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Bound excitons in GaN

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Abstract
The electronic structure of bound excitons in GaN is discussed, with reference to available optical data. Emphasis is given to the neutral-donor and neutral-acceptor spectra, which are the most prominent ones in the experimental photoluminescence data. Two dominant donor bound excitons are observed with photoluminescence lines just above 3.47 eV at 2 K in unstrained samples, tentatively associated with Si and O shallow donors. Several acceptor bound excitons are present; the most prominent one with a photoluminescence line at about 3.466 eV is tentatively assigned to the Mg acceptor. We attempt an explanation of the available data from magneto-optical experiments on this line in terms of a spin-like acceptor hole, as observed in independent magnetic resonance data. Characteristic deep emissions related to P and As doping are reported; they may be interpreted in terms of isoelectronic bound excitons. Excitons bound to structural defects in GaN are also briefly discussed.

1. Introduction

Bound excitons are multi-particle electronic excitations of defects in semiconductors, which are very useful for studying the detailed electronic structure of shallow and deep impurities, as well as other defects. Bound-exciton photoluminescence spectra are also convenient signatures for these defects, by which they can easily be recognized in a particular sample. The concept of bound excitons in semiconductors was first discussed more than four decades ago [1, 2], and the topic has already been studied intensively, during the 1960s [3]. Thousands of papers covering bound excitons for different defects in a large number of semiconductor materials in great detail have since been published, and several reviews on the topic have appeared [4–6].

The current strong interest in III nitride semiconductors has prompted new investigations of defect properties in these materials; in fact the understanding of defects is a major area in this field, very important for the improvement of these materials needed for the desired performance of devices. Although a substantial amount of work has been done concerning specific defect studies on these materials during the last decade, as discussed in recent reviews [7–11], detailed information about the electronic structure of defects, in particular the bound-exciton properties, are still scarce. The reason is that material of sufficiently low (or sufficiently

controlled) defect density has so far not been commonly available. Below, we shall attempt to discuss the present understanding of bound excitons (BEs) in GaN, being the most developed material in the III nitride group. We shall concentrate on BEs related to shallow dopants, but also mention a few cases involving other classes of defects, such as isoelectronic defects and extended structural defects.

2. Expected electronic structure of bound excitons in GaN

The electronic states of the bound excitons depend strongly on the semiconductor material, in particular the band structure. For dopants we distinguish the cases of donors and acceptors; their BE structures are different. The cases of isoelectronic defects, other deep-level defects and dislocation defects are in turn again different. We therefore need to discuss all these cases separately to cover the variety of expected electronic states.

In figure 1 we show schematically the electronic configuration of BEs in GaN, for three different cases: neutral donors, neutral acceptors and neutral 'isoelectronic' defects. (Excitons bound to charged defects are also possible, but rarely observed to be prominent in semiconductors.) The BE states are observed in optical transitions, mainly photoluminescence (PL). Such transitions occur between the excited state, i.e. the donor BE (DBE) state, and the neutral-donor ground state for the case of donors (figure 1). Both these electronic states need to be discussed in connection with the experimental optical spectra for the BEs.

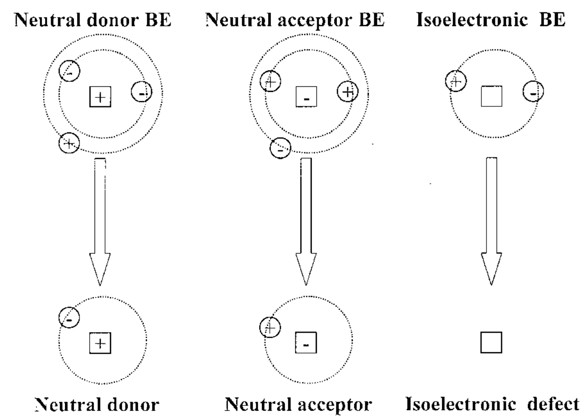


Figure 1. A sketch of the electronic structure of bound excitons. The bound exciton states as well as the corresponding defect ground states are shown, for neutral donors, neutral acceptors and neutral 'isoelectronic' defects.

Another important background item for the modelling of BEs is the band structure of the material. Figure 2 shows the basic properties of conduction and valence bands of GaN close to the respective band edges, which are relevant for the discussion of electronic states for most defects. The conduction band structure of GaN is simple (figure 2), and can be approximated with a single spherical band with an effective mass $m_n = 0.22\ m_0$. The shallow donors therefore also have a simple structure, with a single 1S ground state, and hydrogenic excited states nS, nP etc, which are expected to show moderate energy shifts compared to the ideal effective-mass donor, due to the small anisotropy of the conduction band.

The valence band top of GaN shows three non-degenerate bands within 30 meV, due to the small values of the crystal-field-splitting parameters and the spin–orbit splitting. This will have a fundamental influence on bound hole states, acceptor states as well as acceptor BE (ABE)

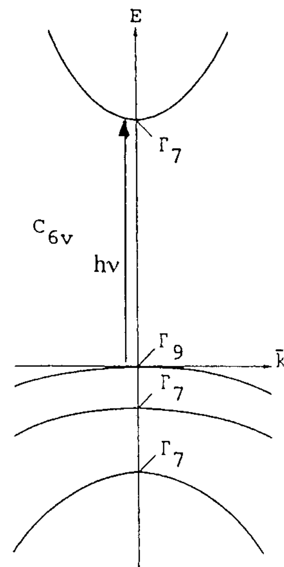


Figure 2. A sketch of the band structure of GaN, showing the simple single lowest conduction band, and the three highest bands, Γ_9, Γ_7 and the spin–orbit split-off Γ_7, respectively, at the valence band top.

states. In the cubic semiconductors, where the valence band top is degenerate, there is a single 1S ground state for the bound hole at neutral single acceptors. This is not true for wurtzite materials like GaN, with a non-degenerate valence band top. Neutral shallow acceptors may show more than one 1S bound hole state (with different binding energy), one for each branch of the valence band top.

