Spontaneous emission in GaN
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Part 1

Introduction

The technological potential of GaN as an opto-electronic material was anticipated for the last 30 years, but only in the recent decade, improved crystal growth techniques have allowed several leading groups to achieve device-quality films. Progress was due to reduction of the high background electron concentration, persistent in the GaN grown in the seventies, and these reduced electron concentrations were accompanied by enhanced carrier mobilities. The problems with p-type doping delayed, however, practical use of this material. A real breakthrough came when the low resistivity of acceptor doped material became available. In recent five years many subsequent challenges in the area of materials science and device fabrication were successfully resolved. Following the commercialisation of light emitting diodes (LEDs) in 1994, the mass production of the present GaN-based LEDs yields devices with quantum efficiency exceeding 10 %, comparable to the most efficient semiconductor light sources on the market today. In 1999 we witnessed another industry breakthrough, the commercial introduction of the blue laser diode. It can be expected that this event will revolutionise the optical memory devices by considerably increasing the amount of information that can be stored in optical disks.

The advantages of high bandgap energy and good thermal properties in GaN and related III-V nitrides are still accompanied by a relatively poor material quality. GaN materials grown using both MBE and MOCVD methods was proven to contain high densities of dislocations, partly related to a lack of suitable substrate material with matching lattice constants and thermal expansion coefficients. The successful utilisation in electronic and opto-electronic industry of materials with such high dislocation density, is puzzling. Consequently in this review we concentrate on the optical properties of GaN and related nitrides. We start with a basic discussion of various recombination processes important in GaN. We describe the ways of distinguishing between these processes. This is very important in the case
of GaN, because due to large differences between materials a given photoluminescence (PL) transition is often observed at quite different spectral positions. Next, we discuss the relationship between structural (morphological) properties of GaN films and optical transitions. We survey the role of dislocation in radiative and nonradiative recombination transitions and the influence of piezoelectric effects on rate of radiative recombination and emission energy. Finally, we analyse two deep emissions of GaN - the yellow and blue emission, observed in acceptor doped samples.
Part 2

Recombination processes in the bandgap region

In this part we discuss examples of photoluminescence processes in gallium nitride selected to exemplify the different types of recombination. The non-radiative as well as radiative centres will be considered. We will concentrate in this section on methods that use photoluminescence and other emission data and on quantitative information about GaN films and their defect structure and processes that can be obtained from these studies.

The term photoluminescence denotes the radiation emitted by a crystal after an optical excitation. It is produced as a result of recombination of photoexcited electron-hole (e-h) pairs. From the analysis of the luminescence spectrum as a function of different parameters (temperature, excitation energy, excitation intensity, temporal evolution, external fields, etc), general information on the material quality can be gained. It may give some insight into the defects involved in the growth process or produced by typical processing steps and by post-growth treatments. It gives information mainly on minority carrier properties and their influence on, or relationship to, defects. For example, the minority carrier lifetime, diffusion length, and quantum efficiency can be deduced from the study of the recombination pathways. All these quantities are affected by the defects as well as the doping level. Importantly, photoluminescence spectroscopy is capable of distinction between the chemical species of impurities. Owing to its sensitivity, photoluminescence may be used at very low defect densities, sometimes even as low as $10^{13} - 10^{14}$ cm$^{-3}$.

It is not always straightforward to extract quantitative information from the photoluminescence measurements alone. The values of the doping density or the trap concentration may require a very accurate calibration or careful lineshape studies. Sometimes extensive analysis and supplementary mea-
measurements using other techniques are required. The important non-radiative recombination processes can be studied only indirectly and accessed through their effect on transition rates for the radiative processes. For example, the non-radiative processes are more pronounced in the proximity of extended defects and thus may be visualised in the topographic distribution of the luminescence intensity. Owing to this effect, the imaging techniques, and more particularly cathodoluminescence, have provided detailed information on dislocations and other extended defects and their spatial distribution.

In an idealised semiconductor at least four coupled radiative recombination channels may be active, these are band-to-band, free exciton, bound exciton, and impurity-to-band transitions, as illustrated in Figure 2.1. These channels may or may not be spectrally distinct in a particular film. We now present some background information on these four processes.

2.1 Free excitons

Free excitons assemble from the excited electrons and holes as a result of the Coulomb interaction. The Wannier-Mott free exciton can be described within the effective mass approximation, and its bound states (in the case of non-degenerate band extrema and at the exciton wavevector \( k = 0 \)) have binding energies \( E_n \) given by [1]:

\[
E_n = \frac{1}{n^2} \frac{\mu}{m_0} \frac{1}{\epsilon_0} R_H.
\]

(2.1)

In Equation 2.1 \( R_H \) is the Rydberg constant of the hydrogen atom, \( m_0 \) is the electron mass, \( \epsilon_0 \) is the static relative dielectric constant, and the exciton reduced mass \( \mu \) is given by

\[
\mu = \frac{m_e m_h}{m_e + m_h}.
\]

The free excitons at non-zero wavevectors can not be directly observed in the emission spectra. The emission of the recombining free excitons (at \( k = 0 \)) occurs below the band gap energy \( E_g \), at the energy \( E_X \) given by:

\[
E_X = E_g - \frac{R_H}{n^2}.
\]

GaN in wurtzite structure has its valence band split into three subbands. The splitting is caused by the axial crystal field and the spin-orbit interaction. The valence band splitting leads to three free excitons A, B and C,
associated with each of the three subbands. The exact energy of these three excitonic transitions was obtained from reflectance and photoluminescence (PL) studies performed on thick GaN epilayers and homoepitaxial epilayers [2-7]. Accurate values of energies of the excitonic transitions have been determined due to full strain relaxation in such epilayers. The highest precision measurements were carried out in homoepitaxial GaN samples, where very sharp PL lines are observed, with linewidths below 1 meV [8, 9]. The values of exciton energies of 3.478 eV (A exciton), 3.484 eV (B exciton) and 3.502 eV (C exciton) have been obtained with the accuracy of about 2 meV [10]. Consequently, the binding energy of all three (A,B,C) free excitons in GaN is determined to be about 25-27 meV [10, 11].

With technological advances in GaN layer quality resulting in sharp spectral features, it became possible to observe fine structures in the excitonic transitions. Examples of such fine structures include the polariton longitudinal-transverse splitting and the singlet-triplet exchange splitting. The fine structure of the A exciton was determined from reflectivity and polarised PL investigations by Hoffmann and co-workers [11, 12]. Hoffmann et al. [11] have identified the PL peaks at 3.47904 eV and 3.47892 eV with the lower transverse branch of the spin singlet state and with the spin triplet state of the A exciton, respectively. Such identification gives the value of the exchange splitting of about 120 µeV with the accuracy of about 100 µeV. The PL peak at the energy of 3.48000 eV was assigned to the longitudinal branch of the spin singlet state of the A exciton [11]. This identification yields the value of the longitudinal-transverse splitting of the A exciton to be about 1.0 meV, with the uncertainty of 0.1 meV [11, 12], while other authors [13] quote the value of about 1-2 meV.

2.2 Bound excitons

A free exciton can be bound at a neutral or ionised donor or neutral acceptor, giving rise to an exciton-impurity complex. An exciton bound to an ionised donor is a complex of an ionised donor ion, an electron and a hole; an exciton bound to a neutral donor consists of an ionised donor ion, two electrons and a hole, or otherwise of a neutral donor, an electron and a hole. An ionised donor-bound exciton can only be formed if the effective mass of a hole is considerably larger than the effective mass of an electron, as in the case of GaN. By analogy, ionised acceptor-bound excitons can be stable only if the effective mass of electrons is larger than that of holes. This situation is not realised in GaN. Thus, excitons bound at neutral acceptors are stable, while ionised acceptor-bound excitons may not be formed in GaN.

Recombination of bound excitons is an important process in the near-gap spectral region. It becomes more pronounced with an increasing impurity
concentration. In GaN, as in other semiconductors, bound excitons often dominate the low temperature band-edge spectra. They appear as sharp spectral lines in close proximity of the band edge, particularly at low donor and acceptor concentrations. The sharp bound exciton emission lines are found at the energies $\hbar \omega$ given by:

$$\hbar \omega = E_X - E_{BX},$$

where $E_{BX}$ is the exciton binding energy required to remove the exciton from the impurity centre. The binding energy of donor-bound excitons obtained from spectroscopic measurements is 11.7 meV, while the thermal activation energy is 10.7 meV [14]. The binding energies of excitons bound to acceptors are slightly larger, namely 19 ± 4 meV for the Mg acceptor, and 34 ± 4 meV for the Zn acceptor [15]. According to the Haynes' rule, well established in semiconductors such as silicon and gallium phosphide [16], the exciton binding energy is a linear function of the donor binding energy. We note that the Haynes' rule is, strictly speaking, not applicable to all semiconductors. Nevertheless, a linear relationship for common intentional donors and acceptors in GaN has been empirically identified, as shown in Figure 2.2. Exciton binding energies correlate well with ionisation energies for shallow donors in GaN, and also for the substitutional Mg and Zn acceptors with binding energies of 200 meV and 340 meV, respectively. The latter values are associated with ionisation energies for substitutional Mg acceptor of 200 meV, and for Zn acceptor of 340 meV. Such correlation suggests that the empirical Haynes' rule [17] can be applied to GaN.

In pure materials, with low impurity densities, individual bound exciton complexes interact relatively weakly. Mutual interaction becomes important when the average impurity separation approaches the bound exciton radius given by

$$a_{BX} = \frac{\hbar}{(2m^*E_{BX})},$$

where $m^*$ is the reduced effective mass of the bound particles. Values of $a_{BX}$ in excess than several or even tens of nm are common. In the absence of interactions, the bound exciton lines can be spectrally very narrow. Such sharp bound exciton lines may serve as useful indicators of strain. Their sensitivity to local strains in the sample is often exploited to reveal the microscopic stresses, and particularly their nonuniformity.

