Evidence for Two Mg Related Acceptors in GaN

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The optical signatures of Mg-related acceptors in GaN have been revisited in samples specifically grown on bulk GaN templates, to avoid strain broadening of the optical spectra. Bound-exciton spectra can be studied in these samples for Mg concentrations up to $[\mathrm{Mg}] \approx 2 \times 10^{19}$ cm^{-3}. Contrary to previous work it is found that instabilities in the photoluminescence spectra are not due to unstable shallow donors, but to unstable Mg-related acceptors. Our data show that there are two Mg-related acceptors simultaneously present: the regular (stable) substitutional Mg acceptor, and a complex acceptor which is unstable in *p*-GaN.

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In the recent strong development of III-nitride based light emitting devices efficient *p* doping is recognized as a bottleneck for obtaining high radiative output. Mg is so far the only acceptor that has been successfully applied for *p* doping in GaN [1]. Unfortunately Mg is known to cause a rather deep acceptor level (about 200 meV) in GaN, limiting the hole population at room temperature to a few percent of the Mg concentration [2]. While the electrical properties (such as Hall data) of Mg-doped *p*-GaN can be reasonably well understood using a standard model with a single acceptor level with an activation energy varying with doping between 170 and 130 meV [2], the corresponding optical signatures for Mg acceptors are far from understood. Early studies of photoluminescence (PL) of *p*-GaN showed that the characteristic shallow donor-acceptor pair (DAP) or free-to bound (FB) emission peaking at 3.27 eV was unstable against annealing above 500 °C [3], while the Mg acceptor responsible for the electrical hole activation was known to be activated and stable in this temperature range, by release of H from Mg-H complexes [4]. Several subsequent studies of the instability of the 3.27 eV PL concluded that the instability was caused by unstable shallow donors, believed to be related to H or to N vacancies [5–7]. No direct evidence for this idea was presented, however. In this work we present strong evidence that the instability versus annealing instead is connected with the acceptor involved in the 3.27 eV PL, while the shallow donors involved in the low-temperature PL data are shown to be stable, and in fact are the usual Si and O residual donors. As a consequence, it is found that Mg doping introduces two acceptors with similar binding energies in GaN, one of them is unstable in *p*-GaN.

In the previous studies mentioned above the bound-exciton (BE) spectra were not studied, although these generally give the most precise information about the optical properties of dopants [8]. This work includes studies of BEs in Mg-doped GaN, and in order to avoid the large strain induced broadening and energy shifts of BE transitions typically observed in heteroepitaxial samples, we have exclusively employed about 1-μm-thick Mg-doped layers grown by metal-organic chemical vapor deposition (MOCVD) on strain-free thick (200–300 μm) *c*-plane bulk GaN templates. Samples were grown at Meijo University as well as at Bremen University. Mg-doping levels between 10^{17} and 10^{20} cm^{-3} were studied, but BE spectra were observed only up to Mg concentrations $<2 \times 10^{19}$ cm^{-3}. The Mg concentrations were estimated within about a factor 2 from the growth conditions, which were calibrated against SIMS data for specific samples. Thermal annealing at Meijo University was done at 800 °C for 10 min in N_2 atmosphere, at Bremen University RTA annealing was done during 2 min at 800 °C. The samples from the two sources show consistent PL spectra. Stationary PL spectra were measured with above band gap cw UV excitation (laser photon energy of 4.65 eV), at temperatures from 2 to 300 K. PL transient measurements were done using femtosecond pulses from an amplified and frequency tripled Ti:sapphire laser (frequency 250 kHz, and photon energy 4.65 eV), and detected with a UV sensitive Hamamatsu streak camera with a slow sweep unit.

Typical near band gap PL spectra at 2 K of such samples in the [Mg] range 1×10^{17}–2×10^{19} cm^{-3} are shown in Fig. 1(a). Apart from the donor BE (DBE) lines due to residual Si and O donors at about 3.472 eV, a dominant

