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Optical signatures of dopants in GaN

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Abstract

The characteristic optical spectra for shallow donors and acceptors in GaN are discussed. The most accurate photoluminescence (PL) data are obtained from samples grown on freestanding GaN substrates, where strain shifts are absent and a low spectroscopic line width is obtained. Recent PL data for excitons bound to the O and Si donors are discussed in some detail, giving accurate values for the binding energies and excited bound donor states. The Mg-acceptor is the most important one for p-doping, but the related optical spectra are controversial. We show that there are two acceptors present in Mg-doped GaN, with two different acceptor bound exciton peaks, and also two corresponding lower energy donor–acceptor pair spectra. We give tentative evidence for their interpretation.

Keywords: GaN; HVPE; Exciton; Donor; Acceptor

1. Introduction

The development of the III-nitride semiconductors has been very active during the past two decades, due to the strong interest of these materials for many devices, such as optical emitters covering a broad spectral range from UV to IR [1,2]. The material quality has been severely limited by the lack of native substrates, however, leading to a high dislocation density and problems in controlling doping and point defects. Only recently native GaN substrates are becoming available, so that epi-layers and multi-layer device structures can be grown with a dislocation density in the $10^6\,cm^{-2}$ range, or lower. This development is very helpful for the optical characterization of material properties, and much efforts are currently directed towards a more accurate characterization of GaN, in particular the optical properties of dopants and other defects. The improved material quality allows more reliable data to be obtained from optical spectroscopy, mainly due to a strongly reduced spectroscopic line width.

In this paper we shall review some recent developments on establishing the optical signatures

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for common donors and acceptors in GaN. The most common shallow donors are O and Si, their most easily accessible optical signatures are the near bandgap bound excitons (BEs) observed in low temperature photoluminescence (PL) spectra [3]. Recent optical data on strain free halide vapour phase epitaxy (HVPE) GaN samples have established the energy level structure of these donors in considerable detail. We shall show some recently obtained data on the O and Si donors illustrating this situation. Other shallow donors are less well known. The situation with acceptors is considerably worse than for the shallow donors. The most detailed optical work has been done on the Mg acceptor, the only acceptor so far found to be useful for p-doping. The present confusing picture of the optical signatures of Mg will therefore be discussed in some detail, in connection with new data. Other substitutional acceptors will be only briefly discussed.

2. Samples and experiments

Samples of different origin were studied in this work. For the detailed study of shallow donors a 1 mm thick nominally undoped GaN layer grown by HVPE at Furukawa Ltd., Japan, was used, the total (unintentional) shallow donor concentration in this sample was less than $10^{16}\,cm^{-3}$. For the study of residual acceptors a set of O-doped GaN layers of thickness 1–2 μm were grown on sapphire with low-temperature buffer in a MOCVD system at Meijo University, Nagoya, Japan, as described previously [4]. The doping was carried out by addition of H_2O or CO_2 diluted with H_2 carrier gas and mixed into the ammonia inlet [4]. Ex situ furnace annealing of these high resistivity samples was performed in N_2 for about 10 min at temperatures ranging from 450 to 850 °C. The concentration of O, C and Si impurities was determined by secondary ion mass spectroscopy (SIMS) measurements. The positron annihilation spectroscopy (PAS) was employed to probe Ga-vacancy related defects in the layers, as described in detail previously [5]. Mg-doped samples were also grown with MOCVD on sapphire substrates, and annealed at 800 °C during cool-down from growth to activate the Mg doping. Additionally a set of Mg-doped GaN samples were grown by MOCVD at Bremen University on freestanding bulk GaN substrates produced at Linköping University.

PL spectra were measured with the fourth harmonic ($\lambda = 266$ nm) of a cw Nd:Vanadate laser. The PL signal was dispersed by a 0.55 m monochromator and detected by a UV enhanced liquid nitrogen cooled CCD camera. The samples were placed in a variable temperature cryostat for measurements in the temperature range 2–300 K.