Bound excitons can recombine either directly or through other associated recombination channels such as the "two electron" or "two-hole" transitions [17]. The low intensity two-electron (hole) satellites reflect the recombination of bound excitons in which the donor (acceptor) is left in an excited state. The two-electron (hole) transitions, if observable, provide a wealth
of detailed information on the donor and acceptor centres. Their spectral signatures appear on the low energy side of the main exciton line and they sometimes coincide with the high energy tail of other (for example the donor-acceptor pair) transitions. The two-electron (hole) satellite spectra in GaN are difficult to be observed, possibly because the overall level of unintentional defects/impurities is typically too high and strain-induced broadening prevents observation of sharp low-intensity lines. The two-electron transitions were identified in GaN only very recently [18]. Selective excitation to the no-phonon absorption lines associated with a given defect species has been successfully used in other semiconductors [17, 19] to enhance the "two-electron" luminescence, and may be attempted in GaN. The present authors are confident that this research direction will be further developed once better quality GaN material becomes available.

In addition to two-electron (hole) transitions, radiative recombination of excitons bound at neutral donors or acceptors competes with a highly efficient, non-radiative Auger process, in which the energy of exciton recombination is transferred to a second carrier bound at the site [17]. This strong competition prevents the use of bound exciton transitions in any practical light-emitting devices.

2.3 Free to bound transitions

Free to bound transitions are observed as broad spectral features, also located in close proximity of the band gap energy. The spectrum of a free-to-bound transition is described by the following relationship (given here in the case of an electron-acceptor transition) [20]:

\[ I_{eA} \propto (\hbar \omega - E_g + E_A)^{1/2} \frac{8 \sqrt{2}}{\pi^2} \frac{a_A^3 m_H^{3/2}}{\hbar} \exp \left( -\frac{\hbar \omega - E_g + E_A - E_F}{kT} \right). \]  

(2.3)

Here, \( E_A \) is the acceptor energy, \( E_F \) is the Fermi energy, \( a_A \) is the acceptor Bohr radius, \( m_H \) is the effective mass of holes, and other symbols have their usual meanings.

The free to bound transitions are often seen emerging from the donor-acceptor pair spectra as the temperature is raised, provided that the shallow defect ionisation energy is small enough. The free to bound transitions were identified for example in GaN:Mg [21] at 3.21 eV, where they are associated with the shallow impurity Mg. The same authors show another free to bound transition at 2.95 eV. Kaufman et al [22] identified a free to bound transition at 3.242 eV (see Fig 2.3), and they were able to preferentially excite either the free to bound or the donor-acceptor pair transition by varying the excitation energy.
The deep defect-related band at 2.8 eV in GaN:Mg was studied in Ref. [23] and the band was attributed to a free to bound transition involving a deep donor and the valence band. The PL excitation intensity dependence and temperature dependence of PL emission measurements were carried out. Under high excitation the band was shown to undergo a blue shift of 200 meV and potential fluctuations were found to be responsible. The luminescence quenching is observed at high temperatures with the activation energy of 0.3-0.4 eV. This identification of the blue PL (BL) in Mg doped GaN is however still controversial and it contradicts the results of several other groups. The nature of BL will be discussed in detail in a separate section.

The free to bound transitions can be used to optically determine a degree of compensation [20]. Such studies in GaN:Mg has been carried out by Obloh et al [24]. In their work the Mg-related photoluminescence bands have been investigated as a function of Mg concentration. The hole density was found to reach a maximum at the Mg level of $3 \times 10^{19}$ cm$^{-3}$ and then continued to decrease with increasing Mg content, suggesting self-compensation. At the same density of Mg, the dominant radiative recombination mechanism was found to change, from a free-to bound to a donor-acceptor pair transition. The authors suggest that the deep donor involved in self-compensation is a nearest neighbour associate of a Mg$_{Ga}$ acceptor with a nitrogen vacancy. We will return to this model later in the discussion of compensation mechanism in highly p-type doped GaN.

### 2.4 Band to band transition

Band to band transitions are commonly observed in other direct gap semiconductors. The theoretical description based on the Fermi golden rule and assuming a parabolic density of states and a single hole band gives the following expression for the radiative recombination rate $R_{sp}$ [25]:

$$R_{sp} \propto (\hbar \omega - E_g)^{1/2} \exp \left( -\frac{\hbar \omega - E_g}{kT} \right).$$  \hspace{1cm} (2.4)

The peak energy ($\hbar \omega_p$) and the half-width ($\Delta E$) of the band-to-band recombination is given by:

$$\hbar \omega_p \approx E_g + \frac{1}{2}kT,$$  \hspace{1cm} (2.5)

$$\Delta E \approx 1.8kT.$$  \hspace{1cm} (2.6)

The exponential energy dependence in Equation 2.4 makes it possible to determine the carrier temperature, by the analysis of the high energy slope of the emission spectra. The carrier temperature can be used to evaluate the
rate of energy thermalisation under high excitation conditions, important, for example, in laser operation.

Band to band transitions dominate at room temperature, and they are also one of the key processes thought to be responsible for gain in GaN blue lasers [26]. The identification is not trivial, as the binding energy of the other prospective candidate - the FE emission - is about $kT$ at RT (20 meV) [27–29]. Under high carrier injection conditions the competing processes of biexciton and excitonic molecules formation are not very efficient.

### 2.5 Donor-acceptor pair spectra

The recombination processes involving donors and acceptors compete strongly with the bound exciton processes at high compensation ratios, and particularly when the concentration of both donor and acceptor species is high. The early work by P.J. Dean [16] offers a comprehensive review, focused on properties of GaP, where the donor-acceptor spectra are particularly pronounced. The donor-acceptor pair spectra are explained by Coulomb interaction of ionised donor-acceptor pairs in the final state, leading to the following dependence of the transition energy $\hbar \omega$ on the pair separation $r$:

$$\hbar \omega = E_g - (E_A + E_D) + \frac{e^2}{er} - E_{vdW}. \quad (2.7)$$

Here, $E_D$ is the donor binding energy. The van der Waals polarisation interaction term can be modeled as:

$$E_{vdW} = \frac{6.5e^2}{er} \left( \frac{a_D}{r} \right)^5, \quad (2.8)$$

where $a_D = \frac{\hbar}{\sqrt{2m_eE_D}}$ is the Bohr radius of the shallower impurity in the pair. The intracentre distance takes only discrete values leading to a structured donor-acceptor band. In consequence, a fine structure of donor-acceptor pair transitions can be observed at the high energy wing of the PL band, as observed in GaN in homoepitaxial epilayers [30]. At higher donor - acceptor separations $r$, the individual spectral components merge and form a wide asymmetric band. The envelope of this unresolved band is given by [20]:

$$I(\hbar \omega) =$$

$$\int_0^\infty 4\pi r^2 N_D \frac{e_0}{e^2} \hbar \omega W(r) - \frac{N_D - N_A}{W_{nr} + W_{DA}(r)} \times \exp \left( \frac{-4\pi N D r^3}{3} \right) \delta [\hbar \omega - \hbar \omega(r)] dr. \quad (2.9)$$

Here $N_D(A)$ is the donor (acceptor) concentration, $W(r)$ is the overlap integral between the donor and acceptor wavefunctions, $W_{DA}(r)$ is the donor-acceptor pair transition rate at a separation $r$, and $W_{nr}$ is the non-radiative
recombination rate. The radiative rate for hydrogenic donor and acceptor impurities is given by \( W_{D,A}(r) = W_{D,A}(0) \exp(-2r/a_D) \) and it was found to correctly describe the close donor-acceptor pairs in GaN:Mg \([31]\). The recombination rate quickly decreases with relative distance, and, therefore, distant pairs, while numerous, have very low recombination rates. Such pairs are thus very easily saturated, and, consequently, the DA pair band shifts to higher energies at increasing excitation levels by as much as several meV per decade. The blue shift of the PL is often considered as a proof of the donor-acceptor pair origin of the emission. This argument was used to identify the yellow emission in wurtzite phase GaN \([32]\) and red emission in cubic phase GaN \([33]\).

The intensity \( J \) dependence of the peak of the donor-acceptor transitions can be described as \([34]\):

\[
J \propto \frac{(E_{DA} - E_\infty)^3 \exp[-2E_D/(E_{DA} - E_\infty)]}{E_D + 2E_\infty - 2E_{DA}},
\]

where \( E_\infty = E_g - (E_A + E_D) \), with \( E_A \) and \( E_D \). With an increasing excitation level, the donor-acceptor band maximum saturates at the energy of \( \hbar \omega_\infty + \frac{E_D}{2} \).

An important special case relevant to GaN is that of donor-acceptor pairs involving a shallow centre as well as a deep centre. Due to a localised character of deep impurities, their electronic states may couple strongly to the lattice. As a result, optical transitions may involve strong phonon cooperation. Such transitions between a ground state of a strongly lattice-coupled defect and another weakly coupled or uncoupled defect at a fixed separation \( r \) produce a PL spectrum with a zero phonon line and phonon sidebands. The relative strength of the zero-phonon line and the sidebands is given by the Huang-Rhys factor \( S \) \([35]\). The lineshapes for increasing values of \( S \) vary, and, for strong lattice coupling, the vibrational contributions give rise to a Gaussian shape of the PL band. In these conditions the zero-phonon line is too small to be observable. The maximum of the broad band does not correspond to the electronic transition energy, but is related to the energy of a higher phonon replica. The half-width of the band varies with temperature as:

\[
\Delta(T) = \left[ 8 \ln 2 \left( \hbar \omega_{ph} \right) 2S \coth \left( \frac{\hbar \omega_{ph}}{2kT} \right) \right]^{1/2}.
\]

Here, \( \hbar \omega \) is the energy of the participating phonon.