The energy position of the BE is traditionally defined as related to the free-exciton energy, with a BE binding energy defined as the energy difference between the FE ground-state energy and the BE ground-state energy. Reliable predictions of such binding energies are very difficult, since bound many-particle complexes are hard to describe with sufficient accuracy in terms of wavefunctions and potentials. Empirically it has been found that the BE binding energy has a simple linear relation to the respective binding energy for the single particle at shallow donors and acceptors; this so-called Haynes' rule is valid in particular for the indirect-bandgap materials Si and GaP [4]. There is no real theoretical justification for this experimental rule in the literature. Indeed for several direct-bandgap materials the rule is not found to be valid [4]. Consequently we do not expect this rule to necessarily apply for shallow dopant BEs in GaN.

A basic assumption in the description of the bound exciton states for neutral donors and acceptors is a dominant coupling of the like particles in the BE states, as indicated in figure 1. For a shallow neutral donor the two electrons in the BE state are assumed to pair off into a two-electron state with zero spin. The additional bound hole is then assumed to be weakly bound in the net hole-attractive Coulomb potential set up by this bound two-electron aggregate (figure 1). The main set of excited states would in this picture be the higher shallow bound hole states. Since for shallow dopants all three particles are shallow, with a substantial wavefunction overlap, other interactions do exist which may lead to additional excited configurations, as observed in most direct-bandgap semiconductors [12, 13].

The magnetic behaviour of the DBEs is in this simple model expected to be dominated by the magnetic moment of the bound hole in the BE state, which for a shallow DBE should

be effective-mass-like and related to the properties of free holes at the valence band top. The magnetic properties of the principal DBE state should reflect the corresponding properties of the Γ_9 top valence band, with an anisotropic g-tensor typical of a Γ_9 $J = 3/2$ hole [14].

Due to the proximity of the split bands at the valence band top, additional BE ground states related to the Γ_7 valence bands should also be observable below the bandgap. Such DBEs then exhibit separate complete sets of electronic states at higher energies, with a binding energy related to the respective higher free exciton states. Excited DBE states are also expected to occur at higher energies, just below the $n = 2$ FE states.

Neutral shallow ABEs are expected to have a two-hole state derived from two Γ_9 holes from the topmost valence band. Only one such state with $J = 0$ is allowed by the Pauli principle (in contrast to the case of zinc-blende semiconductors, where $J = 2$ is possible as well). For deeper acceptors with a spin-like hole, a similar $J = 0$ two-hole state is expected. The additional electron in the ABE state then contributes its unpaired spin, so the ABE state has $J = 1/2$. The ABE state is then expected to have a nearly isotropic g-tensor, ideally reflecting the shallow-donor g-value for GaN, $g = 1.95$ [15].

A single $J = 1/2$ ABE ground state is consequently expected in this picture. Interactions between the particles in the ABE state may lead to a substructure, but the hole–hole exchange splitting is expected to be small (i.e. <0.1 meV), at least for a very shallow state with two Γ_9 holes. The electron–hole exchange interaction is also expected to be similarly weak, due to a limited wavefunction overlap. An excited ABE state is expected when the two-hole state has one hole from the lower Γ_7 valence band (this state is denoted as I_{1B} in the CdS literature [3, 16]); in this case an exchange splitting of the order 1 meV may be expected for this state. The energy position of this state is expected to be shifted from the ABE ground state by an amount comparable to the energy difference between the A and B excitons in GaN, i.e. about 7 meV.

For other wurtzite semiconductors (like CdS) a large number of excited neutral ABE states have been observed in the energy range between I_{1A} and I_{1B} [16]. The origin of these is not definitely clarified, but is suggested to be related to molecular-like excited configurations of the three-particle ABE complex, in analogy to the situation with excited states of the DBE [12].

Another class of BEs is constituted by the neutral 'isoelectronic' defects, where the neutral ground state of the optical excitation has no extra electronic particle, unlike donors or acceptors. Well-known classical examples are the N_P defect [17] and the Zn–O nearest-neighbour pair defect [18] in GaP. Such defects have a simple BE configuration with two particles only, an e–h pair. Different electronic states are expected, depending on the localization of the particles, and the character of the bound hole [5, 6]. A strongly bound electron gives rise to a pseudo-acceptor situation, where the hole is bound as a secondary particle with a set of effective-mass-like hole states derived from the valence band top ($J = 3/2$). The reverse situation applies if the hole is strongly bound (in this case often a spin-like $J = 1/2$ hole); then the electron behaves as a shallow-donor electron (pseudo-donor) [5, 6]. There are also cases where both particles are strongly localized [19]. If at least one of the particles is strongly localized, the phonon coupling in the related optical BE transition is also typically strong. Such defects appear to be present in GaN as well, as we will briefly discuss below.

Excitons may also be associated with extended defects, such as dislocations or stacking faults. Such cases have previously been observed in many semiconductors [20, 21], although no complete understanding of these spectra has as yet appeared. Dislocations give rise to a strong local strain field, causing an effectively one-dimensional electronic potential that may bind excitons. In addition, localized states due to dangling bonds or other defect states on a dislocation line may bind carriers or excitons. We shall mention below some optical spectra in GaN which are explained in terms of such extended defects.