3. Experimental results on shallow donors

The most common residual shallow donors in GaN are Si_{Ga} and O_N. Both can be readily used as dopants for n-GaN, in practice Si is typically used since O produces compensating acceptors as well, via complexes with the Ga vacancy [6]. A proper donor BE (DBE) linewidth (<1 meV) is obtained for doping levels $<10^{16}\,cm^{-3}$ in strain-free material. PL spectra for such a sample (a 1 mm thick undoped HVPE GaN sample) are shown in Fig. 1. The two peaks at about 3.4714 and 3.4723 eV have previously been identified as the neutral donor BE signature of O and Si, respectively [7,8]. The data shown in Fig. 1 is for a sample with nearly equal concentration on O and Si, both below $10^{16}\,cm^{-3}$. A lineshape fitting procedure reveals the presence of additional weaker lines in the vicinity of these strong lines (not shown here), presumably DBE lines associated with other residual donors. We do not speculate on the identity of these other donors.

The sharp DBE lines at around 3.47 eV are riding on a broader background signal, that is not clearly understood at present (Fig. 1). There are also

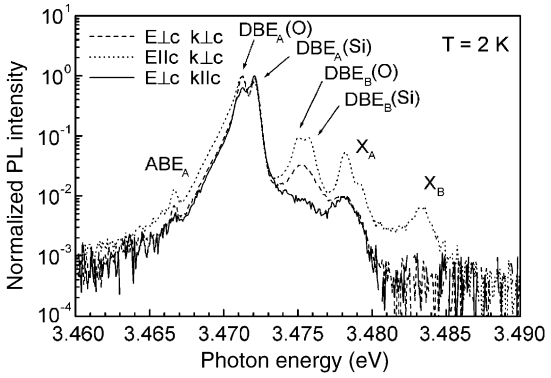

Fig. 1. Near bandgap time-integrated photoluminescence spectra at 2 K for a 1 mm thick nominally undoped GaN sample, for three different polarization geometries: α (E⊥c, k||c), σ (E⊥c, k⊥c), and π (E||c, k⊥c). The Si and O-related DBEs are clearly resolved for both sets of hole states (A for DBE_A peaks and B for DBE_B peaks), the former are strongest for σ-polarization, while the latter are clearly enhanced in the π-polarization.

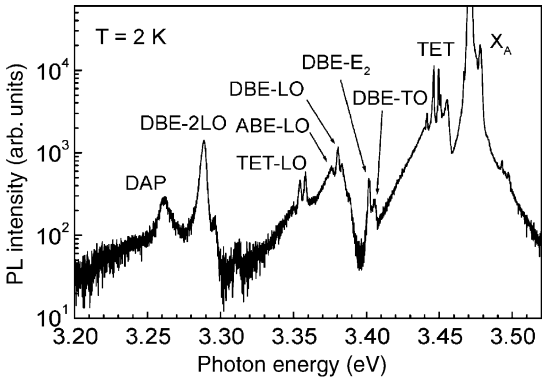

Fig. 2. Photoluminescence spectrum at 2 K fort the same sample as in Fig. 1, over a wider energy range. The spectrum shows the overall TET line shape, and the coupling of the DBEs with different phonon modes.

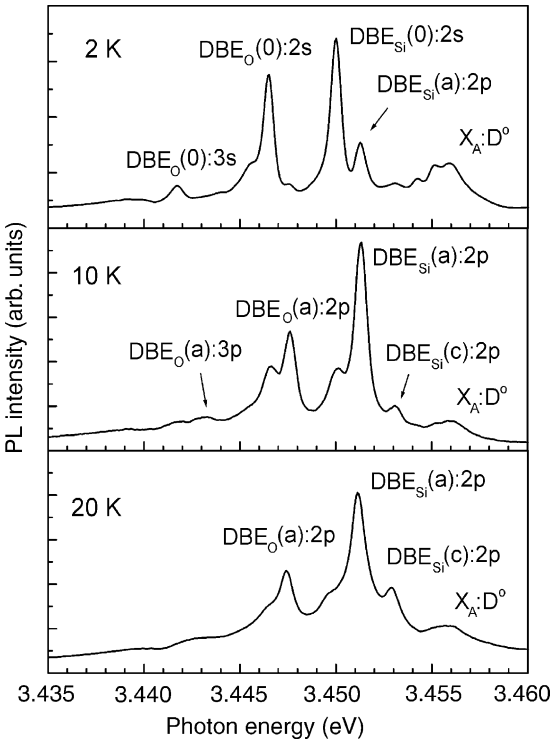

Fig. 3. Photoluminescence spectra for the two-electron transitions of the O and Si DBEs at three different temperatures, 2, 10, and 20 K. Clearly two sets of lines appear, one set for each donor. The principal DBE state connects with the s-like excited donor final states, while the excited DBE configurations (denoted a and c) connect with the p-like excited donor states.

