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Properties of the main Mg-related acceptors in GaN from optical and structural studies

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The luminescent properties of Mg-doped GaN have recently received particular attention, e.g., in the light of new theoretical calculations, where the deep 2.9 eV luminescence band was suggested to be the main optical signature of the substitutional Mg_{Ga} acceptor, thus, having a rather large binding energy and a strong phonon coupling in optical transitions. We present new experimental data on homoepitaxial Mg-doped layers, which together with the previous collection of data give an improved experimental picture of the various luminescence features in Mg-doped GaN. In *n*-type GaN with moderate Mg doping ($<10^{18} \text{ cm}^{-3}$), the 3.466 eV ABE1 acceptor bound exciton and the associated 3.27 eV donor-acceptor pair (DAP) band are the only strong photoluminescence (PL) signals at 2 K, and are identified as related to the substitutional Mg acceptor with a binding energy of $0.225 \pm 0.005 \text{ eV}$, and with a moderate phonon coupling strength. Interaction between basal plane stacking faults (BSFs) and Mg acceptors is suggested to give rise to a second deeper Mg acceptor species, with optical signatures ABE2 at 3.455 eV and a corresponding weak and broad DAP peak at about 3.15 eV. The 2.9 eV PL band has been ascribed to many different processes in the literature. It might be correlated with another deep level having a low concentration, only prominent at high Mg doping in material grown by the Metal Organic Chemical Vapor Deposition technique. The origin of the low temperature metastability of the Mg-related luminescence observed by many authors is here reinterpreted and explained as related to a separate non-radiative metastable deep level defect, i.e., not the Mg_{Ga} acceptor. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862928>]

I. INTRODUCTION

Mg is so far the only acceptor dopant that can be used for *p*-doping in III-nitride based devices, such as light emitting diodes (LEDs) and laser diodes (LDs), for visible and ultraviolet (UV) wavelengths. Although much work has been done in an attempt to clarify the electronic and optical properties of Mg acceptors, there still remain open questions regarding the interpretation of experimental data on the properties of Mg-doped III-nitride materials. This holds true even for GaN, the most developed III-nitride compound in terms of crystal perfection and doping control. In this paper, we shall concentrate on the optical properties of Mg-doped GaN, specifically on luminescence with laser excitation (photoluminescence (PL)) and with electron excitation (cathodoluminescence (CL)). Such optical data give the most detailed information on the energy level structure of acceptors via their characteristic spectra, and also on the related recombination mechanisms of carriers and excitons.

The main PL (or CL) spectra related to acceptors in semiconductors are the acceptor bound exciton (ABE) and donor-acceptor pair (DAP) spectra, as reviewed for GaN in Ref. 1. These PL signatures for Mg-related acceptors were

established only in recent years,^{2–4} with the ABE1 peak at 3.466 eV in unstrained GaN at 2 K and the corresponding DAP peaking at about 3.27 eV. The latter PL emission was studied in detail already four decades ago^{5,6} and established as a DAP emission, but the connection with the Mg acceptor was not definitely known at the time. An unusual feature with Mg acceptors is that there are two ABEs present at high Mg doping, the additional one being a broader ABE2 peak at about 3.455 eV at 2 K.⁴ Another puzzling observation is the instability of the Mg related spectra vs. UV excitation or electron excitation in the low temperature region for *p*-type materials, manifesting itself as the emission intensities going down with excitation time.^{4,7–9} This effect is particularly strong before the Mg-activation anneal of the samples, and has raised questions whether the above-mentioned optical signatures are related to the substitutional Mg_{Ga} acceptor or possibly to an unstable Mg-related complex.⁴

At lower photon energies additional spectra in Mg-doped GaN are noted. A broad peak at about 2.9 eV is commonly observed at high Mg doping concentrations in Metal-Organic Chemical Vapor Deposition (MOCVD) grown samples.^{10,11} This has most often been assigned to the presence of Mg–nitrogen vacancy (Mg-V_{N}) deep donor

complexes in the material.¹⁰ In the deep red spectral region there is a broad band observed at about 1.8 eV, suggested as related to a deep Mg-related complex defect.^{12–14}

In this paper, we will present additional PL and CL data obtained from MOCVD-grown GaN:Mg samples on low defect density bulk GaN substrates. These data allow a more definite identification of the above-mentioned characteristic ABE and DAP spectra for GaN:Mg. Furthermore, the reason for the apparent presence of two acceptor species will be discussed in terms of interaction between Mg acceptors and structural defects induced by the acceptor doping. For comparison, we also include new data from Mg-doped GaN samples grown by Halide Vapor Phase Epitaxy (HVPE).