The analysis of the donor-acceptor pair luminescence decay in Mg-doped GaN was reported by Shin et al \([36]\) and Godlewski et al \([37]\). The results of the latter studies are shown in Figure 2.4. This figure shows the energy
dependence of the measured PL decay time for the blue and yellow PL observed in lightly Mg doped GaN, reflecting the donor-acceptor origin of the two emissions. Closer donor-acceptor pairs, contribute to the PL at the high energy side of the Gaussian band and they show shorter PL decay times, in agreement with the outlined theory. Thus, the PL decay studies help identify the donor-acceptor pair processes, through their characteristic energy dependence of the PL decay time.

2.5.1 Temperature evolution of photoluminescence signatures

Band gap
Temperature evolution of spectral features in emission is often taken as a strong indicator of their origin. Central to this concept is the evolution of energy gap with temperature. The temperature dependence of energy gap \( E_G \) is generally described by the Varshni’s semi-empirical relation [38]:

\[
\Delta E_G(T) = E_G(T) - E_G(0) = \frac{\alpha T^2}{\beta + T},
\]

where \( \alpha \) and \( \beta \) are parameters. This formula provides a benchmark for the bandgap evolution with temperature. The best experimental techniques to study bandgap variations with temperature include reflectance and its derivatives - photo- and electro-reflectance [39-41]. The parameters \( \alpha = 8.32 \times 10^{-4} \) eV/K and \( \beta = 835.6 \) K were obtained from photo-reflectance studies [39, 40]. There appears to be some degree of inconsistency between the band gap evolution measured in GaN grown by different techniques. While the Varshni formula appears to be generally applicable, the detailed temperature studies of the bandgap reveal specimen-related variations. The temperature dependence of the fundamental band gap in heteroepitaxial GaN on sapphire was studied, for example, by Herr et al [42] through the PL study of excitons. They have obtained the Varshni expression with \( \alpha = 7.3 \pm 0.3 \times 10^{-4} \) eV/K and \( \beta = 594 \pm 54 \) K. Similar sample dependency was shown in the study by Manasreh and Sharma [43]. The Varshni parameters in bulk GaN obtained from the temperature dependence of the fundamental absorption edge [44] were found to be \( \alpha = 10.8 \times 10^{-4} \) eV/K and \( \beta = 745 \) K. These values differ considerably from those reported for epilayers grown on lattice mismatched substrates, indicating a strong influence of strain conditions on bandgap properties of GaN. The differences between various films were further explored by Buyanova et al [45] who revealed variations between films grown on SiC and those grown on sapphire, due to different thermal expansion/contraction. These differences are presented in Figure 2.5. Despite these sample-dependent differences, the donor-acceptor pair transitions and excitonic emissions are easily distinguished by their temperature evolution, as the latter decrease in energy with increasing temperature, while the donor-acceptor pair bands shift to higher energies.
Bound excitons

The bound exciton lines rapidly decrease in intensity with increasing temperature, whereas the free exciton emission is observable up to room temperature. This behaviour reflects the small localisation energies of bound excitons.

The PL intensity as a function of temperature \( I(T) \) may often be analysed using a two-channel dissociation Arrhenius model:

\[
\frac{I(T)}{I(0)} = \frac{1}{1 + c_1 \exp(-\Delta E_1/kT) + c_2 \exp(-\Delta E_2/kT)},
\]

(2.13)

where \( c_1 \) and \( c_2 \) are the prefactors, and \( \Delta E_1 \) and \( \Delta E_2 \) are the activation energies. The two activation energies are easily understood if we examine the process of bound exciton creation. Excitation above the band gap creates either free excitons or free carriers. The process of their localisation at neutral donors involves the localisation energy. At elevated temperatures localisation at neutral donors reduces the number of available neutral donors, a process competing with thermal ionisation. Therefore the donor binding energy should also be involved in the process of thermal deactivation of bound exciton emission. The temperature dependence of the PL intensity of a bound exciton complex can be used to identify the kinetics of its thermal dissociation and thus provides a valuable insight into the origin of the complex. Such analysis is, however, possible only if two activation energies differ noticeably. Otherwise, both ionisation processes occur at the same temperature range, and their separation is not possible.

Sometimes it may not be easy to distinguish a priori whether a given exciton is bound at a neutral donor or at an ionised donor. In the latter case, the dissociation energy corresponds to the break off of a loosely bound hole. In these circumstances, the temperature dependence of PL emission may be analysed using a single-channel dissociation model:

\[
\frac{I(T)}{I(0)} = \frac{1}{1 + c_1 \exp(-\Delta E_1/kT)},
\]

(2.14)

The same single-channel model is sometimes applied to the excitons bound at neutral donors, if the emission is examined only in a limited temperature range. While this approach may be justified for individual defect-bound excitons, the conclusions as to the nature of the recombination processes need to be treated with caution. It is known, that in excitons bound to certain isoelectronic traps in GaP [46] thermal release of the hole may be favoured over exciton delocalisation. Therefore if the single-channel model is to be applied a priori, close agreement is required between the activation energy of thermal dissociation with the exciton binding energy, obtained for
example from the wavelength separation of the observed emission line with respect to the free exciton line. The reference [14] describes a recent study of thermal evolution of bound exciton emission in GaN carried out along these lines.

**Phonon replicas**

The phonon replicas of free exciton transitions are associated with the exciton-photon (polariton) coupling. The relative strength of the phonon replicas is a measure of phonon scattering needed to get across the bottleneck in the lower exciton-polariton branch to the radiative branch of the dispersion curve [47]. A linear temperature dependence of the ratio of one longitudinal optical (1LO) phonon replica of the free exciton emission to the two-phonon replica (2LO) is expected in the temperature range below 100 K [48] and observed in Ref. [13], supporting the classical exciton/polariton model. Monemar notes the relatively strong no phonon free exciton line compared with the 1LO and 2LO phonon replicas [13]. This effect points to an enhanced scattering rate of exciton polaritons into the radiative branch of the no-phonon A exciton. High defect density may offer a plausible explanation as it assists in polariton scattering and provides the required momentum transfer.

Investigations of phonon-assisted photoluminescence in wurtzite GaN were reported by Liu [49]. They studied the free exciton linewidth due to exciton-phonon interaction. The LO-phonon assisted satellite lines associated with bound excitons were also observed. Their study of the 2LO phonon replicas provided information on the recombination lifetime of free excitons in GaN.

### 2.5.2 Photoluminescence intensity dependence on excitation power

Excitation intensity dependence of individual spectral emission components may help identify the corresponding recombination processes. Two quantities may be analysed, these are energies of the spectral features and their integrated intensities. The excitonic energy does not vary with increasing excitation power, but the peak energy of donor-acceptor pair transitions does, as described in Equation 2.10. This difference can form a basis of a test to identify the nature of unknown recombination processes. The integrated intensity may be analysed with a varying degree of sophistication. In a simple analysis, a power law may be applied to all near-gap emission lines where the intensity of the line, \( I \) and the excitation power, \( J \) are related through:

\[
I \propto J^k.
\]  

(2.15)
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The coefficient $k$ may also depend on $J$ if the excitation intensity is varied by many orders of magnitude. This relationship is underpinned by a set of rate equations describing details of the relevant recombination processes, and the relationships between them. Typically, simplifying assumptions are necessary.

The excitation intensity dependence may not be the most precise tool to identify a given transition, nor to analyse the nature of the recombination processes, but some general properties have, nevertheless, been identified [50]. It was found that in the case of above-gap excitation the exponent $k$ in Equation 2.15 for free and bound excitons is generally between 1 and 2. A strictly linear dependence of the free exciton recombination on the excitation level was shown by Smith et al [51]. At low excitation intensities, where the effects of photoneutralisation are insignificant, the exponent $k$ is the same for free and bound excitons. On the other hand, for free to bound and donor-acceptor pair recombinations, the exponent $k$ is less than unity. The difference in the ensuing spectra is illustrated in Figure 2.6 (a). Measurements of the emission intensity to identify the exponent $k$ need to be done in the wide spectral region, as sometimes the excitation-induced changes include large spectral shifts (Fig. 2.6 (b)).

A more detailed analysis was used by Müllhauser et al [52]. They plotted the intensity and quantum efficiency (taken as the ratio of intensity at a given temperature to the intensity at 4K) of the near band-edge luminescence against the excitation intensity (see Fig 2.7, where a clear deviation from the power-law dependence is easily noted). The data have been fitted with the model based on rate equations [53] and an estimate of non-radiative lifetimes was obtained. This work sets an example on how to extract quantitative information about the nonradiative processes by using the radiative emission data.

Excitation dependence and temperature dependence were used jointly to identify the cathodoluminescence emission lines in cubic and hexagonal GaN grown on GaAs (001) by MBE [54]. The peak energies in the cubic material at 5K were: 3.263 eV (bound exciton), 3.234 eV (donor-band), 3.208 eV (acceptor-band), 3.150 eV (D-A pair). Similar photoluminescence studies of cubic GaN on (100) GaAs by MOVPE [55] identified the bound exciton emission at 3.274 eV, the donor-acceptor pair emission at 3.178 eV and two additional lines at 3.056 eV and at 3.088 eV, also tentatively attributed to donor-acceptor pairs, possibly with other residual acceptors. Such differences in bound exciton and donor-acceptor pair energies are commonly found and not fully explained at present, and it is believed that poor control of strain and strain relaxation conditions may play a role.
2.5. DONOR-ACCEPTOR PAIR SPECTRA

Smith et al [56] have shown that at room temperature the band-to-band transitions dominate in their high quality undoped \( (n=5\times10^{16} \text{ cm}^{-3}) \) wurtzite GaN grown by low pressure MOCVD. The temperature evolution in its own right is insufficient as grounds for distinction between the (free) excitonic and band-to-band mechanisms, as the line is too broad. However, additional identification is feasible by varying the excitation intensity. For band-to-band transitions the peak position of the emission line shifts towards lower energies with increasing excitation intensity, due to enhanced many-body effects and screening of free carriers. The analysis of the exchange energy of electrons and holes lead to the expression for the PL peak emission energy \( E \) to be:

\[
E = E_g(n = 0) - \alpha I_{exc}^{1/3},
\]

where \( \alpha \) is the proportionality constant [56]. The experimental data are in excellent agreement with the above formula. The excitonic transitions do not obey this type of relationship, so it provides a criterion for their identification. The value of the bandgap energy at \( n = 0 \), \( E_g(n = 0) \), is determined as 3.429 eV. Additionally, the excitation dependence, \( I_{exc} \), of the total PL intensity yields \( I_{PL} \propto I_{exc}^{\beta} \) with \( \beta=2.32 \), consistently with band-to-band transitions. The full width at half maximum (FWHM) also increases linearly with \( I_{exc} \), as expected for band-to-band transitions, since increasing \( I_{exc} \) would increase the energy distribution of the electrons and holes and hence the linewidth. Smith et al argue that the radiative recombination rate for band-to-band transitions should be comparable with the recombination rate of excitons. They also suggest that band-to-band transitions may actually be more probable in less pure or less perfect crystals where local fields can lead to exciton dissociation into free carriers. The opposite view was held by Monemar et al [13] who argued that a band-to-band transition would be manifested as a new peak at about 25-30 meV higher than the energy of the A exciton, and this peak would gradually take over the main PL intensity at the expense of the excitonic transition with increasing excitation level. However, in their work the PL studies as a function of excitation intensity were not carried out.