3. Excitons bound at shallow donors

We shall restrict ourselves to the case of neutral shallow donors, the case normally observed in donor BE (DBE) spectra. Such DBE spectra are observed in PL from heteroepitaxial as well as homoepitaxial GaN samples. The photon energy region for such DBE spectra is about 3.470–3.472 eV at 2 K for strain-free GaN [7, 9]. It is believed that different shallow donors contribute to the spectra observed in this region in different samples, but actually the detailed work required to determine the characteristic DBE line for a particular shallow donor has so far not been done properly. HCVD-grown thick layers are the best heteroepitaxial samples for spectroscopy, with an optical linewidth of about 1 meV or less (see figure 3). Experience indicates that there are often two dominant DBE lines, as in figure 3, with a spectroscopic distance of about 1 meV. A natural suggestion is then that these are connected with what are commonly believed to be the two most dominant residual shallow donors in GaN, O and silicon. Additional careful doping experiments are necessary to verify this assumption, however.

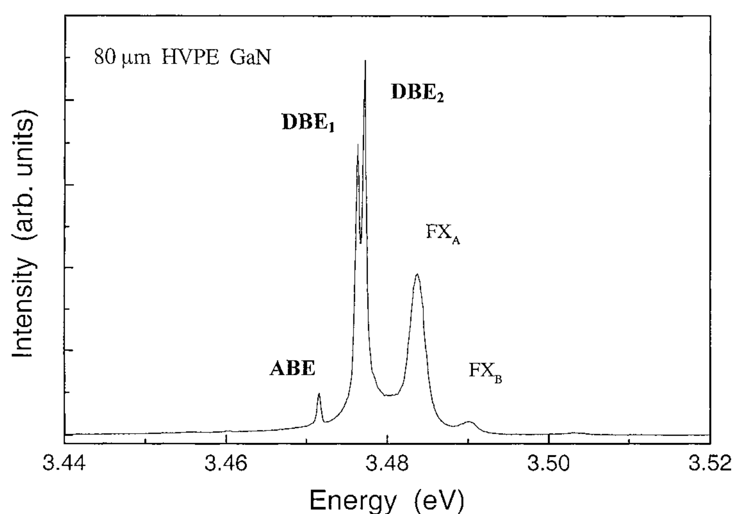


Figure 3. The photoluminescence spectrum of a thick nominally undoped HVPE-grown GaN layer, showing the two dominant donor bound excitons, and the most common acceptor bound exciton at lower energy. Note that the spectra are shifted up in energy by about 6 meV compared to those of unstrained GaN, due to a residual biaxial strain field in the layer.

In homoepitaxial GaN samples grown by MOCVD on strain-free bulk GaN substrates a better spectral linewidth is achieved; down to 0.2 meV has been observed for the DBEs. In this case one dominant line is observed at 3.4709 eV, and several additional lines are seen (figure 4) [22]. The additional lines are weaker, but clearly resolved. The lines occur on a broad background of different origin. These additional lines could be due to additional donor species present as residual impurities [23].

Important additional spectroscopic information is available from the two-electron satellites, where the DBE recombines leaving the remaining donor electron in an excited $n = 2$ state. This gives direct spectroscopic information about the binding energy of the donor electron, which can be extrapolated as ≈4/3 times the distance between the two-electron replica and the principal DBE line, assuming ideal effective-mass behaviour. The spectrum in figure 5 gives a binding energy of about 29 meV for the dominant donor in that sample. Comparison with ir absorption data for Si donors gives a good agreement for the binding energy [23]. These

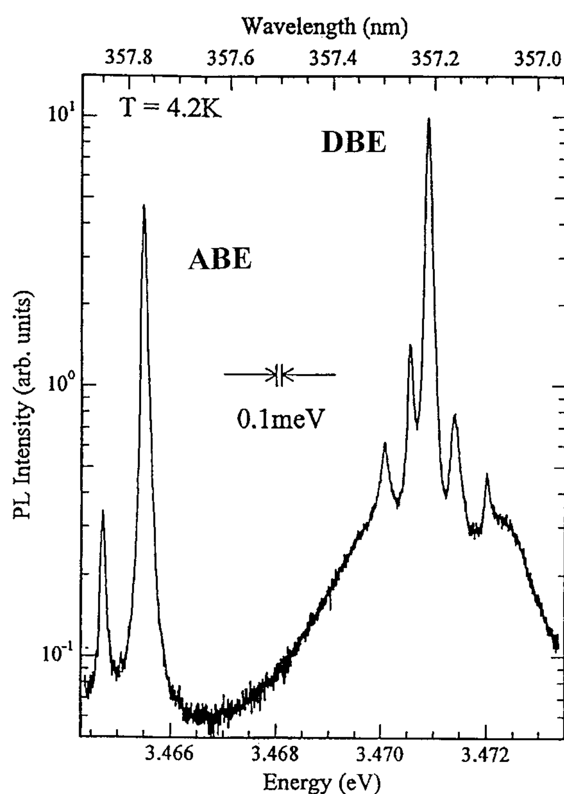


Figure 4. A high-resolution photoluminescence spectrum of a homoepitaxial MOVPE-grown GaN sample, showing the dominant ABE line close to 3.466 eV and the strong DBE line close to 3.471 eV. (From Kornitzer *et al*, reference [22].)

data allow a tentative identification of the 3.4709 eV DBE as due to the neutral silicon donor. It is likely that the often-observed second DBE peak at 3.4718 eV in unstrained GaN [7] is then related to the O donor, but this remains to be proven.

The weaker BE lines in the vicinity of 3.47 eV (figure 4) are most likely due to separate donor states. A careful study of the two-electron satellites related to these donors indicates that their binding energies are nearly identical to those of the Si donor [24]. It was therefore tentatively suggested that these weak lines are due to Si donors in a slightly perturbed structural environment [24].