II. SAMPLES AND EXPERIMENTAL PROCEDURE

The MOCVD samples, used in this work, were grown on thick ($>300\ \mu\text{m}$) bulk GaN templates. Some of these thick GaN substrates were grown with HVPE at Linköping University, and removed from the sapphire substrates with a laser lift-off technique, as reported previously.¹⁵ Other bulk *c*-plane GaN substrates were supplied by Furukawa Co., Ltd., Japan. The *c*-plane Mg doped MOCVD samples were grown at Meijo University as well as at Bremen University, details of the growth procedure can be found in previous papers.⁴ The *m*-plane GaN:Mg samples were grown at Virginia Commonwealth University, on *m*-plane bulk GaN substrates provided by Kyma, Inc.¹⁶ Some HVPE grown thick (about $11\ \mu\text{m}$) GaN:Mg layers on sapphire were provided by Oxford Instruments, the growth conditions are described in Ref. 17.

Thermal annealing at Meijo University and Linköping University was done at 800°C for 10 min in N_2 atmosphere. At Bremen University Rapid Thermal Annealing (RTA) was done during 1 min at 800°C . Stationary PL spectra were measured with above band gap continuous wave UV excitation (laser photon energy of 4.65 eV) at temperatures from 2 K to 300 K, and detected by a UV enhanced liquid nitrogen cooled Charge Couple Device (CCD). 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. Cross-sectional Transmission Electron Microscope (TEM) analysis was done with a high resolution FEI Tecnai G2 200 keV Field Emission Gun (FEG) instrument. CL spectra were measured using a MonoCL4 system integrated with a LEO 1550 Gemini scanning electron microscope (SEM) and equipped with a liquid-He-cooled stage for low-temperature experiments. A fast CCD detection system or a Peltier cooled photo-multiplier tube (PMT) was used for spectral acquisition.

III. EXPERIMENTAL RESULTS

A. Photoluminescence spectra in the near bandgap region

The main features of Mg-related bound exciton (BE) spectra in GaN were discussed in Ref. 4. In Fig. 1(a), we

FIG. 1. Low-temperature near-bandgap spectra of nominally undoped (a) and Mg-doped ($[\text{Mg}] = 3 \times 10^{18}\text{ cm}^{-3}$) (b) homoepitaxial layers grown by MOCVD on *m*-plane bulk GaN substrates.

show new PL data that illustrate the difference in PL spectra at 2 K for nominally undoped GaN and highly Mg-doped GaN, in this case for *m*-plane samples. Separate Secondary Ion Mass Spectroscopy (SIMS) data on other samples indicate that for a nominally undoped GaN layer grown on a bulk GaN substrate the residual Mg concentration can be at most about $1 \times 10^{17}\text{ cm}^{-3}$ at the interface between the layer and the substrate, and decreases to low 10^{16} cm^{-3} upon further growth. This Mg contamination can be ascribed to the well-known Mg memory effect in MOCVD growth,¹⁸ and varies from sample to sample. The PL of the nominally undoped sample in Fig. 1(a) does indeed show the two silicon and oxygen related donor BEs (DBEs) at 3.472 eV and 3.471 eV, respectively, but also clearly the Mg-related ABE1 peak at 3.466 eV (in fact, consisting of two separate peaks, as may be expected for ABEs in GaN (Ref. 19)). We note that in this spectrum there is no trace of the second ABE2 peak previously reported for more highly doped GaN:Mg.⁴ Likewise, there is no trace of other sharp line spectra related to Mg doping, previously reported in the region 3.35 eV to 3.42 eV.²⁰ In *n*-type samples with low Mg-doping, the metastable properties of the Mg-related luminescence are also absent. Another sample with a controlled Mg doping of $[\text{Mg}] = 1 \times 10^{17}\text{ cm}^{-3}$ shows very similar spectra as in Fig. 1(a).