2.5.3 PL intensity and dopant concentration

It is difficult to establish the dopant concentration by measurements of the photoluminescence intensity alone. Firstly, experimental measurements of absolute intensity are difficult and require the use of specialised techniques. Secondly, differences in the nature and strengths of recombination channels may play an important role in films with the same dopant concentration, but with different defect structures. The photoluminescence intensity saturates once the concentration of a particular type of a centre is increased to a point where the recombination through it accounts for the generation rate of free carriers. In typical conditions such as the lifetime of 1 ns, typical of
exciton states, this concentration may be as low as $10^{15}$ cm$^{-3}$. However, the ratio of spectral signatures of free and bound excitons turns out to be an acceptable measure of the impurity content. A careful analysis of the ratio of the bound exciton to the free exciton emission intensity in Si yielded the following relationship [57]:

$$\frac{I_{BE}}{I_{FE}} = N_f^m$$

(2.17)

where $I_{BE}$ is the bound exciton intensity, $I_{FE}$ the free exciton intensity, and $N_f$ is the ionised donor concentration, $m$ is a constant close to unity. It needs to be noted that this empirical relationship applies only to films with relatively low compensation level. To the best of our knowledge similar work in GaN has not yet been reported.

2.5.4 Lineshape

We have presented the expressions for the energy-dependent PL intensity in the important recombination mechanisms, however they need to be treated with some caution. The measured emission spectrum may depart from theoretical predictions if affected by the reabsorption effects and photon recycling effects. The reabsorption is easily quantified, and the measured spectrum $I_{\text{meas}}$ and the emitted spectrum $I_{\text{em}}$ are related through [58]:

$$I_{\text{meas}}(\hbar \omega) = [1 - R(\hbar \omega)] I_{\text{em}}(\hbar \omega) \frac{1 - \exp[-\alpha(\hbar \omega)d]}{\alpha(\hbar \omega)d}.$$  

(2.18)

Here $d$ is the film thickness, $R(\hbar \omega)$ is the sample reflectivity and $\alpha(\hbar \omega)$ is the energy-dependent absorption coefficient. Owing to the high bandgap absorption coefficient of GaN, in excess of $1 \times 10^5$ cm$^{-1}$, the reabsorption effects in typical GaN films in the micrometer thickness range are very pronounced, and many authors discuss their influence on the fine details of the emission spectra [59].

In principle, the free exciton emission spectrum can be obtained from its absorption spectrum through the van Roosbroeck-Shockley formula 2.19. This formula relates the absorption coefficient $\alpha(\hbar \omega)$ to the spontaneous emission spectrum $I(\hbar \omega)$:

$$I(\hbar \omega) = \frac{8\pi n^2(\hbar \omega)^2 \alpha(\hbar \omega)}{\hbar^3 c^2 \left[ \exp\left(\frac{\hbar \omega - \Delta E_F}{kT}\right) - 1 \right]}.$$  

(2.19)

Here $\Delta E_F$ is the energy difference between the electron and hole quasi-Fermi levels, $n$ is the refractive index. The simulation of the emission spectrum from the absorption spectrum is, however, possible only for highly perfect materials with a homogeneous PL line width and provided excitons are not localised [60]. If localisation effects are strong then the absorption or reflectivity probes the density of free excitons, whereas the PL emission is
dominated by recombination of localised excitons, i.e., the PL emission is related to the density of localised states and its energy distribution. In such case there is no simple relation between absorption spectrum and the resulting PL emission spectrum. Fortunately, such complications can easily be identified from the comparison of the absorption/reflectivity and the PL spectra, since their spectral positions are shifted by an averaged localisation energy (Stokes shift). Localisation of excitons, caused by alloy fluctuations or quantum well width fluctuations, is a common property of excitons in quantum well structures of III-V [60] and II-VI semiconductors [61]. It is also critical for excitons in InGaN and GaN epilayers, and will be discussed separately.

The extrinsic broadening of exciton lines caused by crystal imperfections, strain and impurities results in a Gaussian shape of the exciton line [62, 63]. The effect dominates in strongly localised excitons.

2.6 Lifetime and recombination time

2.6.1 Background

The photoluminescence efficiency is an important measure of quality of a semiconductor material. It is therefore not surprising that significant amount of research is devoted to its studies, particularly through time-resolved emission measurements. The photoluminescence efficiency is determined as:

$$\eta = \frac{1/\tau_r}{1/\tau_r + 1/\tau_{nr}},$$

(2.20)

where $\tau_{nr}$ is the non-radiative lifetime and $\tau_r$ is the radiative lifetime. A critical parameter in determining the PL efficiency is the total lifetime $\tau_{tot}$:

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{nr}} + \frac{1}{\tau_r},$$

(2.21)

In lightly doped materials in the low injection limit the radiative recombination time is given by a simple rule

$$\tau_r = \frac{1}{BN_D},$$

(2.22)

where $B$ is the radiative recombination coefficient. The value of $B$ can be determined using a detailed balance principle and the van Roosbroeck-Shockley formula [64]. The approach is based on computation of the spontaneous emission spectrum from the measured absorption spectrum followed by fitting of the result to the experimental PL spectrum. If the two match closely, then the absolute calibration of the measured PL intensity can be
carried out. Consequently, the integral of the spontaneous emission spectrum renormalised to the absolute value of the emission intensity gives the total radiative recombination rate \[ R_{\text{rad}} = B n p \] (2.23)

Using this method, Muth et al \cite{66} calculated \( B \) to be \( 1.1 \times 10^{-8} \text{cm}^3/\text{s} \) and the radiative lifetime for the electron concentration \( n = 1 \times 10^{17} \text{ cm}^{-3} \) to be 0.9 ns, in contrast with GaAs where the radiative lifetime for the same concentration is in the order of 100 ns. The value of the radiative constant \( B \) of \( 4.4\times10^{-11} \text{cm}^3/\text{s} \) at 300 K is given in Ref. \cite{67}. The upper bound value of \( B \) in Ref. \cite{68} was given as \( 2.4\times10^{-11} \text{cm}^3/\text{s} \) at 300K. Such analysis of the excitonic decay time is not valid in the case of exciton localisation, as commonly encountered in InGaN and GaN epilayers and in their quantum well structures. The influence of localisation effects on exciton dynamics in low dimensional structures is discussed in Ref. \cite{69}.

\subsection{2.6.2 Non-radiative recombination}

In addition to radiative recombination, the photoexcited carriers may recombine non-radiatively through a variety of processes such as trapping and recombination at defects, surface recombination, diffusion away from the excitation spot and Auger recombination. As a result, the PL decay time is often regarded as one of the most sensitive tests of film quality. Generally speaking, any imperfection of the crystal/film results in reduction of the PL decay time of free excitons, due to the increased importance of localisation and/or non-radiative processes.

The non-radiative recombination time, \( \tau_{\text{nr}} \) is determined by the non-radiative recombination centres, these are typically mid-gap levels involved in the Schottky-Read-Hall recombination \cite{70}. An insight into the nature of the non-radiative recombination centres was given by Klaun et al \cite{71} who suggested that structural defects such as edge dislocations and stacking faults do not act as non-radiative centres but are electronically inert. The enhanced non-radiative recombination in the proximity of dislocations can be explained by their decoration with impurities. The role of dislocations in recombination processes in InGaN and GaN will be discussed later.

At low injection conditions, when the photoexcited e-h density is smaller than the doping density, \( \tau_{\text{tot}} \) is dominated by recombination of minority carriers. These conditions are often met in experiments at higher temperatures. In such circumstances a certain simplified analysis may be applicable, as shown by Hangleiter et al \cite{68}. They have measured the temperature dependence of the bandedge PL intensity \( I(T) \), assumed the quantum efficiency \( \eta(0) \) at low temperatures as unity and taken \( \eta(T) \) as \( I(T)/I(0) \). If
the measured decay time is approximately equal to the non-radiative time, then the radiative time is approximately given by:

\[
\tau_{rad} = \tau_{nr} \left[ \frac{1}{\eta} - 1 \right].
\] (2.24)

The radiative time thus obtained can be plotted as a function of temperature and compared with models. The conventional theory [72] predicts a \( T^{3/2} \) dependence for free excitons, however the experimental data of Hangleiter et al show some deviations at higher temperatures (see Figure 2.8). These deviations were explained by thermal dissociation of excitons into free carriers. Since electrons and holes forming an exciton are strongly localised, free excitons are expected to have a much smaller radiative lifetime than free carriers at a given carrier density. The quantitative theory is presented in Ref [73]. The fit yields the free exciton dissociation energy of 27 meV.