weaker DBE-related lines at somewhat higher energies, related to higher rotational excited states of the DBEs [9], not shown in Fig. 1. A different set of DBE lines are related to the B valence band, at about 3.475 eV (Fig. 1). The two lines at about 3.4745 and 3.4753 eV directly correspond to the strong DBE lines for O and Si at lower energies, but with a weakly bound hole from the B valence band. These two lines are relatively stronger at somewhat elevated temperatures, and has a more dominant π-polarization, as opposed to the lower energy main DBEs which are dominantly σ-polarized (Fig. 1).

At still lower photon energies there are several sharp lines correlating with the two strong DBEs related to the O and Si donors at 3.4714 and 3.4723 eV, the so-called two-electron transitions (TETs) in the range 3.445–3.453 eV (Fig. 2). These transitions are so-called shake-up processes where the DBE recombination leaves the neutral shallow donor bound electron in an excited state after the recombination event [10]. Both s-like and p-like excited donor states are involved, in addition excited DBE states are also active [7]. The s-like excited donor states connect to the principal DBEs, while the p-like excited donor states mainly participate in transitions from the excited DBE rotational states, as seen in Fig. 3 for the energy range of the TET transitions at three different temperatures, 2, 10 and 20 K. Clearly several sets of PL lines occur with different intensity at different temperatures. The identification of these lines in Fig. 3 agrees with the scheme suggested by Freitas et al. [7] from similar data recorded in the temperature range 5–25 K. These results confirm the binding energies of the O and Si donors in the ground and excited states as shown in Table 1.

The higher energy lines in Fig. 3 (above 3.454 eV) were also identified as DBE TET transitions by Freitas et al. [7], but with phonon participation. From a study of these lines in different samples we conclude that this suggestion is not correct. These lines rather correlate with the PL intensity of the free excitons, and are properly identified as shake up transitions involving the recombination of free A excitons scattering at neutral donors, which are left in an excited state after the recombination event. Such a process was previously suggested by Skromme et al. [11]. We will not discuss these lines in detail here.

In the lower energy range in Fig. 2 (3.41–3.44 eV) there is a clear tail in the range 3.41–3.44 eV beyond the lower energy TET transitions involving the $n = 3$ excited donor states. This tail is the signature of TET transitions in the limit that the donor electron in the final state is excited to the conduction band,

Table 1
Binding energies in meV of different donor states obtained from analysis of the TET spectra

Donor	1s	2s	2p
Si	30.2	7.4	7.4
O	33.2	7.8	7.5

The accuracy is better than 0.2 meV.

i.e. a bound exciton Auger transition. In Fig. 2 are also shown the phonon replicas of the DBE transitions, involving mainly the 92 meV LO phonons, but also the TO and E_2 modes. The very strong enhancement of the 2LO replica of the DBEs is remarkable. We will not discuss the details of the phonon coupling for the DBEs here.

4. Acceptors in GaN

The optical signatures for acceptors in GaN are much less clear than for the O and Si donors discussed above. The optical studies have so far been severely limited in quality by the presence of a large concentration of structural defects in heteroepitaxial samples. Neutral acceptor bound excitons (ABEs) are therefore not assigned with any level of confidence for the various acceptors in GaN. Donor–acceptor pair (DAP) emissions have been observed for several acceptor dopants, providing an estimate of binding energies of the acceptors, assuming the participating donors are either O or Si. In Be-doped GaN there is clearly a DAP emission peaking at about 3.38 eV at low T, evidence for a shallow acceptor with binding energy about 100 meV [12]. The identity of this acceptor is unclear, it could be the Be_{Ga} acceptor, but it could also be a complex acceptor involving Be. No p-type GaN has been convincingly demonstrated for Be-doped GaN, presumably due to self-compensation problems [13].

