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# Mg-related acceptors in GaN

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Photoluminescence spectra of *c*-plane Mg doped GaN samples grown by MOVPE on bulk GaN templates reveal previously unknown properties, like the presence of several Mg-related acceptors. The use of unstrained samples allows a study of both bound exciton (BE) and donor-acceptor pair (DAP) spectra. Two main acceptors A1 and A2 are observed strongly in BE spectra as well as in DAP spectra, they have similar binding energies, i.e. about 220 meV. The common assignment of the deeper blue PL emission at 2.8 – 3.0 eV to a deep donor-shallow acceptor transition is questioned, and discussed in connection with the compensation problem in p-GaN. It seems like the Fermi level in p-GaN is controlled by a set of Mg-related acceptors at energies 0.2 – 0.6 eV from the valence band top.

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**1 Background and experiments** The generally accepted picture in the literature is that Mg doping causes a moderately shallow acceptor (about 200 meV) in GaN, and in addition there are compensating shallow and deep donors, the latter also Mg-related [1, 2]. It is also well known that the Mg acceptor can be activated via a thermal annealing process at elevated temperatures, such as 800°C [3]. Recently it was discovered, however, that Mg doping introduces at least two acceptors in GaN, with different properties [4]. These results call for a reevaluation of the Mg-induced defect levels in GaN. In this paper we present some additional optical data, and discuss the compensation problem in p-GaN with reference to earlier work.

The samples used in this work were *c*-plane Mg-doped Ga-face GaN layers grown with metal-organic vapor phase epitaxy (MOVPE) on bulk GaN templates in two laboratories, Meijo University and Bremen University. Details of the sample preparation, annealing conditions, and also on optical measurement techniques were reported in Ref. 4.

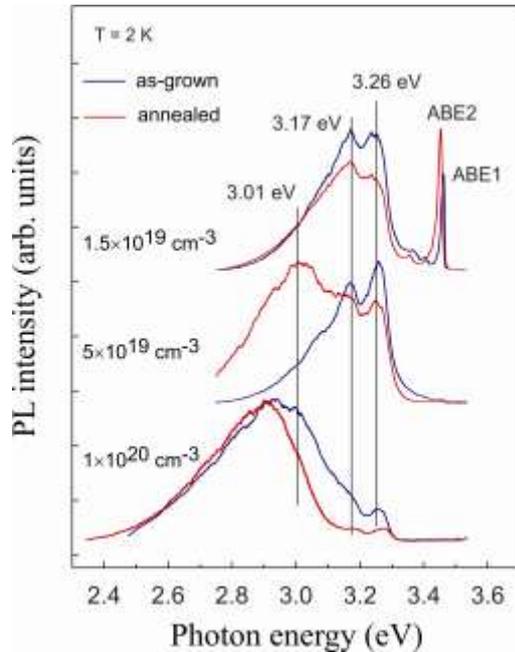
**2 Optical spectra related to Mg acceptors** In Fig. 1 are shown low temperature photoluminescence (PL) spectra for p-type GaN:Mg at three different doping levels. Below  $[Mg] \approx 2 \times 10^{19} \text{ cm}^{-3}$  free and bound excitons are present in the spectra, at higher doping only transitions of

donor-acceptor pair (DAP) type are seen. The spectra are a superposition of several peaks, dominated by the A1 and A2 related DAPs [4], at the highest doping the so-called blue band at 2.9 – 3.0 eV dominates. The PL spectra in Fig. 1 show a strong general shift towards higher photon energy when the excitation intensity is increased by about 3 orders of magnitude (not shown in Fig. 1). This result is in line with some similar previous studies in highly Mg-doped GaN [5-8].