The significance of non-radiative recombination can, to some extent, be controlled by the excitation intensity as it may be possible to (partially or fully) saturate the non-radiative channels, or to occupy the localised states, if their density is low. It needs to be noted that the experimentally observed PL decay time \( \tau_{PL} \) may also be affected by the effects of sample geometry, and particularly, by surface recombination. In the case of a parallel slab of a thickness \( d \), the observed decay time is given by:

\[
\frac{1}{\tau_{PL}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} + \frac{2S}{d}.
\] (2.25)

Here, \( S \) is the surface/interface recombination velocity. This formula is applicable if the diffusion constant \( D_e \) is much larger than the product of \( Sd \). At low surface/interface recombination velocity \( S \), the measured \( \tau_{PL} \) approaches the bulk minority carrier lifetime \( \tau_{tot} \). It is known that photon recycling can, in general, change the carrier lifetime \( \tau_{tot} \) to give:

\[
\frac{1}{\tau_{tot}} = \frac{1}{\tau_{nr}} + \frac{1}{\Phi(d)\tau_r}.
\] (2.26)

where \( \Phi(d) \) is the recycling factor [74].

### 2.6.3 Examples of applications

The radiative and non-radiative relaxation of excitons in GaN was examined in Ref. [75]. The excitonic quantum efficiency was studied as a function of the specimen parameters such as the sample and buffer thickness, buffer material, and residual oxygen content. Predictably, thicker and less contaminated samples gave improved quantum efficiencies, and homoepitaxial GaN [6] gave better values than GaN on an AlN buffer. Interestingly, in GaN
epilayers the quantum efficiencies were generally in the 20 % range, whereas bulk GaN shows 25 % quantum efficiency for the free A exciton and 50 % for the neutral donor bound exciton complex. The latter result indicates a rather reduced role of Auger-type non-radiative recombination in excitons bound at neutral donor centres. Similar conclusions were reached by Pau et al [76] who found that the free exciton decay dynamics at the front surface of the film and at the interface side were significantly different. The interface decay time was much shorter, in concert with an increased density of the non-radiative centres.

The time-resolved photoluminescence measurements of exciton recombination at low temperatures [6, 77] show a broad perspective of the exciton behaviour and illustrate the methods available in time-resolved emission studies. The observed emission channels consist of free excitons and donor and acceptor bound excitons. At low temperatures, bound excitons are found to dominate, but are subject to quenching at 50 K and above. At higher temperatures free excitons are the most pronounced feature. Generally, non-radiative processes dominate in epitaxial layers, and the decay times of about 100 ps are typically observed [6, 77]. In thick bulk samples, the free exciton lifetime of about 200 ps is observed, close to the radiative decay time of free excitons [77]. The donor and acceptor bound excitons decay more slowly, with the decay constants of 250 ps and 1200 ps, respectively. Bergman [77] and Godlewski et al [6] observed that at increasing temperatures the donor bound exciton emission is quenched, but at the same time the free exciton recombination increases, giving an almost constant total PL intensity. This effect illustrates a strong interaction between free excitons and donor bound excitons through an important free exciton recombination mechanism of capture to a donor (or acceptor). An interesting effect is observed with increasing excitation intensity, where an increase in the free exciton recombination time is observed [77]. This phenomenon is interpreted as due to partial saturation of the non-radiative recombination channels, most likely dislocations. Further increase of the excitation intensity make it possible to observe the actual radiative recombination time. Saturation of traps at dislocations with increasing number of injected carriers has recently been invoked to explain high performance of GaN optoelectronic devices despite the abundance of dislocations [78]. We will return to this problem later.

The temperature dependence of the free exciton lifetime reflects the capture of free excitons at deep defects, donors and acceptors. This temperature dependence is also affected by exciton localisation, due to poor crystalline quality of GaN epilayers. At low density of structural imperfections and defects, only a weak temperature evolution is observed. If the free exciton decay time is purely radiative, then it should increase with temperature due to thermal redistribution of excitons, caused by scattering with acoustic
2.6. LIFETIME AND RECOMBINATION TIME

phonons. This effect reduces the relative number of excitons with small momenta, the only excitons involved in radiative recombination. Bergman [77] found that the free exciton decay time increases only up to 20 K and, at higher temperatures, it starts to decrease due to the onset of non-radiative processes.

The donor bound exciton and the free exciton decay curves have a different character, free excitons are characterized by a rapid rise followed by an exponential decay, while donor bound excitons have a longer rise time, following the free exciton decay. Bergman [77] concluded that this indicates the population increase of donor bound excitons formed by the capture of free excitons. This result indicates that impurities should be avoided in active parts of the opto-electronics devices, since donor and acceptor bound excitonic recombination processes compete with free excitonic transitions.

The value of 200 ps for the radiative time of free excitons in GaN is much shorter than in GaAs (3.3 ns at 2K [79]). An increase in the recombination probability in GaN compared to GaAs is related primarily to the higher bandgap photon energy. The free exciton decay time \( \tau \) depends on the photon energy \( \hbar \omega \), the exciton absorption coefficient \( \alpha_{ex} \) and the refractive index \( n \) as:

\[
\tau \propto \frac{1}{(\hbar \omega)^2 n^2 \alpha_{ex}}.
\]  

(2.27)

This expression explains the factor of 1/20 compared to GaAs.

The recent value of 200 ps for the radiative exciton lifetime in GaN is possibly one of the longest reported (other authors give the values of 35 ps for FE and 55 ps for BE or even about 5 ps [80]), but still it falls well short of the actual theoretical prediction for the radiative lifetime. These were presented in Ref. [81]. The expression for the radiative lifetime is [82, 83]:

\[
\tau_r = \frac{2\pi \epsilon_0 m_0 c^3}{n \epsilon^2 \omega^2 f},
\]  

(2.28)

where \( f \) is the oscillator strength, and other symbols have their usual meaning. The oscillator strength for the free excitons, calculated within the effective mass approximation, is given by:

\[
f = \frac{E_p}{\pi \hbar \omega} \times \left( V/a_X^3 \right),
\]  

(2.29)

where \( E_p \) is the Kane matrix element, \( V \) is the volume of the unit cell and \( a_X \) is the effective Bohr radius of the free exciton. The effective Bohr radius of the free exciton in GaN was estimated by \( a_X = 0.528(m_0 \epsilon / \mu \epsilon_0) \) Å, where \( \epsilon = n^2 \approx 5.8 \epsilon_0 \) and \( \mu \) is the reduced effective mass of \( \approx 0.16m_0 \). With the
value of $a_X = 20\text{Å}$ thus obtained and $E_p \approx 18$ eV, the oscillator strength $f$ is 0.012 and $\tau_r \approx 800/f$ (ps). For bound excitons an estimate only is given, and, assuming that the oscillator strength is in the range of unity, the radiative lifetime of approximately 1 ns is obtained. We note here that these theoretical predictions show an opposite trend to that observed in [77], where the bound exciton lifetime is longer than that of free excitons. This is a clear indication of non-radiative relaxation processes for free excitons which, at low temperature, are trapped at donor/acceptor centres, forming bound excitons. The capture of excitons, in addition to trapping of carriers by non-radiative centres (defects and impurities) thus plays a major role in the population decay of free excitons examined in [81].

The dynamics of fundamental optical transitions probed by picosecond time-resolved photoluminescence was also studied by other authors, for example by Jiang and Lin [84] and Mair et al [85]. The latter work is focussed on the properties of ionised donor-bound excitons in GaN doped with both Mg and Si at concentrations $5 \times 10^{18}\text{cm}^{-3}$ and $1.5 \times 10^{17}\text{cm}^{-3}$, respectively. The ionised donor-bound exciton is identified approximately 11.5 meV below the neutral acceptor bound exciton and 20.5 meV below the free exciton peak. The free excitons decay rapidly, within 20 ps, as a result of rapid capture by acceptors and ionised donors. The ionised donor bound excitons decay much more slowly than the acceptor bound exciton (with the decay time of 180 ps), suggesting that the state is stable at low temperatures. Reduction of the acceptor bound exciton PL decay time by a competing Auger-type transition provides a possible explanation. In the process, the energy of the recombining electron-hole pair is transferred to a second hole bound at the same centre. The hole is then excited into a valence band state. Such process leads to ionisation of acceptors while the exciton energy is dissipated by phonon thermalisation.

The temperature dependence of radiative lifetime in GaN was also examined by Brandt et al [86]. They carried out the lifetime analysis in conditions where different recombination processes (band-to-band, free exciton, bound exciton) could not be spectrally resolved. In such circumstances, the measured radiative lifetime is a composite of individual lifetimes. The observed decays showed a bi-exponential behaviour, with the decay times in the order of 250 ps. Such bi-exponential decays are typical of capture processes in multilevel systems, and require a nonstandard analysis. Brandt et al have taken the radiative decay rate as equal to the peak intensity of the transient PL signal divided by the incident fluence. This approach is valid, provided the exciting pulse is much shorter than any recombination processes in the sample. To normalise the radiative rate at 0K, the value of 250 ps was used as calculated using the theory of Rashba [87]. The rate equations described the formation and dissociation of free excitons, capture
and emission of free excitons by neutral donors and capture and emission of electrons by charged and neutral donors. As all capture coefficients are unknown, the authors assumed that capture is much faster than recombination; under these conditions the population in each level decays with a common time constant. They also used the principle of detailed balance to obtain analytical expressions for the common radiative decay rate \( \gamma_{\text{eff}} \). Importantly, these expressions make it possible to quantify the contribution of each of the recombination channels. Below 20 K the bound excitons dominate the recombination, and between 20 K and 50 K the bound excitons have largely dissociated and free excitons become dominant. The free carriers become important at 100 K, but even at room temperature the free excitons contribute to the radiative rate. The free excitons spectrally dominate in all samples except in the highly doped case, where high electron background reduces the free exciton decay rate. Free to bound (donor-hole) transitions are insignificant in all films except in the highly doped, where they contribute between 100 K and 300 K. The temperature dependence of the radiative lifetime and the result of the fit to the analytical formula is shown in Figure 2.9.