At slightly higher energies there is another DBE state at about 3.474–3.475 eV (figure 5). This is generally interpreted as the principal DBE state related to the B free exciton, i.e. the bound hole is from the Γ_7 valence band. Additional excited states below the A free exciton are not resolved in figure 5, but clearly seen in selective excitation spectroscopy, where four additional states are seen in the energy range 1–5.5 meV above the principal DBE line at 3.471 eV [25]. These particular states are tentatively explained as due to rotational states of the Γ_9 hole in the DBE [25].

In figure 5 there are also seen a couple of peaks at much higher energies, 3.492–3.494 eV, just below the excited $n = 2$ state of the A exciton. These are tentatively explained as very extended DBE states in a configuration related to the $n = 2$ A free exciton. Such states have also been observed for GaAs [26].

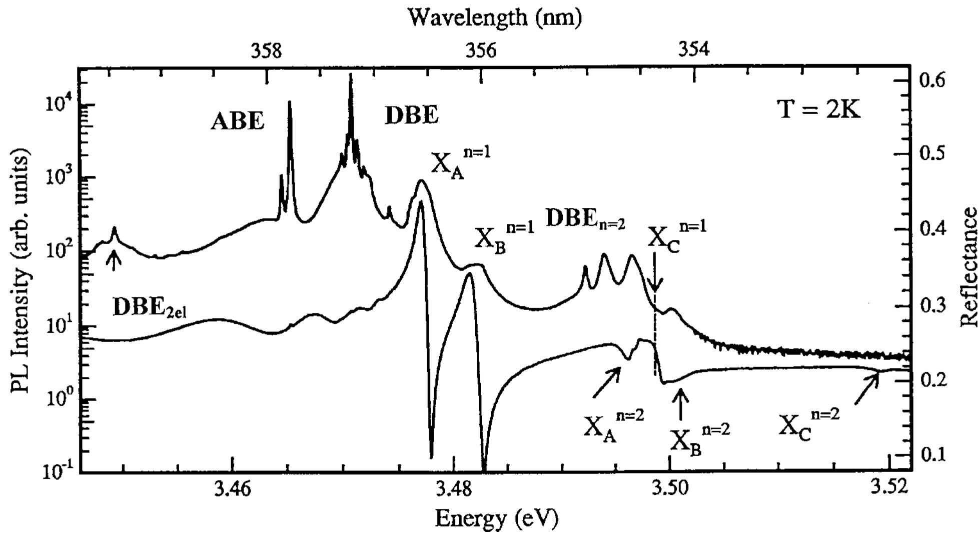
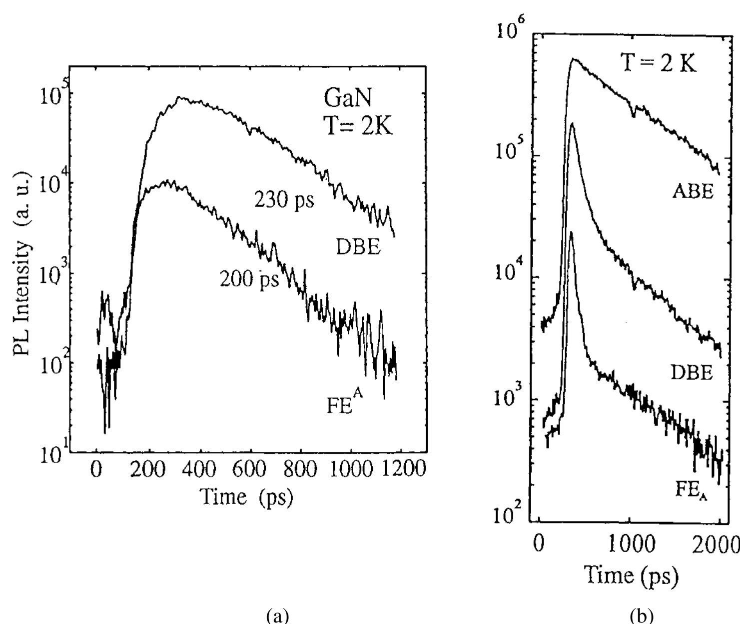


Figure 5. Photoluminescence from the same sample as in figure 4, in a wider spectral range. In addition to the intrinsic exciton peaks and the BE peaks shown in figure 4, excited DBE states related to the $n = 2$ free excitons are observed close to 3.494 eV. A DBE related to the B free exciton is seen at about 3.475 eV, and a two-electron replica related to the principal DBE at 3.471 eV is observed at about 3.450 eV. (From Kornitzer *et al*, reference [22].)

The magnetic properties of the donor BE have recently been studied [24, 27]. A Γ_9 hole should determine the magnetic properties of the DBE state, since the electron spins are paired off (figure 1), and the hole is expected to be very shallow. For the case of $\boldsymbol{B} \perp \boldsymbol{c}$ the effective hole g-factor is then expected to be zero, and the splitting observed for the BE PL line is due to the final-state donor electron, expected to have an isotropic g-factor of $g \approx 1.95$. The observed lack of thermalization and an effective g-factor of $g_\perp = 1.87$–2.07 between different experiments seem to nicely confirm this prediction [24, 27]. For the case of $\boldsymbol{B} \parallel \boldsymbol{c}$ both the hole on the BE state and the final-state donor electrons split, and thus the effective g-factor is the difference of these two splittings. The thermalization behaviour confirms a splitting in the excited state as well, and the effective g-factor $g_\parallel$ is found as 0.64, being the difference between the g-factor for the DBE state and the donor electron g-factor. Thus the effective g-factor for the hole in the BE state is derived as $g_{\parallel h} = 2.5$. This agrees with the expected value for a completely anisotropic Γ_9 hole, i.e. $g_{\perp h} = 0$ and $2 \leqslant g_{\parallel h} \leqslant 4$, depending on the degree of admixture of the Γ_7 holes [14].