In the *m*-plane sample doped with Mg to a concentration of $3 \times 10^{18}\text{ cm}^{-3}$ there is a broad ABE2 peak (Fig. 1(b)), in agreement with earlier data on *c*-plane samples.⁴ This ABE2

FIG. 2. PL spectra of *c*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 1 \times 10^{19} \text{ cm}^{-3}$) measured at different temperatures after annealing.

peak has a very similar polarization behavior as the ABE1 peak (dominantly $E \perp c$), indicating that both are somehow related to a substitutional Mg_{Ga} acceptor. Moreover, there is also a series of rather strong peaks in the region 3.35–3.42 eV, in addition to the broadened phonon replicas related to free and bound excitons present in the same energy range. The origin of these lines is different basal plane stacking faults (BSFs), as discussed in Ref. 21.

Shown in Fig. 2 is the temperature dependence of PL for a *c*-plane MOCVD sample, with a Mg concentration of approximately $1 \times 10^{19} \text{ cm}^{-3}$. The sample is annealed, which in this case enhances the relative intensity of the ABE2 peak.⁴ The spectral PL development with temperature is very much the same for the two peaks ABE1 and ABE2, and they both disappear at about 50 K, leaving behind only the DBE peak in the near bandgap region. Note that the narrower ABE1 peak is observed at the high energy flank of the broad ABE2 peak. These temperature dependent data are a support of the ABE nature of the broad ABE2 peak, which due to the spectral broadening cannot be established with standard spectroscopic means (e.g., via resolving the electronic substructure of the no-phonon line¹⁹). We note that the DBE PL features in GaN are stable up to much higher temperatures, e.g., 150 K in samples with low doping.²²

In order to obtain a complete experimental picture, the spectra from an 11- μm -thick HVPE grown GaN:Mg layer on sapphire was studied as well, as shown in Fig. 3. The Mg concentration was not exactly known in this sample, but the hole concentration was measured as $2 \times 10^{18} \text{ cm}^{-3}$ at room temperature, which is consistent with an Mg concentration of about $2 \times 10^{19} \text{ cm}^{-3}$.¹⁷ The spectra clearly show the two Mg related ABEs with a similar appearance as in the MOCVD Mg-doped sample in Fig. 1(b). Previous work in literature also shows the presence of both the ABE1 and the ABE2 peak in Molecular Beam Epitaxy (MBE) grown GaN:Mg at high doping concentrations, although the identity

FIG. 3. Near-bandgap PL spectra of as-grown HVPE GaN:Mg layer ($[Mg] = 2 \times 10^{19} \text{ cm}^{-3}$) at different temperatures.

of the peaks was incorrectly labeled.²³ Therefore, the presence of two Mg-related acceptor bound exciton near bandgap PL signatures in GaN appears to be universal.

B. The DAP spectrum at 3.27 eV

A common feature in all acceptor related luminescence spectra in semiconductors is that the ABE spectra in the near bandgap region are accompanied by DAP spectra at lower energies, i.e., there is one DAP emission and one ABE peak for each particular acceptor species. For low Mg doping levels, the relation between the ABE1 peak at 3.466 eV and the 3.27 eV DAP peak (with accompanying LO phonon replicas at lower energies) has been established in the literature.²³ For Mg doping at concentrations $[Mg] < 10^{18} \text{ cm}^{-3}$ these are the only acceptor related PL features in this energy range, and therefore have to be assigned to the substitutional Mg acceptor.

For higher Mg concentrations, the connection between the ABE2 peak and a weak broad background under the low energy part of the 3.27 eV peak has also been suggested.⁴ In order to shed more light on this, we have carried out new time resolved PL measurements in the DAP region for an Mg-doped sample with $[Mg] = 2 \times 10^{19} \text{ cm}^{-3}$, see Fig. 4. From these data, it is obvious that at longer delay times (several μs) a broad spectrum peaking at about 3.15 eV is dominant, which is then suggested to correspond to a broad DAP emission related to the A2 acceptor with a larger binding energy, consistent with the larger ABE2 binding energy (compared to ABE1) observed in the near bandgap spectra. A longer decay time for deeper DAP emissions is a general observation in semiconductors.¹ A discussion on the suggested interpretation of the corresponding deeper acceptors in terms of Mg_{Ga} acceptors interacting with structural defects is presented below.