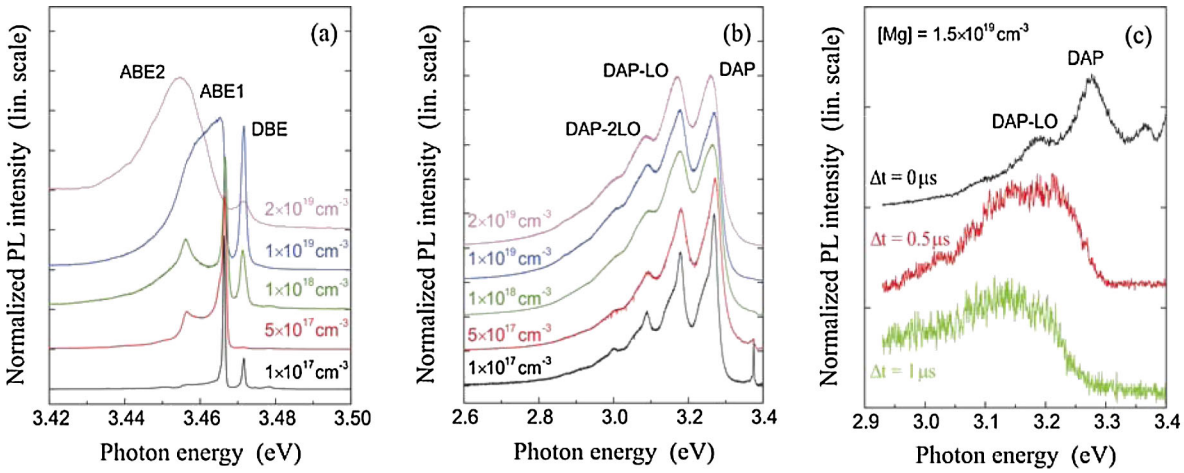

FIG. 1 (color online). Low-temperature (2 K) PL spectra in the bound-exciton (a) and DAP (b) regions of unannealed homoepitaxial GaN:Mg layers with different doping levels (Partial annealing may occur during the cool down of the samples to 300 K). Time-resolved PL spectra are shown in (c) for an annealed sample with $[\mathrm{Mg}] = 1.5 \times 10^{19}$ cm^{-3}. All spectra are normalized and vertically shifted for clarity.

acceptor BE (ABE) line is observed at 3.466 eV, here called ABE1 and related to an acceptor here called A1, which completely dominates the acceptor related PL at low to moderate Mg doping. This ABE1 has been studied previously in some detail [9], and generally regarded as related to Mg [10]. The direct evidence for the ABE assignment is the presence of two no-phonon BE lines, only possible for ABEs [11,12]. Also it exhibits a temperature quenching below 50 K, and a strong LO phonon coupling, typical for ABEs. A second broadened BE peak (ABE2) is observed at about 3.454 eV [13]; it becomes dominant for increasing Mg doping, and is broadened and slightly downshifted in energy at the highest doping [Fig. 1(a)]. It is suggested to be related to a second acceptor A2 dominating at high Mg-doping level. It appears in the energy range for most other ABEs in GaN [8,14], and has the typical temperature quenching below 50 K. In Fig. 1(b) the corresponding PL spectra at 2 K in the range of the DAP transitions are shown. They are dominated by the 3.27 eV DAP peak and its LO replicas for all five samples. We have recently in a separate study concluded the correlation between the ABE1 and the 3.27 eV DAP spectra; i.e., they are most likely related to the same acceptor [15]. This is also consistent with a previous PL study of Mg-implanted bulk GaN layers [14]. A weaker background exists peaking at around 3.15 eV in Fig. 1(b), more clearly resolved in time-resolved PL [see Fig. 1(c)]. This broad peak is tentatively assigned as the DAP transition related to the A2 acceptor.

The spectra for moderately doped samples ($[\mathrm{Mg}] < 1 \times 10^{19}$ cm^{-3}) which are n-type or high-resistive do not show any strong variation upon annealing; i.e., the involved dopants are stable. For samples with Mg concentration above about 1×10^{19} cm^{-3}, however, there is a pronounced difference between the spectra taken before and after annealing. These samples are typically p-type after annealing. Figure 2 shows the near band gap PL spectra at 2 K for a sample with $[\mathrm{Mg}] = 1 \times 10^{19}$ cm^{-3}, both before and after annealing. Even though the spectral broadening is increased at these doping levels, several facts are clear from these results. First, the DBE peak is at about 3.472 eV; i.e., the donors responsible are the usual residual donors in GaN, O, and/or Si [8]. Furthermore, no difference in the DBE spectrum is observed before and after annealing; i.e., there is no sign of unstable shallow donors. The ABE spectra at lower energies show a dramatic sensitivity to the annealing, however. The ABE1 peak at 3.466 eV observed for the unannealed condition is broadened due to acceptor interaction [16], and shows a characteristic high energy cutoff due to a mobility edge related to ABE excitation transfer [17]. The ABE2 peak at about 3.454 eV dominant in the annealed condition is also se-