### 2.6.4 Recombination rates and excitation dependence of emission intensity

The importance of various recombination mechanisms can be identified through the calculations of recombination rates which have appeared in recent literature. One of the examples is described in the work by Griesbacher et al [88] who discussed competition between the edge and yellow luminescence in GaN. The principal claim in this work was that the yellow band emission is the principal recombination channel competing with the bandgap emission. This is a rather common assumption, since yellow emission in GaN is considered parasitic, however, surprisingly, it has not yet been experimentally verified. The rate equation model introduced by Griesbacher et al took into account the electron/hole populations in the bands and on shallow donor states, and the population of deep stats involved in the yellow PL. Contrary to the accepted view, the authors assumed that the transition takes place from a band to a deep level. This assumption was supported by the absence of saturation at higher intensities; we will show further that such character of the yellow PL is observed only in bulk GaN samples with metallic n-type conductivity. The rate equations gave the power law dependence of the PL intensities on the generation rate:

\[
I \propto G^n,
\]

where \( n \) can assume the values of 0.5, 1 or 1.5, depending on the doping level and excitation conditions. It was found experimentally that the band-to-band emission increases linearly with the excitation level over the entire
range of excitation intensities. The yellow emission follows a linear dependence at low intensities and changes to a square root dependence at high intensities. Such behaviour is consistent with the proposed rate equations. Similar model was put forward by Banas et al [89]. Further works [90, 91] revealed that the observed yellow and bandgap emissions are coming from different regions of the film; the bandgap emission is reabsorbed and comes from the top layer of the film (within a fraction of a \( \mu m \)), while the yellow emission is particularly strong at the interface. These effects are ignored by the rate equation model [88].

2.6.5 Photoluminescence excitation spectroscopy

The photoluminescence excitation spectroscopy yields information about the intrinsic excitonic structure, also available through reflectivity and absorption measurements. It provides information on the relaxation dynamics towards the impurity-related photoluminescence lines. If the energy transfer processes are efficient, then, for example, excitation of free excitons leads to bound excitonic or other impurity-related PL emissions. Such observation is then considered a direct proof of the energy transfer. In the case of GaN, such transfer was observed from A excitons to the centres active in the yellow emission, but only at elevated temperature [92], which complicates the discussion of the role of the yellow emission as a parasitic transition in GaN films.

The PL excitation spectra give a direct estimate of the localisation energy in a given material. A typical value of the localisation energy in common semiconducting materials is about few meV [61]. It was thus highly unexpected that the values of more than 100 meV were reported in structures with InGaN quantum wells. The origin of such large Stokes shifts and the accompanying effects, such as the temperature-induced PL blue shift and the red shift of time resolved PL with time is still disputed and was discussed by several authors (see for example Refs [41, 93-103]). It is now understood that the effect comes from both piezoelectric fields in the structure and very strong fluctuations of the In fraction in InGaN quantum wells caused by the phase separation effects. This issue will be discussed separately.

2.7 Strain effects

A particular recombination process in a semiconductor is typically expected to give rise to a sample-independent emission line (band) at a certain sample-independent photon energy. In GaN films grown on lattice mismatched substrates this is no longer the case. Differences in the lattice constants and in thermal expansion coefficients induce strain in the film. The associated hydrostatic strain component modifies the band gap energy compared to
bulk GaN, and, consequently, the position of all emission lines associated with the band edges. Variations of the bandgap as high as 25 meV can occur. The influence of strain on the A, B and C excitonic transitions in GaN was systematically examined by Bigenwald et al [104]. The strain in the samples can be modified by variations in growth conditions, leading to a substantial scatter of the reported free and bound exciton energies. As a result it is often impossible to judge the identity of a recombination process from the energy of the spectral feature alone and reliable assignments are possible only through additional studies. This explains a large number of works devoted to general photoluminescence studies of bandgap emission, for example Ref. [105]. In this work, growth of undoped and Si-doped films was carried out by magnetron sputtering on (0001) sapphire. Donor and acceptor bound excitons were observed at low Si levels at 3.488 eV and at 3.456 eV, respectively. Two donor-acceptor and band-acceptor transitions were observed at 3.364, 3.368, 3.375 and 3.383 eV and explained by two acceptor ionisation energies of 120 meV and 135 meV, while a donor ionisation energy of 14 and 18 meV was obtained. The temperature dependence of the yellow band yielded an activation energy of 11 meV, consistent with the shallow donor energy. Other works focussed on identification and classification include Ref. [106] and numerous others. The benchmark values for various emission energies are available from studies of homoepitaxial nominally strain-free GaN [107]. The values are: 3.483 eV for the free exciton B, free exciton A - 3.4785 eV, donor bound exciton - 3.4718 eV, donor bound exciton (second donor) - 3.4709 eV, acceptor bound exciton 3.4663 eV. In Ref. [107] the identity of donors and acceptors remains undetermined. It is important to note that homoepitaxial films can also be partly strained depending on the contamination level of the film and substrate or due to the fact that Ga- and N-side grown films exhibit different properties. Moreover, the GaN bulk crystals grown at high pressures have a relatively high density of dislocations, in the order of $10^4$ to $10^5$ cm$^{-2}$ [108].

A valuable study performed on films grown with controlled influence of strain was reported by Lee et al [109]. These authors made use of the fact that doping (with Si) is accompanied by a systematic change in strain conditions as measured by X-ray diffraction. The residual strain $\Delta c/c_0$ varied between $1.1 \times 10^{-3}$ to almost zero. This change led to variation of the in-plane stress estimated from the simple expression based on the elasticity theory [110]:

$$
\sigma_\parallel = \left[ \Delta c/c_0 \right] B_M/\nu,
$$

(2.31)

where $c_0$ is the strain-free lattice constant of the bulk GaN, $\Delta c$ is the change in the lattice constant, $B_M$ is the bulk modulus, and $\nu$ is the Poisson ratio. The bound exciton peak energy was found to vary approximately linearly with the compressive in-plane stress at a rate of 42 meV/GPa (see Figure...
2.10). The bound exciton in undoped layers was already shifted with respect to its bulk value by 17 meV, due to large differences of the thermal expansion coefficients of sapphire and GaN. The overall shifts of about 20 meV have been reported.

Advances in understanding of lattice-mismatched film growth have identified a number of other growth parameters that affect strain in the films, and, consequently, the excitonic energies. It was found, for example that GaN films grown on (0001) sapphire but using two different buffers, GaN and AlN, are subjected to different strain, and films deposited on AlN are more strained [111]. Variations of the V/III ratio in a MOCVD growth process have a pronounced effect; if this ratio decreases, the exciton features and the bandgap can blue shift by as much as 20 meV [111]. Finally, GaN layer thickness is an important factor, and the thicker is the layer the smaller its residual strain. Some factors are still not well understood, for example recrystallization of the buffer prior to growth affects the strain as well [111]. In addition to shifts of peak energies, other effects, such as strain-induced variations of the oscillator strength of the B and C exciton have also been reported [112].
Figure 2.1: Basic recombination processes induced by shallow donor and acceptor species in a semiconductor.
Figure 2.2: Localisation energy as a function of binding energy for acceptor and donor bound excitons. After Ref. [114].
Figure 2.3: Photoluminescence spectra of a GaN:Mg sample recorded with two different excitation intensities and normalised to the same peak intensity. After Ref [22].
Figure 2.4: Energy dependence of PL decay time measured of the blue emission in magnesium doped bulk GaN crystals. The PL decay curves were taken at maximum of blue emission band (top curve), at two positions along the low energy wing of the PL (second and third curve) and at the spectral position of the yellow PL (bottom curve). After Ref. [37].
Figure 2.5: Temperature dependent energies of intrinsic excitonic transitions determined by PL spectroscopy in GaN/SiC epilayers and bulk GaN. For comparison data from Ref. [113] obtained in a GaN/sapphire heterostructure using reflectance measurements are also shown.
Figure 2.6: Photoluminescence spectra at 15 K for nominally undoped GaN (a) and highly doped GaN:Mg (b) with various excitation densities. After Ref. [115].
Figure 2.7: Intensity (top) and quantum efficiency (bottom) of the near-band edge luminescence against excitation density (symbols) compared to model calculations. Squares - hexagonal GaN, circles: cubic GaN. After Ref. [52].
Figure 2.8: Temperature dependence of the radiative lifetime. The dashed line indicates the $T^{3/2}$ dependence expected for free excitons or free carriers in a direct gap semiconductor. The full line is the result of theory presented in Ref [68]. After Ref [68].
Figure 2.9: Measured (symbols) and calculated (lines) radiative lifetime versus temperature for four GaN samples. After Ref. [86].
Figure 2.10: Bound exciton peak energies for undoped ($J_2$ line) and Si-doped GaN films as a function of the compressive in-plane stress. The triangle denotes the value for a fully relaxed sample. After Ref. [109].
Part 3

Common deep emission bands in GaN

In addition to the edge emission comprising of various excitonic and other transitions, GaN films usually show deep emission bands. The most commonly studied deep emissions include the yellow PL band (YL), recognised in very early studies in the sixties. The precise nature of this band has not been clearly identified yet. Another deep emission of interest, blue PL (BL) is observed in heavily acceptor doped GaN samples. Below we discuss the nature of these two PL emissions of GaN, emphasising a close relationship between material properties, such as growth and doping conditions, and the nature and strength of these two PL recombination transitions.