C. Deeper Mg-related spectra

At higher Mg doping levels, in the range of 10^{20} cm^{-3} for MOCVD samples, a strong broad PL band at about 2.9 eV is

FIG. 4. Time-resolved PL spectra of *m*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 2 \times 10^{19} \text{ cm}^{-3}$) obtained with a time delay of $1 \mu\text{s}$ between each curve. (The repetition rate of the femtosecond laser excitation was 250 kHz.)

noted and sometimes dominates the PL spectra.^{10–14} We show such spectra in Fig. 5 for MOCVD grown samples, measured under different excitation conditions. In the sample with moderately high doping ($1.5 \times 10^{19} \text{ cm}^{-3}$) clearly both the 3.27 eV and the 2.9 eV emission band are seen separately, while in the highly doped sample ($1 \times 10^{20} \text{ cm}^{-3}$) only the 2.9 eV emission is present. This shows that these are two separate emissions, and that they are only moderately affected by potential fluctuations in the material.^{12,24} The connection to Mg- V_N complexes often suggested for the 2.9 eV emission (see, e.g., Ref. 10) also seems less probable, since such complexes are expected to have a low concentration after annealing.^{25–27} The deep 2.9 eV emission seems to be strong only for highly doped MOCVD grown GaN:Mg, and not observable (or at least very weak) for the corresponding doping in MBE (Refs. 23 and 28) or HVPE grown materials (see, Fig. 6). This situation presumably reflects the very different growth conditions in these three growth techniques.

IV. DISCUSSION

A. Tentative model for the second deeper Mg related acceptor responsible for ABE2

Acceptor bound excitons at high doping level have previously been studied for other compound semiconductors like InP and ZnTe.^{29,30} In these cases, a substantial broadening of the ABE peak (corresponding to ABE1 in our case) is observed; it broadens out towards lower energy and there is also some downshift in the mean peak position. The broadening on the low energy side is explained as an effect of the dispersion of the distances in the lattice for interacting acceptor pairs binding the excitons at high doping.^{29,30} Our observations for the Mg acceptors in GaN with two distinct

FIG. 5. Low-temperature spectra of *c*-plane MOCVD homoepitaxial GaN:Mg layers measured at different excitation powers: (a) $[Mg] = 1.5 \times 10^{19} \text{ cm}^{-3}$ and (b) $[Mg] = 1 \times 10^{20} \text{ cm}^{-3}$.

FIG. 6. Low-temperature bound-exciton and DAP spectra of as-grown and annealed HVPE GaN:Mg layer ($[Mg] = 2 \times 10^{19} \text{ cm}^{-3}$). (The modulation of the spectra is due to the interference effect.)

ABE peaks (ABE1 and ABE2) over the entire doping range, i.e., say $1 \times 10^{18} \text{ cm}^{-3}$ to $2 \times 10^{19} \text{ cm}^{-3}$, are clearly different from the above traditional description of ABEs at interacting acceptors in the III-V and II-VI compounds. There is no appreciable shift of the main ABE1 acceptor peak with increased Mg doping, and the second ABE2 peak is well separated from ABE1 over this range of concentrations. So we conclude that the two ABE peaks correspond to two different acceptor species caused by the Mg doping. At an Mg concentration above about $2 \times 10^{19} \text{ cm}^{-3}$, the ABEs interact strongly so that a Mott-like transition occurs and excitons (ABEs) are no longer bound to the acceptors, thus the near bandgap ABE spectra disappear.

The unusual situation that two different acceptor levels are created by one acceptor dopant in the case of Mg-doped GaN has prompted new structural investigations of GaN:Mg.^{31,32} The observation that the second acceptor responsible for the ABE2 signature is only observed in highly doped GaN:Mg suggests the possibility of a correlation with structural defects, that have also been observed in the GaN:Mg samples studied here.³² These structural defects appear only significantly for $[\text{Mg}] > 10^{18} \text{ cm}^{-3}$, and are dominantly BSFs in the case of homoepitaxial material.^{31,32} Some of these SF defects are very small in the *c*-plane samples (a couple of nm in size), and those could also be pyramid features, as reported for GaN:Mg grown on sapphire.³³ These defects are presumably induced during growth by the introduction of Mg atoms in the lattice.³²