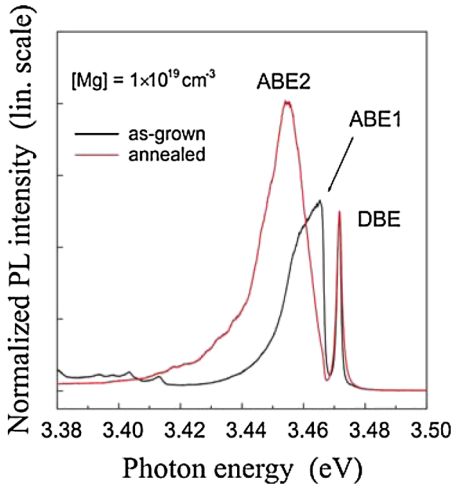

FIG. 2 (color online). Low-temperature PL spectra in the bound-exciton region of as-grown and annealed GaN:Mg layers with Mg-doping concentration of 1×10^{19} cm^{-3}. The PL intensities are normalized to the DBE peak.

verely broadened due to a high acceptor density. The appearance of ABE1 dominantly before anneal and ABE2 only after anneal gives clear indication that the acceptor A1 is unstable against the annealing, and also that A2 shows properties expected for the regular Mg acceptor (i.e., Mg substitutional at Ga site), being activated upon the annealing procedure [4].

The stability of the optical spectra can also be observed via studies of the changes in PL versus UV laser excitation time [18]. In Fig. 3(a) is shown the change in the near band gap PL spectrum for an unannealed sample with [Mg] about 1.5×10^{19} cm^{-3} and continuous excitation up to 1 h. A clear transformation of the BE spectra is observed:

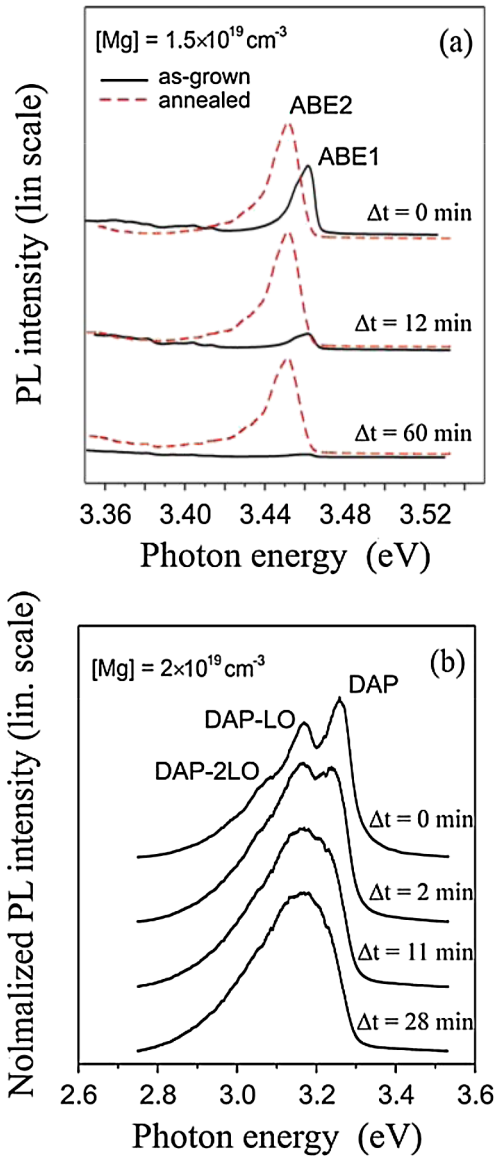

FIG. 3 (color online). (a) Transformation of the near band gap PL spectra at 2 K during UV laser excitation up to 1 h for a sample with [Mg] = 1.5×10^{19} cm^{-3}. (b) Corresponding transformation of the PL in the DAP spectral range for an unannealed sample (that was partly activated during the cooldown from growth). PL intensities in (b) are normalized.

