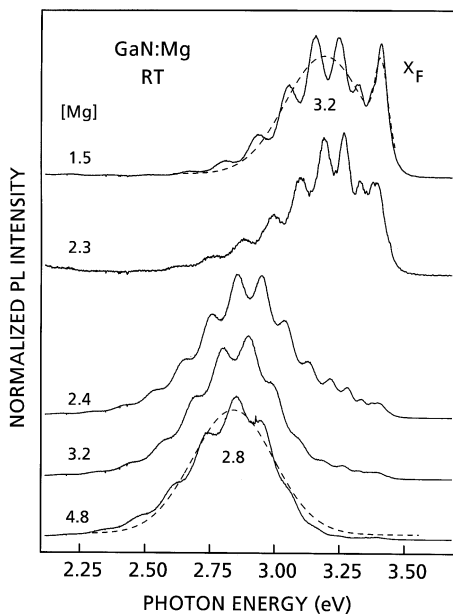


Fig. 2. PL spectra at RT for various GaN : Mg films measured at constant power density. Mg concentrations in units of 10^{19} cm^{-3} are indicated to the left. The spectra reveal the free exciton X_F and the broad Mg induced bands peaked at 2.8 and 3.2 eV. The oscillations superimposed on the broad bands are Fabry–Perot interferences. Curves fitted neglecting interference effects are shown by dashed lines.

Since the Mg related 3.2 eV band is already observable for Mg concentrations in the low 10^{18} cm^{-3} range, we assign it to isolated Mg acceptors. Its missing peak shift with changes in excitation power density, compare Fig. 3, excludes that it has D–A pair character at RT and suggests a free to bound recombination process (Mg^0, e) in line with previous assignments. The 2.8 eV band cannot simply originate from free electron recombination at a deeper Mg related acceptor complex. In this case, the dependence of its peak position on power density, see Fig. 3, would be expected to be the same as that of the 3.2 eV band. This is evidently not the case. Rather, the peak position of the 2.8 eV band shifts to higher energy with increasing power density. This is a characteristic typical for (D–A) pair recombination involving electrons and holes trapped at distant donors and acceptors, respectively. The reason for this behavior is the Coulomb inter-

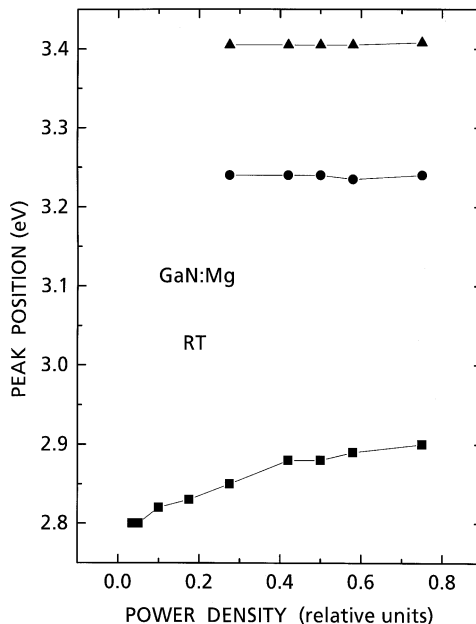


Fig. 3. Plot of peak energies of the 2.8, 3.2 and 3.4 eV PL band versus excitation power density.

action $E_C = e^2/\epsilon r$ where r is the mean separation between D and A in neutral pairs. With increasing power density, r decreases and E_C increases. As a consequence, the recombination energy $h\nu = E_G - (E_D + E_A) + E_C$ shifts to higher energy. Peak shifts up to 130 meV have been observed, indicative of intrapair separations r as short as 2 nm and deep donor concentrations around 10^{19} cm^{-3} . The 2.8 eV band has therefore been assigned to D–A-recombination involving isolated Mg acceptors and deep donors D_d (430 meV) presumably induced by self-compensation. Based on the results of theory [3] and in analogy to acceptor-doped high gap II–VI compounds like ZnS : Ag [4], it appears likely that D_d consists of Mg_{Ga} associated with a nearest-neighbor nitrogen vacancy (V_N). V_N is the only native defect with a relevant concentration in p-GaN [3] and the $\text{Mg}_{\text{Ga}}-V_N$ associates are expected to form since at a growth temperature around 1000°C the constituents are oppositely charged and V_N is mobile. The present interpretation of the 2.8 and 3.2 eV band provides a qualitative explanation for the concentration induced switching between

these two bands in Fig. 2. As long as the Mg content is moderate the concentration of deep donors D_d ($Mg_{Ga}-V_N$ associates) is low, and the D_d – Mg_{Ga} intrapair separations are relatively large. Consequently, the probability of recombination for trapped electrons and holes is low because of their small wave function overlap. Therefore, free electrons will preferentially recombine directly with holes on Mg^0 (3.2 eV band). However, with increasing Mg concentration, the Fermi level moves towards the valence band edge thus also increasing the V_N concentration [3]. Therefore, the D_d concentration increases and consequently the D_d – Mg_{Ga} intrapair distances decrease. Correspondingly, the pair recombination probability increases and eventually exceeds that of the direct $e-A^0$ recombination process such that the 2.8 eV band becomes dominant.

4. Conclusions

PL and Hall effect data on Mg-doped GaN layers indicate that the difficulties in achieving reproducible hole densities significantly above $4 \times 10^{17} \text{ cm}^{-3}$ appear to be primarily related to self-compensation rather than to hydrogen passivation. There is clear evidence that a deep donor D_d is formed with increasing Mg content. In our view,

the best model for D_d is a nearest-neighbour associate of Mg_{Ga} and a nitrogen vacancy V_N .

Acknowledgements

The authors are grateful to T. Fuchs, Ch. Manz, B. Santic and R. Schmidt for their support with SIMS, PL and Hall effect measurements. We would like to thank J. Wagner for fruitful discussions, G. Weimann for continuous support and encouragement, and the German Ministry for Research and Education for financial support.

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