The observed properties of the A2 acceptor discussed here may be understood in a similar way as for the BSF-related PL in *n*-type GaN.³⁴ In that case, it was argued that the localization of electrons (and subsequently excitons) to BSFs in *n*-GaN is mainly induced by donor potentials in the vicinity of the BSF.³⁴ In the case of acceptor doping the acceptor potential is much more localized, within $< 1 \text{ nm}$, meaning that the acceptor hole may not easily delocalize to the BSF plane, but will distort the local potential at the BSF, thus assisting the BSF hole (and exciton) localization, so that the BSF luminescence is observed.³² The acceptor will, in turn, be perturbed by the nearby BSF potential mainly governed by the spontaneous polarization field,²¹ positioned on the average a few nm away in *p*-GaN with an Mg doping of 10^{19} cm^{-3} . This perturbed potential should be sufficiently different from an unperturbed Mg acceptor to give rise to the A2 acceptor and its characteristic ABE2 spectrum.

We note that there is independent evidence for the stimulation of BSF luminescence by acceptor doping, as recently observed in a series of *n*-type *m*-plane homoepitaxial GaN samples.³⁵ Also in our *m*-plane Mg-doped samples there are strong BSF-related spectra in the range 3.3–3.42 eV, apparently stimulated by the Mg doping (Fig. 7). These BSF PL spectra are different from the ABE2 peak, again emphasizing that the A2 acceptor is likely to be associated to a specific site of the Mg acceptor in relation to the BSF plane, i.e., not randomly distributed acceptors. The microscopic geometry of the A2 acceptor center remains to be revealed by future studies.

The PL spectrum of the unperturbed A1 acceptor has the appearance expected for an isolated Mg acceptor.¹⁹ The complex defect aggregate (Mg acceptor plus BSF), on the other

FIG. 7. Low temperature CL spectra of *m*-plane MOCVD homoepitaxial GaN:Mg ($[\text{Mg}] = 1 \times 10^{19} \text{ cm}^{-3}$).

hand, is suggested to explain the additional binding energy (ABE2 is deeper than ABE1), and the broad lineshape of ABE2 (see, Figs. 1(b), 2, and 3). The peculiar lineshape observed for ABE2 may originate from a strong transfer process for excitons between different sites (from shallower BEs to deeper ones). Such excitonic transfer has been observed previously in other III-V and II-VI semiconductors and explained in terms of acoustic phonon assisted exciton tunneling.^{36,37} Transient PL spectroscopy on a highly doped GaN:Mg sample clearly demonstrates decay processes dominated by such transfer, see Fig. 8. The range of acoustic phonons in GaN has been determined to cover phonon energies up to above 30 meV (Ref. 38) therefore the ABE2 peak at 3.455 eV is well within the range of a transfer process involving the ABE1 at 3.466 eV as the main original state. The intensity profile of ABE2 has a high energy portion, which is, continuously rising from ABE1 all the way down to the ABE2 peak. The position of ABE2 is rather well defined in all samples, and the acceptor binding energy (as well as the ABE2 binding energy) should be determined by the specific configuration of the defect center, i.e., the Mg acceptor–BSF combination.

The PL decay traces in Fig. 8(a) clearly show the fast initial decay of the shallower DBE and ABE1 signal, much faster than the radiative decay times observed in samples with lower doping.³⁹ In Fig. 8(b), a time resolved development of the ABE1–ABE2 pair of peaks is shown. These data show directly the spectral shift of the PL signal from the ABE1 position to ABE2, mostly during the first 100 ps. This is naturally explained as exciton transfer, as discussed above.

The broad ABE2 PL peak has a very specific dependence on excitation intensity, i.e., at low excitation levels the peak is just barely seen, while it increases superlinearly at high excitation levels (Fig. 9). This is again consistent with the exciton transfer processes. At low excitation levels there are few neutral acceptors and ABEs, and therefore the distance of an ABE site to another neutral acceptor is long. This means a low probability for transfer because the overlap matrix element is very small. With increasing excitation the

FIG. 8. (a) PL decay curves taken at different photon energies for *c*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 1.5 \times 10^{19} \text{ cm}^{-3}$) and (b) time-resolved PL spectra of the same sample.

occupation probability of both neutral acceptors and neutral ABEs (ABE1) increases, and as a result the distance between ABE1 sites and neutral A2 acceptors becomes favorable for transfer.