The substitutional acceptors Mg, Zn and Cd all produce broad DAP bands due to a strong phonon coupling with a broad range of phonons in the DAP transition [14]. From these DAP bands the binding energies have been estimated in early work as about 0.23 eV for Mg, 0.34 eV for Zn and 0.55 eV for Cd [12,14]. The corresponding ABE peaks are not established very accurately, partly due to the fact that in early work large strain shifts of the PL emissions always were present. Results for Zn-implanted GaN give an ABE peak at about 3.454 eV (corrected for strain shift), claimed to be Zn-related [15]. Also, for acceptors with a strong phonon coupling in the optical transitions it seems that the ABEs have a small oscillator strength. Only Mg is of interest for p-doping, and Mg doping has been studied in some detail. A strong ABE line at 3.466 eV has been observed in Mg-doped GaN, in most papers it has been related to the Mg acceptor [12]. This line, however, appears strongly also in GaN material which has not been Mg-doped [12], it appears to be related to a very common residual acceptor in GaN. The connection of this ABE to Mg therefore needs to be treated with caution. The 3.466 eV ABE is related to an equally common DAP emission at about 3.27 eV, with clear phonon replicas at lower energies (Fig. 4). There is evidence that these two PL emissions are separate signatures of the same acceptor [4,16].

We have recently published results of deliberate O doping of GaN during MOCVD growth [4]. This leads to a very strong enhancement of the two emissions, i.e. the 3.466 eV ABE and the 3.27 eV DAP [4] (Fig. 4). Our preliminary conclusion from that work was that the corresponding acceptor is O-related, i.e. a V_{Ga}–O complex. The presence of Ga vacancies in the samples in concentrations to 10^{16}–$10^{17}\,cm^{-3}$ was confirmed by PAS [4]. O concentrations in the range $10^{17}\,cm^{-3}$ were confirmed by SIMS data [4]. The fact that the 3.27 eV DAP emission is unstable against annealing above

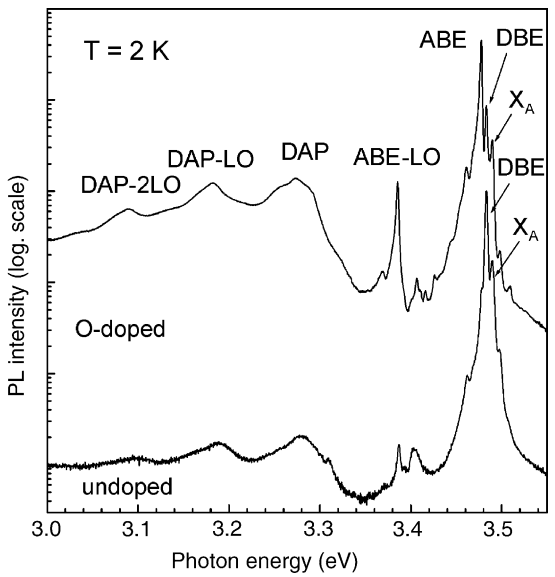

Fig. 4. Photoluminescence spectra at 2 K of a deliberately O-doped sample (top) and a nominally undoped sample (bottom). The ABE at 3.466 eV and the 3.27 eV DAP peak dominate in the O-doped sample, while they are much weaker in the undoped one.

500 °C in p-GaN [17] further indicates that H is part of this complex acceptor. The possibility that the acceptor is a V_{Ga}–O–H single acceptor was put forward to explain these experiments [4]. The main problem with this model is that in p-GaN the concentration of V_{Ga} should be very small from thermal equilibrium considerations [18], yet the 3.27 eV DAP PL is still rather strong in Mg-doped p-GaN. A possible explanation in support of the V_{Ga}–O–H model would be that in samples grown on sapphire Ga vacancies may be created via dislocation motion during growth or cooldown after growth, these vacancies are mobile and can be stabilized by O present in the material. The concentration of V_{Ga} (and related complexes) in p-GaN on sapphire is still uncertain, and has to be thoroughly investigated by future PAS experiments.