Another important property of the DBEs is the recombination dynamics. The low-temperature decay rate for the DBE PL line should give the radiative lifetime τ_{BE} of the DBE, which may also be theoretically predicted by the theory of Rashba and Gurgenishvili [28]. In the simplified form given by Henry and Nassau [29], $\tau_{BE} = \text{constant} \times \lambda/nf_{BE}$, where λ is the photon wavelength, n the refractive index and f_{BE} the BE oscillator strength. For thick HVPE GaN layers (>100 μm) of low dislocation density (in the 10^7 cm^{-2} range), a low-intensity decay time of about 200 ps is observed at 2 K (figure 6(a)), which is believed to be a typical radiative lifetime for DBEs related to shallow neutral donors. This corresponds to a value of f_{BE} of about 10, very similar to that in the case of shallow donors in CdS [29]. In thin strained heteroepitaxial layers with a higher defect density, the observed lifetime is typically shorter [30, 31] (figure 6(b)), indicating an influence of excitation transfer from the DBE to lower-energy states before the radiative recombination takes place. A smaller value of the



(a) (b)

Figure 6. Photoluminescence decay curves at 2 K for two different samples, a thick high-quality HVPE-grown sample (a), and a thin homoepitaxial MOVPE-grown layer (b). Note that in the latter case the DBE decay is much faster, probably due to transfer of the DBE to other defects before recombination.

decay time is also often observed in thick GaN layers on sapphire, if the point defect density is not sufficiently low [32], which is explained by the same argument. Similarly homoepitaxial GaN layers also often show a fast DBE decay at low excitation density, due to excitation transfer to point defects [34]. A slow component is often observed in the DBE decay [33, 34] indicating a slower weakly radiative process overlapping the DBE transition (figure 6(b)). At high excitation intensities the influence of biexcitons gives rise to a slower decay [35]. Being a localized excitation, the BE lifetime should ideally be temperature independent; in practice however an initial increase in the DBE decay time with rising temperature is typically observed, followed by a decrease. The initial increase may be due to the capture of free excitons to the DBE ground state, so the DBE is sensitive to the increased decay time of the FE state. The decreased decay time at higher temperatures is due to thermal excitation to FE states, and further transfer to faster non-radiative recombination sites [32, 34].

4. Excitons bound at acceptors

The situation regarding acceptor BEs (ABEs) in GaN is somewhat less clear than that for the donors. The most prominent neutral ABE is found at about 3.466 eV in unstrained GaN (figure 7; also seen in figures 3–5). There are several arguments that this should be an ABE for a neutral acceptor; one argument involves the magneto-optical properties which will be discussed below. Further, this BE has been found to be dominant in slightly Mg-doped GaN samples [36–38]; it has a low-energy acoustic phonon wing which is very characteristic for ABEs [3, 39] (figure 7). Also it has a rather strong LO phonon coupling (figures 7–9), much stronger than for the DBE, a property which has also been found in previous studies of shallow ABEs in CdS [3]. An alternative interpretation of this BE line as being related to charged

DBEs has recently been proposed by several authors [40–43]. This idea seems to be wrong, because it conflicts with the observed behaviour of the BE line in magneto-optical data [27], as further discussed below.

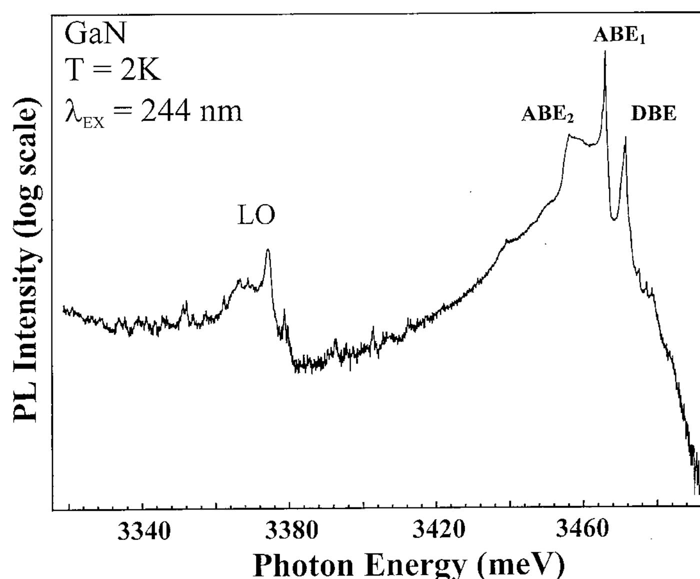


Figure 7. The photoluminescence spectrum at 2 K from a lightly Mg-contaminated MOVPE-grown homoepitaxial GaN layer. The dominant BE line is that of the Mg-related 3.466 ABE_1, but another deeper ABE, ABE_2, is seen at about 3.456 eV. Note the strong acoustic phonon wing related to ABE_1, and also the dominant LO phonon replicas for the ABEs.

The chemical identity of this 3.466 eV ABE is still not definitely confirmed. As stated above, many workers have tentatively associated this ABE with Mg_{Ga} [36, 44, 45]. A difficulty is that most experiments with doped crystals up to now have been performed on heteroepitaxial material, where the ABE peak position strongly depends on the strain. While the shallowest BEs (such as the DBEs) tend to have a nearly constant distance to the FE_A position in strained layers, the ABEs, being deeper, do not follow such a simple behaviour. In samples with a high biaxial strain the ABE binding energy seems to be strain dependent. For example in Mg-doped samples with an A-exciton position at 3.499 eV at 2 K, the Mg ABE is observed at 3.480 eV [46], with a binding energy of 19 meV. In unstrained samples the same distance is observed to be 11–12 meV [22–25, 44]. The fact that this 3.466 eV ABE line is observed in almost all PL spectra of GaN in the literature has then to be explained by the assumption that Mg is a common contaminant in GaN. Recently obtained SIMS data on HVPE GaN have confirmed this situation, i.e. Mg is often present in HVPE GaN, typically at concentrations in the 10^{16} cm^{-3} region [47].