B. The 3.27 eV DAP emission and blue PL band at 2.9 eV

While the relation of the 3.27 eV PL spectrum to the Mg_{Ga} acceptor seems to be well established experimentally, the identity of the blue PL band peaking at about 2.9 eV is confusing within the confines of the available data and their interpretation in the literature. As stated above, the early investigations focused on a DAP recombination model with a deep V_N -Mg donor complex together with a substitutional Mg acceptor.¹⁰ This DAP model is only consistent with a high concentration of these donor complexes ($>10^{19} \text{ cm}^{-3}$), while the investigations that followed estimated the actual concentration of these donors to be as low as 10^{17} cm^{-3} before annealing and much lower after anneal.^{25,26} Further, the Optically Detected Magnetic Resonance (ODMR) investigations of GaN:Mg failed to show any evidence for deep donors.⁴⁰ Recently, another interpretation of this blue PL as

FIG. 9. Excitation intensity dependent PL spectra of *m*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 1 \times 10^{18} \text{ cm}^{-3}$).

a DAP involving shallow donors and the substitutional Mg_{Ga} acceptor was presented, based on theoretical calculations indicating that the Mg acceptor should be deeper than previously believed and have a strong phonon coupling.⁴¹ This interpretation also means that the 3.27 eV DAP is not related to the Mg_{Ga} acceptor, but to an Mg-H complex. The blue PL is only strong in MOCVD grown GaN at high Mg doping, however, while the same material grown with MBE or HVPE does not show the blue PL peak, in spite of the fact that a similar number of Mg_{Ga} acceptors should be present. There are many early papers demonstrating the DAP nature of the 3.27 eV PL.^{5,6} A most relevant recent paper on low Mg doped MBE samples demonstrate clearly both the DAP and the free-to-bound (FB) transition, at different temperatures, confirming the binding energy of the Mg acceptor as $225 \pm 5 \text{ meV}$.⁴² An argument against the interpretation of the 3.27 eV emission as being related to a neutral Mg-H complex is that this complex (from theoretical results⁴¹) is only expected to be found in *p*-type samples with a high Mg doping, while in reality the 3.27 eV PL is also prominent in *n*-type GaN. It is, in fact, the only Mg-related PL emission in *n*-type GaN, and dominates the PL spectrum in all Mg-doped samples, except in very highly doped MOCVD samples where the 2.9 eV band is strong. This behavior is expected if the 3.27 eV DAP involves the Mg_{Ga} acceptor.

Returning to the deeper 2.9 eV band there is some evidence from ODMR data for a DAP recombination, since a shallow donor signal is observed for detection in this peak.^{43,44} Thermal quenching of the emission is observed near room temperature with an activation energy of 0.3–0.4 eV.⁴⁵ This would be consistent with an acceptor level of similar binding energy, deeper than for the Mg_{Ga} acceptor. The oscillator strength for the deeper 2.9 eV transition is naturally weaker than that for the 3.27 eV PL line, explaining the frequently observed spectral upshift in this spectral range upon increasing excitation density.

The annealing studies in H plasma reported in Ref. 11 are interesting. It is shown that the 2.9 eV PL seems to be H-related, and the corresponding defect does not noticeably affect the hole concentration. The authors explain their data regarding a DAP process with an H-related deep donor (binding energy 0.37 eV) and the shallow Mg acceptor, similar to other work.⁴⁵ An alternative model would be a H-related

complex that gives rise to the 2.9 eV PL line, but has a concentration much lower than the [Mg] atomic concentration, and thus does not affect the hole concentration in *p*-GaN.

C. Instabilities of acceptor related luminescence spectra

An important property that needs an explanation is the instability of the PL or CL spectra (ABE as well as 3.27 eV DAP spectra) during prolonged excitation with above bandgap UV light or energetic electrons.^{4,7-9} This is particularly important for MOCVD material which usually contains an appreciable concentration of H. In our previous work, it was suggested that this property could be interpreted as evidence for instability of the acceptor responsible for the ABE1 and the 3.27 eV spectral features.⁴ Since our later optical investigations discussed in this paper are only consistent with a model where the ABE1 and the 3.27 eV PL features are related to the substitutional Mg acceptor, we have tested alternative models to explain these instabilities. In Fig. 10, we show time sequential PL spectra of an *m*-plane Mg doped sample, obtained at time intervals of 10 s during continuous UV excitation. It is obvious that in this case, the dominant feature of this short term instability is a rapid degradation of the PL efficiency in the entire near bandgap region, evidence for a rapid nonradiative process induced by the UV excitation. Such a process is most naturally explained by the presence of a defect possessing instable properties, acting as a non-radiative shunt path for the near bandgap luminescence.