3.1 Yellow emission of GaN

Under photoexcitation GaN often emits a broad yellow luminescence band centred near 2.2 eV. The YL band appears in GaN grown by various techniques, under dissimilar growth conditions and on different substrates. Since the YL is commonly found in GaN samples regardless of their growth technique, it is widely regarded that intrinsic defects such as vacancies, interstitials or antisites may participate in its formation. The contribution of inadvertently introduced chemical species, such as C, O and H can not be easily ruled out as these contaminants are found in many GaN films. A variety of technological procedures was found to affect the YL band, for example ion implantation significantly increases its intensity [116]. The YL band in wurtzite GaN is particularly pronounced in poor quality layers [117], and it is also observed in doped films, where it seems to be correlated with the doping level.

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3.1.1 Models of the yellow emission process

The microscopic models of the yellow emission band in wurtzite GaN remain the subject of a continuing debate. All models assume that there is one yellow emission common in all types of GaN samples studied. We will later show arguments why this may not always be the case, as many experimental results indicate that there are several overlapping PL emission bands, occurring in the YL spectral region.

An important early work by Ogino and Aoki [32] was based on luminescence studies, and attributed the yellow band to transitions between shallow donors and deep acceptors strongly coupled to the lattice. A schematic diagram of energy levels in relation to configurational coordinates is given in Figure 3.1. The Ogino and Aoki model assumes radiative recombination of an electron from a shallow donor (with binding energy of about 25 meV) with a hole on a deep acceptor located 860 meV above the valence band [32]. This model was further supported by PL studies under hydrostatic pressure [118] where the YL band was observed to shift to higher energies with increasing pressure. This shift follows the pressure-induced movement of the band edges and it indicates that a shallow hydrogenic state takes part in the YL recombination. Such observation is consistent with the Ogino and Aoki model, but also with the free (electron)-to-bound (hole on deep acceptor) or deep donor-shallow (hydrogenic) acceptor origin of the YL. Thus precise identification of a detailed microscopic mechanism exclusively through high pressure studies is not feasible. A similar pressure-induced shift was observed in the YL measurements in bulk heavily n-type samples and in GaN epilayers.

An alternative model presented in the work of Glaser et al. [119] was based on the results of optically detected magnetic resonance (ODMR) measurements. According to this work, the principal transition responsible for the yellow emission takes place from a deep donor to a shallow acceptor. The Glaser model [120] implies a two-step process: a non-radiative electron transfer from a shallow donor to a deep double donor followed by radiative transfer from the deep donor to a shallow acceptor. The Glaser model is supported by results of ODMR investigations of Mason et al [121]. Both Glaser et al and Mason et al reported that a deep donor signal was observed in their ODMR studies. This signal appeared as an enhancement of the YL intensity at the magnetic resonance and interpreted as a proof of the donor-acceptor pair origin of the YL. Thus it was concluded that the YL donor-acceptor pair process involves the deep donor - shallow acceptor pair recombination.

Other models of the yellow emission have also been proposed. A most
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A popular approach assumes broadening of the participating defect levels and formation of large potential fluctuations in doped samples. For example, Banas et al. [89] proposed that the YL arises from an ensemble of midgap states and the relevant transition is from these states to the valence band. Their photoluminescence excitation shows a strong peak at 3.36 eV suggesting that a donor state takes part as an intermediate step in the relaxation process. The excitation power dependence of the YL is found to be proportional to the square root of power, a similar dependence is predicted by the rate equations in the midgap state model. A prominent role of potential fluctuations in heavily doped samples was also reported for Si-doped GaN [122].

The recent ODMR studies of Godlewski et al [123] and Bayerl et al [124] in Mg doped bulk GaN samples indicate another possible mechanism of the YL emission, which explains its behaviour in heavily oxygen-contaminated samples codoped with acceptors. In Figure 3.2 we show the ODMR signals observed in heavily Mg doped bulk GaN detected in the spectral region of the YL. An anisotropic ODMR spectrum is composed of a group of resonance lines around \( g = 2 \) and another group at about \( g = 4 \). Such ODMR spectra were previously observed for excitons bound at neutral complex centres and explained by the spin triplet resonance [125]. We thus propose that the new ODMR spectrum observed by us has a similar origin. If so, the ODMR investigations indicate a contribution of a new recombination channel, namely recombination of an electron and hole at a closely associated donor-acceptor pair forming a neutral complex centre. A detailed analysis of the angular dependence of the spectrum could not be performed, due to a large width of the observed resonance. We could not thus identify the microscopic model of the complex active in the YL. However, recent calculations suggest a possible explanation of the observed triplet ODMR spectrum. Recently, the Mg-O complexes were found theoretically to have a fairly low formation energy [126]. The Mg-O complex consists of a single donor, which compensates a single acceptor, thus it is a close analogue of a donor-acceptor pair and a prime candidate for the neutral complex centre observed in the ODMR experiments. If this hypothesis is confirmed, the introduction of Mg into the crystals may not only compensate the charge on oxygen donors, but could also deactivate oxygen centres acting as single donors, if found in close proximity.

The above analysis of the ODMR data leads to an alternative interpretation of the YL in Mg doped samples. The model is based on high probability of finding close donor-acceptor pairs. In such pairs, due to exchange interaction of an electron bound at a shallow, oxygen-related donor with a hole at an acceptor the PL can be no longer described in terms of donor-acceptor pair transitions and the bound exciton model should be introduced [125]. At this stage the identification is tentative and it needs to be further supported.
by calculations of energy states of the Mg-O complex.

Currently, most of experimental evidence confirms the original model by Ogino and Aoki [32], at least in GaN samples which are not heavily doped. In such samples only minor modifications of the model are being proposed. For example, the time-resolved PL and ODMR measurements [127] suggested a double donor rather than a double acceptor, as the centre participating in the YL. The Ogino and Aoki model of the YL is also supported by photocapacitance studies [128], which show a trap at 0.94 eV above the valence band, detected only after light excitation at above 2.5 eV. The photocapacitance signal correlates well with the YL intensity pointing to this trap as a recombination path for the YL. Below we list further properties of the YL emission as observed in various experiments.

3.1.2 Empirical features of the yellow emission band

a) Temperature evolution

Various authors report different evolution of the YL with temperature. According to Seitz et al. [129] the yellow band increases in intensity between 30 and 100 K and then it starts to decrease. This feature is not found in all samples, in some films the YL stays relatively constant and then it thermally quenches at above 120 K. The time-resolved spectroscopy at varying temperatures enabled these authors to distinguish a second band overlapping with the YL with the maximum at 2.35 eV but characterised by a much slower decay time. This is another indication of a more complex nature of the YL.

A more involved mechanism of the YL is also suggested by the PL decay studies. The average lifetime of the YL measured as a function of temperature shows two time constants, a dominant decay of 0.2 ms is almost temperature independent, while the second component with a value of 3 ms at 10 K varies with temperature following an exponential law with the activation energy of 13.7 meV. The same activation energy can be used to model the intensity variations. Such property of the PL decay is easy to account for if we assume that two recombination processes contribute to the YL. The temperature independent and fast component can be attributed to free-to-bound recombination, whereas the slow component with a longer decay time and with the activation energy of about 14 meV, to a shallow donor-deep acceptor pair recombination. At high temperatures these two PL recombination processes should be deactivated by thermal ionisation of a deep acceptor. According to Ogino and Aoki [32] the YL emission intensity
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decreases at high temperatures and is well described by the expression

\[ I(T) = \frac{I(0)}{1 + C \exp \left( \frac{-E^*}{kT} \right)} \]  

(3.1)

Here \( C \) is a constant and \( E^* \) is the activation energy of 860 ± 40 meV [32]. The observed activation energy was consequently related to the ionisation energy of a deep acceptor and the model of shallow donor-deep acceptor was proposed. Considering, the proposed shallow donor-deep acceptor model of the donor-acceptor pair transition, the YL emission should also decrease when shallow donors are ionised. The energy of 13.7 meV reported by Sitz et al [129] can indeed be explained by shallow donor ionisation. Such deactivation process was however not observed by Ogino and Aoki, we believe that this may be due to a strong contribution of free-to-bound transition to the YL in their films.

b) **YL halfwidth**

The YL can be approximately described by a Gaussian line shape, and the PL halfwidth is typically in the order of 0.4-0.5 eV. The PL halfwidth varies with temperature according to the equation:

\[ W_{em}(T) = W_{em}(0) \sqrt{\coth \frac{\hbar \omega_e}{2kT}}. \]  

(3.2)

Here \( \hbar \omega_e \) is the energy of the effective vibrational mode of the excited state (≈ 40 meV). Such temperature dependence is only expected for the donor-acceptor pair mechanism of the YLs, thus it provides a strong argument in favour of such origin. However, the two models of shallow donor-deep acceptor and deep donor-shallow acceptor pair recombination cannot be distinguished in these measurements. A similar PL halfwidth may be observed for free electrons localised by potential fluctuations near the conduction band edges to a deep acceptor strongly coupled to the lattice.

c) **Excitation intensity dependence**

The yellow band shifts to lower energies with increasing excitation intensity, by about 10 meV as the excitation level is decreased by a factor of ten. This result supports the donor-acceptor pair origin of the YL. With increasing excitation density, the distant donor-acceptor pairs are saturated and their relative contribution to the PL decreases. This effect leads to an effective spectral shift of the YL towards the recombination of close pairs.