The 3.466 eV ABE line is in high-resolution spectra observed as two separate lines, one at about 3.4655 eV and another at about 3.4647 eV [22] (figure 4). The position of these two lines varies slightly from sample to sample, due to residual strain. It is possible that these two BEs are due to two different acceptors, which would be supported by the recent finding of quite different relative intensities of the two lines in epilayers grown with Ga and N polarity, respectively [48]. In principle, two ABE lines are possible for the same acceptor, since there may be two separate acceptor ground states in wurtzite semiconductors [34]. Further work is needed to clarify the origin of this doublet of lines.

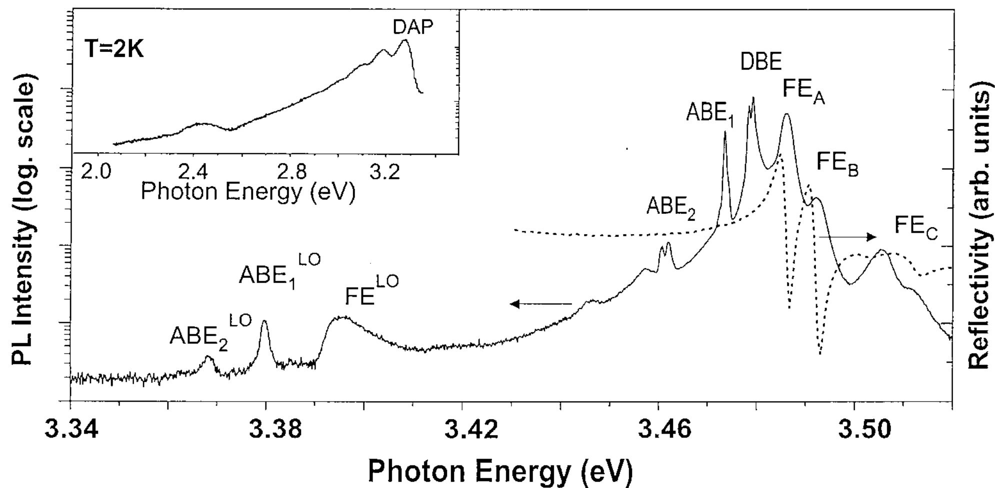


Figure 8. The photoluminescence spectrum at 2 K of a nominally undoped HVPE-grown 80 μm thick layer, showing two DBE lines, and two ABEs, ABE_1 and ABE_2. Note the splitting into two lines for ABE_2. The LO replicas are dominated by the intrinsic FE_A emission and the ABEs. All lines are strain-shifted upwards by about 6 meV for this sample.

There are other deeper BE PL lines in GaN which are probably acceptor related. One example is given in figure 8, where additional ABE peaks are observed at 3.461 eV (a doublet structure) [32]. Since there is a strain shift upwards in the spectrum in figure 4, this is probably the same ABE as is observed in some homoepitaxial layers at 3.455 eV [33], indicating a BE binding energy of about 21 meV. The observed splitting is tentatively related to a splitting in the neutral-acceptor ground state, as supported by the lack of thermalization [32]. The identity of this acceptor is not established, but it is close to the position observed from the dominant ABE in Zn-doped samples, if strain shifts are considered [46]. Therefore it might be due to residual Zn acceptors, present as contaminants in many samples.

In figure 9 there are also shown other weaker PL peaks below 3.44 eV, for another HVPE-grown thinner GaN layer. These may be related to additional deeper ABEs, but more work is needed to clarify the identity. The LO phonon replicas of the ABEs are rather strong; in fact it is apparent that the strength of the LO phonon coupling is larger for the deeper ABEs, as expected due to an increased localization of the ABE wavefunction [49]. The strength of the LO replicas is typically more than an order of magnitude larger than for the DBEs, consistent with the early findings for DBEs and ABEs in CdS [3].

The recently obtained magneto-optical data for homoepitaxial GaN seem to confirm the identification of the 3.466 eV BE as an ABE [27], as already mentioned above. The ABE state has an effective spin of the electron (figure 1), while the acceptor ground state has the effective hole spin. From independent magnetic resonance studies of the Mg acceptor it has been established that the Mg acceptor hole is essentially spin-like, with a g-factor close to 2 and nearly isotropic [50, 51]. This may be expected for a degenerate bound hole state with a rather localized wavefunction [5]. The magnetic field splitting of the ABE PL line should therefore show essentially an isotropic pattern of splitting into three lines, as schematically indicated in figure 10. The experimental data from reference [27] (figure 11) may be interpreted along these lines. For the case of the magnetic field $\boldsymbol{B}$ parallel to the c-axis no splitting is resolved in the data presented, but for $\boldsymbol{B} \perp \boldsymbol{c}$ a splitting into three lines is clearly seen, in agreement with the expected pattern shown in figure 10. More detailed future work with circularly polarized

measurements may be needed to confirm this picture. (The interpretation in reference [27] is different, since the authors assume a Γ_9 hole for the acceptor.) For the case of a charged DBE [40–43] there is no particle in the final state of the PL transition. Therefore the magnetic splitting should be similar to the case for the free excitons [52]. For instance, in the case of $\boldsymbol{B} \perp \boldsymbol{c}$ a splitting into a doublet would be expected, which is not observed in figure 11.