In order to study the acceptor signatures in Mg-doped GaN in more detail, homoepitaxial samples were prepared by MOCVD on freestanding bulk GaN templates, to reduce the strain and the dislocation density in the material. We shall here report on PL spectra for three samples, with Mg doping about $1 \times 10^{17}\,cm^{-3}$ (A), $1 \times 10^{18}\,cm^{-3}$ (B), and $5 \times 10^{18}\,cm^{-3}$ (C), respectively. These samples are compensated n-type. The spectra show two dominant transitions at 2 K: (i) the neutral donor DBEs at about 3.471 eV (or two close lines due to O and Si at 3.471 and 3.472 eV, respectively [7]) and (ii) the neutral acceptor BE (ABE1) at about 3.466 eV [19] (Fig. 5). The latter peak is clearly strongly enhanced by the Mg doping in our samples, while it is very weak in the undoped HVPE GaN template (Fig. 5). In addition a second peak is observed at about 3.4555 eV in the Mg-doped samples, not present in the HVPE grown substrate. We suggest that this second ABE (here called ABE2) is also induced by the Mg doping process.

Somewhat surprisingly an 800 °C annealing step does not seem to affect the dominant near bandgap PL spectra too much. The dominant 3.466 eV ABE1 peak seems not to be affected at all by the annealing, while the lower energy 3.4555 eV ABE2 is enhanced in intensity. The most dramatic effect on the near bandgap PL spectrum is observed with a change in excitation intensity. For sample A the intensity of ABE1 is actually saturating with excitation, indicating that the concentration of the corresponding acceptor has to be rather small in that sample. This is not the case in samples B and C, where both the DBE and the ABE1 increase approximately linearly with excitation intensity.

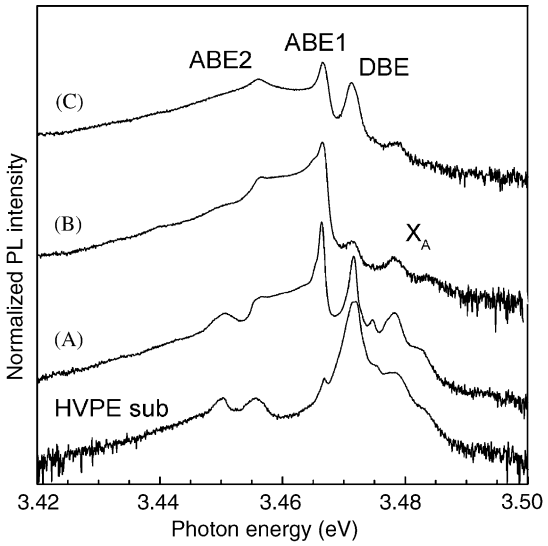

Fig. 5. Near bandgap photoluminescence spectra at 2 K of the freestanding HVPE substrate, and the three Mg-doped samples A–C. The spectra are normalized in intensity and plotted in log scale. The two ABE peaks are clearly observed.

Thus the concentration of the corresponding acceptor is higher in these samples. The ABE2 peak is increasing superlinearly with excitation intensity, and is dominant at the highest excitation for sample C after anneal. It is clearly enhanced with excitation intensity in all three samples, consistent with a high concentration of the corresponding acceptor.

In the lower photon energy region there is a rather strong PL emission at 3.27 eV with characteristic LO phonon replicas at lower energies, the so called "UVL" spectrum [12]. This is a DAP emission [20] involving shallow (O or Si) donors and the same acceptor as responsible for the ABE1 peak discussed above. As seen in Fig. 6 for samples A–C the intensity of this DAP PL strongly increases with the Mg doping, relative to the near bandgap PL. The same DAP PL is present in the HVPE GaN template, but much weaker (Fig. 6). In addition there is a broader background spectrum peaking at about 3.1 eV, most easily observed at low excitation intensity (Fig. 6). This spectrum obviously also increases in intensity with Mg doping, in fact more strongly than the 3.27 eV DAP, and therefore appears to be Mg-related, as also noted previously [21,22]. We assume this broad spectrum is also a DAP transition. The no-phonon line is weak and seems to be at a similar energy as the 3.27 eV DAP peak. In this lower energy range there are thus two different characteristic DAP PL signatures, related