The properties of the two Mg-related acceptors A1 and A2 were discussed in Ref. 4. They are both present in most Mg-doped samples, although the A2 signature seems to be much weaker in n-type GaN. Their binding energies (as defined by the energy position of the no-phonon region in the respective DAP spectra) are similar, i.e.  $225 \pm 10 \text{ meV}$  for A1 and about  $220 \pm 20 \text{ meV}$  for A2 [4]. Otherwise their properties seem to be quite different. A1 has an effective mass acceptor character with rather weak phonon coupling in optical spectra and a strongly anisotropic hole *g*-tensor [4]. A2 behaves more like a deep level with strong phonon coupling in optical spectra (more like the deeper Zn- and Cd-related acceptors [9, 10]), with a rather isotropic hole *g*-tensor [11]. Such defects typically have a thermally activated hole emission, consistent with just a few percent hole activation at room temperature [7]. Much more work is

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needed to determine their relative contributions to the hole concentrations in p-type samples prepared under different conditions. It seems like in p-GaN samples annealed with a standard procedure at 800°C the A2 acceptor dominates in the BE PL spectra [4]. The identity of the two acceptors is not clear. An interesting possibility is that both are related to substitutional  $\text{Mg}_{\text{Ga}}$ , with the slightly deeper A2 acceptor showing a lattice relaxation, with the hole bound essentially to one local bond [12].

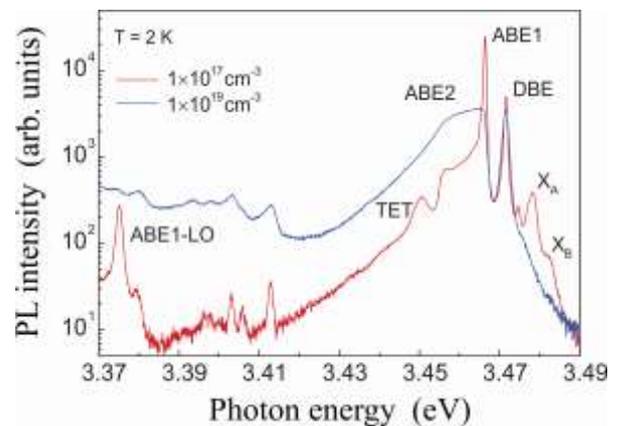


**Figure 1** Low-temperature PL spectra of three GaN layers with different Mg-doping concentrations before and after annealing.

Besides the PL features related to these two acceptors there is a multitude of PL lines present in the range 3.34 – 3.42 eV (Fig. 2). Actually these lines were studied in some detail previously [13], and these authors concluded from an approximate fit of the line energies that the lines were discrete DAP lines associated with an Mg acceptor with a binding energy of 265 meV. The only acceptor that such DAP lines could be associated with is the A1 acceptor, which however has an established binding energy of  $225 \pm 5$  meV. We suggest the five exceptionally strong lines between 3.39 eV and 3.42 eV may have a separate origin, supported by the fact that the temperature dependence of these lines is very similar to ABE1 and ABE2, they all quench at around 50 K (data not shown here). There is no detailed model for these lines at present, however. There is a rather dense background of weaker PL lines in the range 3.34 – 3.43 eV (not well resolved in Fig. 2), these might well be discrete DAP lines.

In addition to A1 and A2 there is optical evidence for deeper acceptors, from the PL structure in the range below 3.1 eV (Fig. 1). So it appears that there are several acceptors related to Mg-doping in GaN. At very high Mg doping

(say  $[\text{Mg}] \approx 10^{20} \text{ cm}^{-3}$ ) the broad peak at about 2.9 eV dominates (Fig. 1). This peak is commonly assigned to a deep donor-shallow acceptor DAP [1], where the deep donor is suggested to be a  $\text{V}_{\text{N}}\text{-Mg}_{\text{Ga}}$  complex with a binding energy about 0.28 eV. This donor is also assumed to be largely responsible for the severe compensation commonly reported in highly p-doped GaN [1, 7, 14]. In later work by positron annihilation spectroscopy (PAS) this donor defect has indeed been identified, but found to have a moderate concentration (about  $2 \times 10^{17} \text{ cm}^{-3}$ ) and to be unstable against annealing above 500°C [15]. Since in Fig. 1 the deep 2.9 eV PL peak is rather enhanced by annealing, it should not be due to any  $\text{V}_{\text{N}}\text{-Mg}_{\text{Ga}}$  donor. In fact DLTS data show a very small concentration of a deep donor at about 0.26 eV in Mg-doped n-GaN [16]. Other DLTS data on highly Mg-doped p-GaN show evidence of several hole traps in the range 0.2 – 0.6 eV from the valence band edge, while the concentration of deep donors corresponding to the  $\text{V}_{\text{N}}\text{-Mg}_{\text{Ga}}$  complex at about 0.28 eV below the conduction band is negligible [17, 18]. The same conclusion is given in Ref. 15. This is consistent with the ODMR data in Ref. 11, where only shallow donor signals (i. e. no deep donors) are observed for highly Mg-doped GaN.