The ABE recombination dynamics has been studied in transient PL data [30–34, 53]. The decay curves are usually clean exponentials for the ABEs (figure 6) (in contrast to the case for DBEs), and presumably reflect the radiative lifetimes of the BEs at the lowest temperatures,

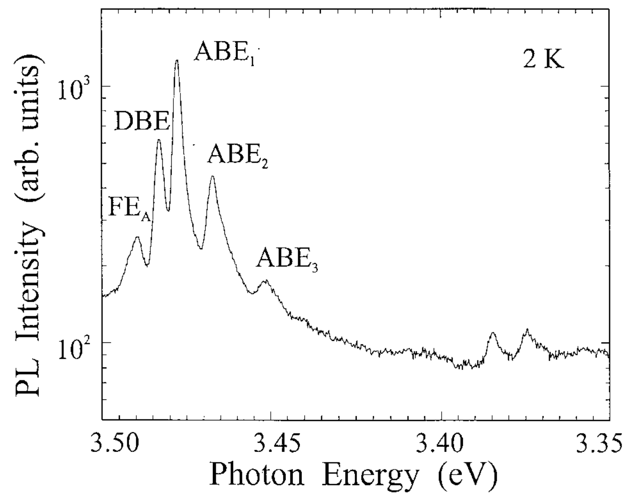


Figure 9. Photoluminescence for a thinner (12 μm) HVPE sample, less pure than the sample in figure 8. The spectrum is dominated by ABE lines; three different acceptors appear to be present in the sample. These are probably the same acceptors as in figures 7 and 8. Note the strong upshift in energy of the spectrum, due to residual uniaxial strain in the sample.

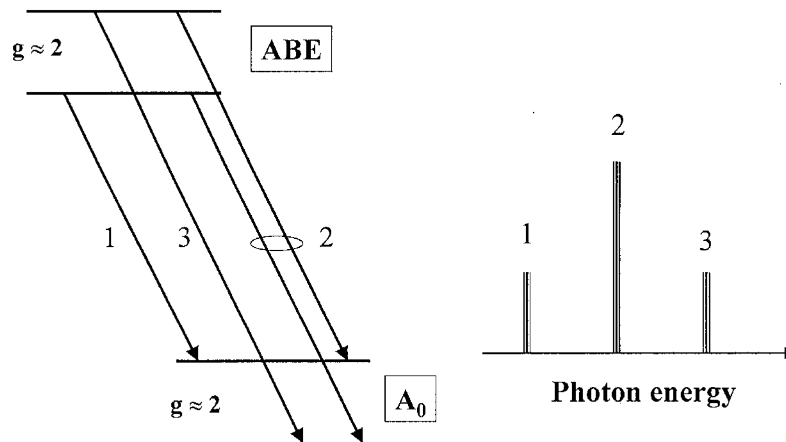


Figure 10. A sketch of the expected photoluminescence lines of a spin-like acceptor in a magnetic field. In this case both the ABE state and the acceptor ground state will have an approximately isotropic splitting corresponding to $g \approx 2$, which leads to essentially a three-line structure of the PL spectrum (right).

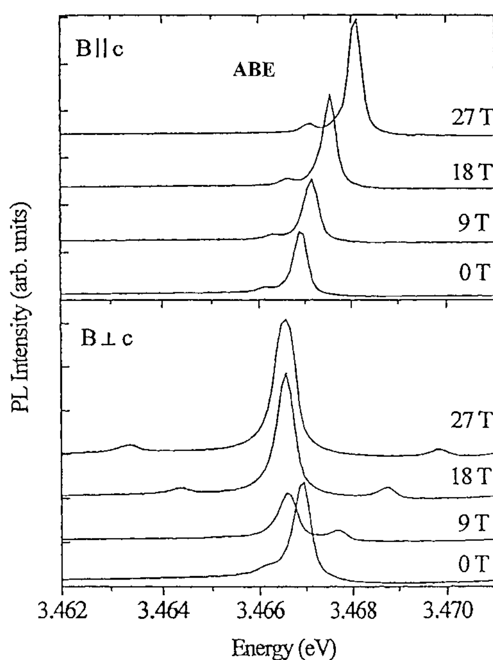


Figure 11. Experimental data for the splitting of the 3.466 eV PL line for a homoepitaxial GaN sample in a magnetic field, for both orientations of the magnetic field with respect to the *c*-axis. In the upper curve only one line is clearly resolved; the additional low-energy line is probably the weaker PL line seen in figure 4. In the lower spectrum, three lines are clearly resolved. (From Stepniewski *et al*, reference [27].)

before thermalization sets in (figure 12) [32]. The observed values of the radiative lifetimes are 0.7 ns for the 3.466 eV ABE [53] and much longer, 3.6 ns, for the deeper 3.455–3.46 ABE (figure 6(b)) [32]. This corresponds to an oscillator strength of the order of 1, very similar to that for the shallow ABEs in CdS [29].

5. Deep levels and bound excitons

Some defects give rise to deep levels in the bandgap. These may be donors, acceptors or neutral isoelectronic defects. Optical transitions associated with such states are typically accompanied by a very strong phonon coupling, which means that the PL emission is a broad phonon envelope, and no sharp electronic line is detected. This makes the analysis of the electronic structure from optical spectroscopy difficult (or impossible). Therefore it is difficult to establish whether such an optical transition is due to a bound-exciton process, or e.g. a donor–acceptor (DA) pair recombination.