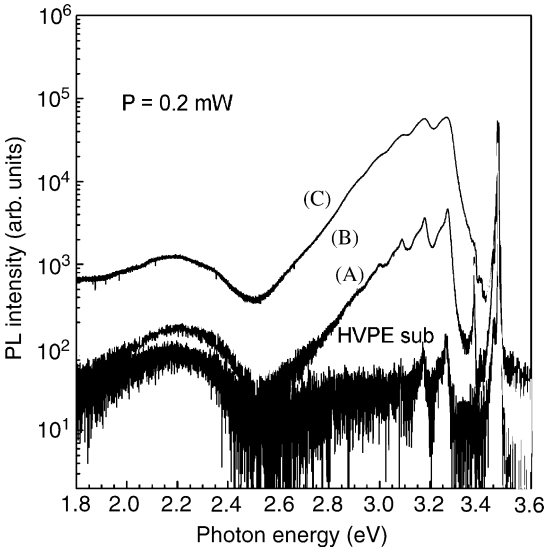

Fig. 6. Photoluminescence spectra at 2 K for the samples A–C, and the freestanding substrate, here shown in a wider photon energy range. The 3.27 eV emission is clearly strong, but is accompanied by a broad background emission peaking at about 3.1 eV, particularly strong for sample C.

to two acceptors, just as observed for the ABE spectra in the near bandgap spectral region.

At lower energies the broad 2.2 eV yellow PL band appears in all Mg-doped samples, it also appears stronger with increasing Mg doping. In the samples B and C there seems to be a shoulder at about 2.4 eV, both spectra presumably related to the deep V_{Ga}–O acceptor [12]. The appearance of these PL bands is evidence for the introduction of V_{Ga}–O acceptors simultaneously with the Mg doping.

The presence of the deeper 3.4555 eV ABE2 peak in Mg-doped GaN seems not to have been given proper attention so far, a similar peak has been observed strongly in Mg-doped GaN previously though [16,23,24]. Similarly the presence of the broad 3.1 eV PL band in Mg-doped GaN has been essentially ignored in recent work, although noticed in the very early papers [21,22].

This work demonstrates that there are two different acceptors in Mg-doped GaN. Our recent work on O-doping in GaN has shown that the ABE1 peak and the 3.27 eV UVL peak are signatures of the same acceptor, in that work it was tentatively suggested to be a V_{Ga}–O–H single acceptor [4]. The O may be introduced into the GaN material via the Mg precursor in the case of Mg-doping, the presence of the ''yellow emission'' PL band in Fig. 6 is evidence for this. The instability of the 3.27 eV PL band in p-GaN at annealing above 500 °C suggests that the corresponding acceptor can hardly be the Mg acceptor, which is known to be stable under these conditions. We suggest that the 3.4555 eV ABE2 peak and the broad 3.1 eV PL band are the signatures of the regular Mg acceptor. They apparently have a much lower oscillator strength than the other acceptor, explaining why the ABE1 peak and the 3.27 eV typically appear so dominant. A low oscillator strength may be the consequence of a strong phonon coupling for the Mg acceptor, analogous to the case of other substitutional acceptors like Zn and Cd on Ga site in GaN [12]. The observed instability of the 3.27 eV PL band in p-GaN strongly suggests that H is involved in that acceptor. The above suggestion of a V_{Ga}–O–H complex as the identity is a possibility, but is problematic in p-GaN, where the Ga vacancy is not expected to form [18]. As already mentioned, introduction of a non-equilibrium V_{Ga} concentration via dislocation motion at high temperatures is clearly possible, that might explain the data for heteroepitaxial samples. An alternative possibility would be a Mg–H complex as the origin of the ABE1 and the 3.27 eV emissions. Further work is in progress to identify the origin of these dominant acceptor signatures in Mg-doped GaN.

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