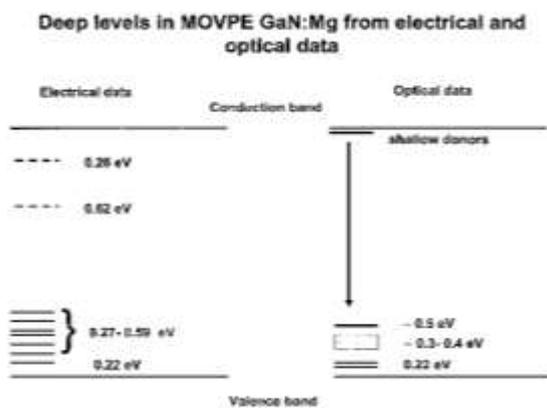


**Figure 2** Low-temperature PL spectra of as-grown GaN layers with two different Mg-doping concentrations. The TET peak denotes two-electron transitions for the donor BEs.

Thus from optical as well as electrical measurements there is evidence for several Mg-related acceptors in *c*-plane MOCVD GaN, which will all affect the hole concentration. A schematic picture of relevant donor and acceptor levels is shown in Fig. 3. A problem at present is that the concentrations of these acceptors deduced from DLTS data in p-GaN is much too low to be realistic, of the order  $10^{16} \text{ cm}^{-3}$  [18]. The reason for this is not presently known. The strong PL spectral shifts with excitation intensity [1, 6] expected in the case of DAPs with a high deep donor concentration may alternatively be explained as a saturation effect of lower photon energy DAPs in the range 2.9 – 3.2 eV in favor of the higher energy transitions (like the 3.27 eV

DAP) with a stronger oscillator strength. As mentioned above there is only weak evidence for the role of a deep donor at about 0.28 eV in compensating Mg-related acceptors. The concentration of such donors seems to be quite small in Mg-doped GaN, nowhere close to the densities in the  $10^{19} \text{ cm}^{-3}$  range deduced from Hall data [7]. In this situation the use of a simplified model with one Mg acceptor and one deep donor for evaluation of Hall data is inadequate.

The Fermi level seems to be controlled primarily by a set of Mg-related acceptors, and the main donor compensation would be caused by residual shallow donors. The situation is schematically illustrated in Fig. 3. It is then important to establish the typical shallow donor concentration in Mg-doped p-GaN. We have investigated the residual shallow donor concentration in optimized p-GaN:Mg material grown on sapphire (as obtained from SIMS data). For an Mg concentration in the  $10^{19} \text{ cm}^{-3}$  range the residual Si donor concentration can be kept well below  $10^{17} \text{ cm}^{-3}$ . Other important donor-like defects in GaN are introduced by O and H. In optimized p-GaN with [Mg] about  $4 \times 10^{19} \text{ cm}^{-3}$  the total O concentration is well below  $1 \times 10^{17} \text{ cm}^{-3}$  [19], only part of this is shallow donors. The H concentration is in the low  $10^{17} \text{ cm}^{-3}$  range after annealing [19]. H is known to be a deep donor in p-GaN, however it will participate in several other complex defects that are not donors. It is then likely that the H-related donor concentration is also not larger than  $10^{17} \text{ cm}^{-3}$  after proper annealing.



**Figure 3** Comparison of energy levels for donors and Mg-related acceptors in GaN, from electrical and optical data (see text).

In summary both optical and electrical data give evidence of several acceptor states in Mg-doped GaN with hole binding energies in the range 0.2 – 0.6 eV. Both shallow and deep donors in optimized MOVPE Mg-doped p-GaN seem to have a typical concentration of the order  $10^{17} \text{ cm}^{-3}$ . The standard charge neutrality formula commonly used to evaluate Hall data leads to a compensating donor concentration of the order  $10^{19} \text{ cm}^{-3}$ , however. Since the

Fermi level seems to be controlled by the different acceptors, a different approach is needed to evaluate Hall data.

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