One example of such a broad PL emission is the As-related spectrum peaking at 2.6 eV in GaN [54–57]. This emission has a weak sharp no-phonon line at 2.945 eV at 4 K (figure 13) [55], which might indicate an exciton transition. As substituting on N sites is isoelectronic, and is suggested to introduce a 0/+ level 0.4 eV above the valence band from theoretical calculations [58]. If this level is neutral it may bind an exciton, and give rise to the observed emission. This mechanism has to be confirmed by further detailed experiments. An alternative mechanism would be the situation where the PL emission is instead related to a double-antisite

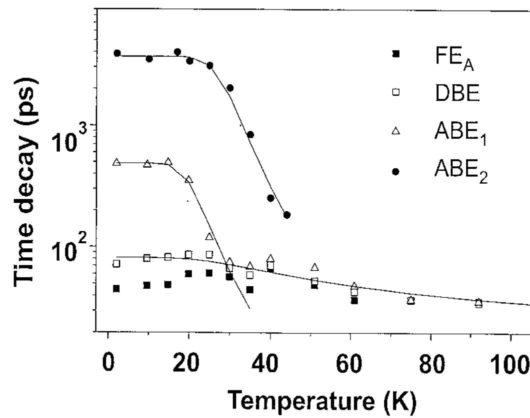


Figure 12. Temperature dependences of the decay time for various exciton states in the same HVPE-grown sample as in figure 8. The ABEs exhibit a constant decay time versus temperature at low T, as expected, while at higher temperatures the thermalization becomes important, and non-radiative processes begin to dominate, shortening the decay time.

As_{Ga} donor. Such a defect is predicted to readily form in cases where the Fermi level is low in the bandgap [59]. Some recent experimental data seem to favour this possibility [56]. If this is the case the PL emission is not from a BE, but rather from an internal donor recombination, as seen e.g. for As_{Ga} in GaAs [60].

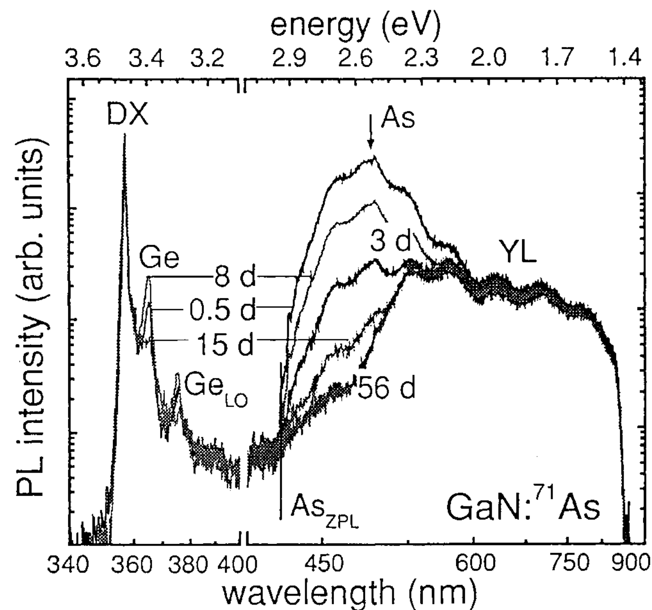


Figure 13. Photoluminescence of As-doped GaN, prepared by isotope implantation. The As-related emission has a sharp no-phonon line at 2.945 eV, with a strong broad phonon sideband. (From Stötzler *et al*, reference [55].)

A quite analogous broad PL emission is observed in GaN doped with P [61]. Here the no-phonon line is at 3.271 eV at 4 K, consistent with the predicted 0/+ level at 0.2 eV above

the valence band [58]. Detailed studies to confirm the identity of the PL process have not so far been presented, to our knowledge.

6. Excitons bound to structural defects

It is well known that dislocation defects of different types are able to bind excitons, and show sharp PL line spectra associated with such BEs. Such line spectra have been seen in Si [62], ZnSe [63] and recently also in GaN [64–66]. In simple terms, the one-dimensional strain field at the dislocation creates a strong local one-dimensional potential, which can bind a charge carrier, like a hole, often quite deeply [67]. Once the hole is bound, an electron follows by Coulomb attraction, so an exciton becomes bound. The defect then resembles an isoelectronic centre of pseudo-donor type [4–6].

In the literature there are many reports on a PL line structure at energies 3.41–3.42 eV at low temperatures in various GaN materials where the dislocation density is high [64–66]. This line may show substructure in some samples, and the energy position varies slightly in energy from sample to sample. It never occurs in high-quality GaN. This line has been associated with dislocation-type defects, although the exact type of defect (stacking fault, screw dislocation etc) is not known. The recombination model may be similar to what has been observed with other semiconductors, i.e. an exciton bound in a one-dimensional strain-induced potential, where the hole is the primary bound particle. The thermal activation energy is found to be about 20 meV, interpreted as the binding energy of the weakly bound electron, while the hole would then be bound by about 60 meV. The PL transient decay time for this emission at low temperatures is found to be about 500 ps, which appears to be consistent with a rather localized hole and a shallow electron.

7. Summary

Bound excitons associated with neutral donors and acceptors in GaN show prominent optical spectra, which will be very useful signatures of the corresponding defects. The spectroscopic studies performed to date are limited by the spectral linewidth, which was only barely adequate for detailed studies (i.e. about 0.1 meV) in the rarely available homoepitaxial MOVPE-grown samples. Nevertheless the main aspects of the electronic structure of the bound excitons are understood for this class of defects, from the preliminary magneto-optical and magnetic resonance data now available. The donor bound excitons appear to have a shallow Γ_9-like hole as the most weakly bound particle. The magneto-optical data for the most common Mg-related acceptor BE are less clear, but seem to be consistent with a spin-like hole in the acceptor state. The tentative identification of the observed BE lines reported here with specific donors and acceptors needs to be confirmed by careful back-doping experiments in the future. P and As dopants give rise to strong characteristic deep PL emissions, which may be related to isoelectronic BEs. Excitons bound to structural defects are clearly present in GaN; the detailed models for such spectra are still under debate.

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