The involvement of another defect (i.e., not primarily the Mg acceptor) in the instability process is further indicated by time-resolved PL data of the DAP emission at 3.27 eV (see, Fig. 11). This figure shows that upon long term excitation there is a clear downshift in energy of the 3.27 eV DAP peak, evidence for a decrease of the hole occupation of the Mg acceptor.^{46,47} This decrease means that the quasi Fermi level is raised in the bandgap during the long term excitation in this experiment, which is understood if another deeper (nonradiative) defect level is active in the recombination process, capturing photoexcited holes to a metastable state, which decreases the hole occupation in the Mg acceptor. This nonradiative defect is then directly

FIG. 10. Low-temperature spectra of *m*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 3 \times 10^{18} \text{ cm}^{-3}$) obtained at time intervals of 10 s during continuous UV excitation.

FIG. 11. Low-temperature spectra of *c*-plane MOCVD homoepitaxial GaN:Mg ($[Mg] = 1.5 \times 10^{19} \text{ cm}^{-3}$) measured upon long term continuous UV excitation showing a clear red shift of the DAP emission.

responsible for the long term instability properties. To reveal specific properties of the defect responsible for the long term instability, more experiments to obtain Deep Level Transient Spectroscopy (DLTS) data are needed.

As mentioned above, this idea with an independent deep level defect responsible for the instability allows the interpretation of the strongest features in PL and CL data of Mg-doped GaN, the ABE1 peak and the 3.27 eV DAP, as connected to the regular substitutional Mg acceptor, a simpler model than the one discussed in Ref. 4. Unfortunately, electrical measurements to reveal properties of the metastable defect are very difficult in the low temperature range involved here, and very limited such data for Mg-doped *p*-GaN are found in the literature.⁴⁸ Metastable defects are also reported for *n*-GaN, suggested to be V_{Ga} -related.^{49,50} Such defects related to V_{Ga} would be unlikely in *p*-GaN (Ref. 51) therefore, more work is needed to explore the identity of the metastable defect in Mg-doped GaN.

V. CONCLUSIONS

We discuss new and previous optical data for the Mg acceptor in GaN, in an attempt to arrive at the simplest possible model that can explain all the data in aggregate. Intriguing properties discussed in previous work were the existence of two different acceptor signatures in low temperature PL spectra for bound excitons (ABE1 at 3.466 eV and ABE2 at 3.455 eV), and the corresponding DAP1 at 3.27 eV and the weaker DAP2 at about 3.15 eV. Since at low Mg doping (*n*-type samples) only ABE1 and DAP1 are observed, the above-mentioned spectra should be related to the substitutional Mg acceptors, i.e., no Mg-H related complexes as previously suggested in relation to the observed instabilities⁴ are needed to explain these optical data. The second deeper set of broadened spectra ABE2 and DAP2 appear at higher doping ($[Mg] > 10^{18} \text{ cm}^{-3}$), simultaneously, as structural defects (basal plane stacking faults) are introduced.³² The

acceptors involved in the ABE2 and DAP2 peaks are therefore assigned to substitutional Mg acceptors perturbed by the induced structural defects (BSFs). This correlation was made possible in this work via the use of homoepitaxy on bulk GaN substrates, thus avoiding the more complex spectral behavior in samples grown on sapphire.⁵² The unusual unstable behavior in the optical spectra at low temperatures for high Mg doping may then be explained by the presence of another nonradiative recombination path via a deeper defect level which is metastable in this low temperature range (<300 K), and affects the PL of the Mg-related spectra via the quasi-Fermi level under optical excitation. Since the deeper radiative PL emission at 2.9 eV only occurs at high doping levels in MOCVD samples (and is not regularly observed in similarly Mg-doped MBE and HVPE samples), it is implausible that this emission is related to the substitutional Mg acceptor, as recently suggested in theoretical work.^{41,53} It may relate to a deeper acceptor of low concentration, introduced primarily in MOCVD growth.

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