ABE1 decreases continuously with excitation time. This is evidence that the A1 acceptor is unstable against electron injection in *p*-GaN, a property well known for H-related complexes [19,20]. If the sample is warmed up to room temperature and remeasured again at 2 K, the original spectrum is restored; i.e., this is a case of metastability. For the same sample measured after annealing ABE2 becomes dominant, as expected if it is related to the regular Mg acceptor, that becomes activated upon annealing. There is no significant change in the PL intensity with excitation time for the annealed sample. Similar observations are made for the lower energy DAP spectra; see Fig. 3(b). These data are from an unannealed sample with [Mg] about 2×10^{19} cm^{-3}. With continuous laser excitation the 3.27 eV DAP spectrum related to A1 gradually disappears during 30 min excitation [18], while the broad background spectrum at about 3.15 eV, suggested above to be related to A2 remains and dominates (compare with TRPL spectra in Fig. 1(c) for a similar sample). Again, the original spectrum is restored after warming up to room temperature and remeasuring the PL at 2 K. This low-temperature metastability of the A1 acceptor is tentatively explained as a stimulated motion of an H atom into a metastable excited state configuration, from where it can be thermally restored at elevated temperatures [18].

The above PL data for the optical signatures of Mg-related acceptors allow the following conclusions. (i) The dominant shallow donors in Mg-doped *p*-GaN are stable, and are the same common residual donors (O and Si) as in *n*-GaN. (ii) There is clear evidence for two separate acceptors in Mg-doped GaN, here called A1 and A2. (iii) A2 appears to have the properties expected for the substitutional Mg acceptor in terms of annealing behavior, while A1 is unstable vs annealing as well as vs UV (or electron [7]) excitation in *p*-GaN. (iv) The instability occurring only in *p*-GaN is evidence that H is involved in the transformation processes described, since H^+ is expected to be highly mobile in *p*-GaN [21]. (v) The two acceptors have very similar binding energies for the hole, which makes their separation in electrical measurements difficult. (vi) The strong phonon coupling for the 3.15 eV DAP spectrum related to the A2 acceptor is similar to what is observed for other substitutional deeper acceptors on Ga site (see, e.g., Ref. [14]).

It appears that the A1 related optical spectra are always very strong in Mg-doped GaN, which argues for the interpretation that A1 is actually Mg related. A2 appears to have the properties expected for the regular Mg acceptor, but its optical spectra are remarkably weak in comparison to A1 for low [Mg]. The main reason for that could be that the A2 acceptor remains largely passivated in GaN, as long as the Fermi level is not sufficiently low in the bandgap. It is known that the oscillator strength related to the A1 spectra is unusually strong [22] in fact the radiative lifetime of ABE1 is shorter than for the shallow donor BEs in GaN [8]. Nevertheless the complete dominance of the A1 related spectra for low Mg doping is surprising, since it suggests

that an acceptor other than the substitutional Mg is important at these lower concentrations. A1 is likely to be a complex acceptor involving Mg and possibly somehow also H. A1 is unstable vs annealing at $T > 500\,^{\circ}\mathrm{C}$, as typical for an H-related complex, and the metastability at cryogenic temperatures is comfortably explaned in terms of a mobile H atom. Other constituents are possible, and it is premature to suggest an identity at this stage.

The A1 related PL spectra are commonly occurring in nominally undoped GaN, and several acceptors (including Mg) have been suggested as its chemical origin [23]. Clearly one specific optical signature should correspond to only one acceptor; we suggest here the A1 signatures (ABE1 and the 3.27 eV DAP) are due to an Mg-related acceptor, different from the regular A2 Mg_{Ga} acceptor. A similar situation with two Mg-related signatures is emerging in the magnetic resonance (ODMR) data reported in the literature. An effective-mass-like acceptor derived from the topmost valence band (Γ_9) is expected to have a completely anisotropic g tensor for the Zeeman splitting of the bound hole state, i.e., $g_\perp$ (the g component perpendicular to the c axis) is close to zero. The g tensor in ODMR data related to the 3.27 eV DAP is strongly anisotropic, as recently observed in Mg-doped GaN [24]. The regular Mg_{Ga} acceptor has a different rather isotropic g tensor, as derived from ODMR and EPR data for highly Mg-doped GaN [25], more typical for a deep acceptor.

The possible identity of the A1 acceptor in GaN should be studied with the aid of theoretical calculations. The studies on Mg-related complexes in the literature are mainly concentrated on donorlike defects, which compensate the Mg_{Ga} acceptors [26]. The presence of two dominant Mg acceptors was apparently not foreseen in the theoretical studies so far.

In conclusion, we present strong evidence for the presence of two different acceptors related to Mg doping in GaN. Surprisingly, one of these seems to be a complex acceptor, possibly involving H, dominating at lower Mg acceptor concentrations, while at high doping the regular substitutional Mg acceptor seems to dominate in annealed samples.

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