The intensity dependence of the YL in a wide range of excitation powers with the focus on competition between the YL and the bound excitons
was examined by Grieshaber et al. [130]. They formulated a detailed rate equation model including the conduction and valence states, deep states involved in the YL and shallow donor states. The YL in their films is found to follow a linear power dependence at low excitation intensities, changes to a square root dependence at higher excitation densities and does not saturate. Surprisingly Grieshaber et al. [130] did not observe any change in the width of the YL for excitation intensities up to 50 W/cm².

d) Photoluminescence excitation spectra

The photoluminescence excitation spectrum of the yellow band reported by Ogino et al. [32] is dominated by the bandedge peak, where, at low temperatures, the three main excitonic transitions, A, B, and C can be resolved. There is also a low energy tail extending down to about 3.4 eV at 4.2 K. In carbon-doped samples with a strong YL, a characteristic excitation band below the bandgap can be observed with the maximum at about 3.19 eV and the width of 0.40 eV. Comparison of the PL and PL excitation bands yields a zero-phonon transition energy of 2.64 ± 0.05 eV. A similar PL excitation spectrum taken at 1.8 K is reported by Hofmann et al. [127]. In addition to a structured edge emission where the three free excitonic transitions A, B and C, as well as an acceptor and donor bound exciton peaks can be observed, a characteristic band extending to 2.4 eV and with a maximum near 2.8-3.0 eV is seen. The most detailed PL excitation studies reported so far were carried out by Colton et al [131]. Using selective PL excitation they were able to resolve the contributions of at least two PL transitions to the YL emission. These authors conclude that with their bandedge excitation the excited YL is dominated by recombination of distant donor-acceptor pairs. However, a new type of YL emission can be selectively excited. This new PL shows a fine structure and is attributed to the recombination of electron-hole pairs at closely associated donor-acceptor pairs. Thus, the PL excitation studies confirm our results of the ODMR investigations, in which a triplet resonance was observed and attributed to the recombination of exciton bound at closely associated donor-acceptor pairs.

e) Time-resolved spectroscopy

The time-resolved studies of YL in GaN epilayers formally agree with the donor-acceptor pair recombination model of this emission, since the results can be analysed using the model of Thomas and Hopfield [132]. Recently, Hofmann et al. [127] showed that the photoluminescence decay of the YL matches closely that expected for pair transitions and that a shallow donor is implicated. However they also underline the apparent lack of Coulombic interaction between the two centres active in the recombination process. The authors failed to observe any shift in energy between the YL observed
at short and long time delays and at different time windows. This led them to conclude that the YL mechanism involves a shallow donor-deep donor recombination. Similarly, Seitz et al. [129] did not observe any shift in their time-resolved spectra. The anticipated shift can be calculated using the shallow donor concentration and the value between 5 meV and 10 meV can be estimated for samples used in Ref. [127]. We emphasise here that in our own measurements on cubic GaN [33] a shift of similar magnitude was, in fact, observed with shorter delay and gate times (see Figure 3.3). We believe that inadequate (too long) time delays and time windows were responsible for the negative result in Refs [127, 129].

In n-type GaN our PL kinetics studies indicate that the free-to-bound recombination process, which we attribute to recombination of delocalised electron with holes at deep acceptors, increasingly contributes to the YL emission. The relevant PL decay curves taken on bulk GaN samples are shown in Figure 3.4. In the nominally undoped highly n-type bulk GaN an energy-independent decay of YL is observed with the PL decay time in the ns range, which we explained by degenerate n-type conductivity of uncompensated bulk crystals [123]. We thus conclude that in the samples with shallow donor concentration, above the Mott transition limit, the YL shows the characteristics of the free-to-bound transition and thus different PL kinetics and temperature dependencies. Due to small ionisation energy of shallow donors, the free to bound transition is observed nearly at the same spectral region as the donor-acceptor pair YL emission.

A very different dependence is observed both for the YL and BL bands in acceptor compensated crystals. The PL decay spectra taken at 2 K in heavily Mg doped crystal show a non-exponential PL kinetics. The fast decay is followed by a slow decay component, with a time constant up to 500 µs. The PL decay time is photon energy dependent. Longer decay times are observed at the low energy tail of the PL emission, a characteristic property of donor-acceptor pair recombination transitions [132].

3.1.3 Microscopic origins of the centre responsible for the yellow emission

The studies of deep traps often give a variety of trap energies that may support almost any model of YL. A variety of thresholds observed in photoemission capacitance spectroscopy and optical transmission ranges from 0.87 to 3.1 eV [106, 133, 134]. Deep level transient spectroscopy and photocapacitance data taken by Calleja et al. [128] show two clear thresholds at 2.5 eV and at 1 eV. The capacitance step amplitude at 1 eV correlates well with the YL intensity. The latter value agrees relatively well with the 1.2 eV energy of the 3− charge state of gallium vacancies in GaN predicted the-
oretically [135]. Other authors give, however, different values for the same state, for example 0.3 eV above GaN valence band is predicted in Ref. [136]. Thus coincidence of energies can not be treated as a definite identification of deep acceptors responsible for the YL. Recently Fleischer et al. proposed a modification of this model. They suggested that a complex of gallium vacancy and oxygen forms a deep acceptor active in the YL [137]. The energy position of this state in the GaN bandgap is not known yet.

Calleja et al. [128] invokes the concept of a broad band of trap states to explain long times needed for capacitance stabilisation. A similar distribution of states was suggested by Qiu et al. [138] to account for the photoconductive response of undoped GaN to photon energies between 1.5 and 3.0 eV. The surface photovoltage spectroscopy in conjunction with PL was recently employed to shed light on the energy distribution of the YL-related levels [139]. The surface barrier height (surface charge density) was found to correlate with the ratio of the yellow to band edge PL intensity, and the surface state density increases with increasing YL/bound exciton ratio.

The donor and acceptor species active in the YL emission could be due to native defects or impurities, or, alternatively, to extended defects such as dislocations or grain boundaries and practically all these alternatives were proposed and analysed. For example, numerous reports point to the YL being enhanced by or associated with extended defects. However, the fact that the YL is present and often very strong in bulk GaN films with a much lower extended defect density than GaN in thin film form strongly suggests that the extended defects themselves are not a unique source of YL. The association can be explained by the well-known affinity of extended defects to attract native defects or impurities forming the Cottrell atmosphere. This effect is stimulated by strain fields surrounding the extended defects, which may facilitate the formation of other native defects or getter impurities. The relative enhancement of the YL with respect to the edge PL emissions can also be due to the destructive influence of local electric fields at charged dislocations on the formation rate of excitons. It is thus possible that a frequently observed anticorrelation between the intensity of the YL and density of extended defects (dislocations) may be due to this indirect influence.

Assuming the shallow donor to deep trap model, no significant changes in the YL signal should be expected with increasing level of n-type doping as the deep trap density should be the limiting factor. However certain doping procedures clearly modify the deep trap concentration. The effects of doping on the PL bands in doped, codoped and undoped GaN provide a very strong argument for the donor-acceptor pair recombination character of the YL (2.2 eV) and also of other red (1.8 eV) and blue (2.8 eV) luminescence bands [140]. According to this report, doping with Si donors
enhances the YL, while Mg acceptor doping generates the blue band and, upon codoping with Si and Mg simultaneously, the red band is induced. It is suggested that the two former bands are self-activated, that is a fraction of the dopant atom is converted into deep centres of with the opposite electrical activity by association with vacancies (self-compensation). The degree of self-compensation in Si doping is small, but it is significant for Mg doping. We will return to this point later, here we only point out that several other authors tried to examine the anticipated correlation between doping procedures and strength of the YL, with varying degree of success. Such studies have, for example, shown that the YL can be suppressed by p-type doping of GaN [141]. This indicates that the YL is associated with a defect, with a low formation energy in n-type material but high formation energy under p-type conditions. This behaviour is characteristic of acceptors; these are more easily formed in n-GaN than in p-GaN due to energy gained by partly compensating donors. By the same argument, donors are more easily formed in p-type GaN. The compensation effects will be discussed again in the context of blue PL in Mg-doped GaN.

The studies of the YL as a function of doping density [142] also show that the density of the compensating centres is proportional to the doping density. This behaviour is consistent with simple acceptors or donors, such as carbon, silicon or oxygen contributing to the YL. We can not reject such interpretation of the YL, but we point out that both p-type and n-type doping shifts the position of the Fermi level in the sample and thus it dramatically affects the formation rate of different intrinsic defects in GaN [136,143–145]. This fact is often ignored in the explanation of the observed results.

Several acceptor centres were proposed to be responsible for the YL. The association of YL with carbon was suggested by Ogino and Aoki [32] and supported by others. This model of the YL has been theoretically investigated by Neugebauer and Van de Walle [143]. They have found that carbon has very high formation energies in a variety of sites, for example at the Ga site where it acts as a donor, and also at interstitial sites. The only configuration with a relatively low formation energy is that of a shallow acceptor at a substitutional N site. As such, carbon can not be directly involved in YL. It can not form complexes with Ga vacancy; as they are both acceptors, they occupy a negative charge state in n-GaN and thus repel each other. This result rules out the involvement of carbon in the YL. The results of Neugebauer and Van de Walle were also confirmed by Boguslawski and Bernholc [146]. These authors confirmed that carbon at a gallium site should behave as an effective mass shallow donor, whereas carbon at a nitrogen site is expected to be a shallow acceptor, with the binding energy below that of a Mg acceptor.
The involvement of nitrogen vacancies in the YL has also been discussed by other authors [147]. In this work the YL band was studied as a function of deposition temperature in the MOCVD process and the microstructure, carbon, oxygen and hydrogen contamination were examined. The YL was found to be stronger at grain boundaries, where high concentrations of hydrocarbons are present. The latter result was not, however, confirmed by other authors. Thermal annealing to 1000°C was found to increase the YL by a factor of 1.5, accompanied beyond 850°C by GaN decomposition through evaporation of nitrogen molecules. This suggests that nitrogen vacancies may play a role in the YL mechanism. The direct involvement of nitrogen vacancies in the YL is not, however, supported by theoretical calculations. Neugebauer and Van de Walle [143] proposed that a native defect, either a Ga vacancy or a related complex is responsible for the YL. Their calculations indicate that a Ga vacancy produces a triply-charged \((V_{Ga}^{3-})\) acceptor level which acts as a compensating native defect in n-type GaN. A variety of complexes such as \(V_{Ga}-O\) and \(V_{Ga}\)-donor [137] (see Figure 3.5) generate close deep acceptor states in the range 0.9 - 1.1 eV. These results rest comfortably with the picture of YL as due to several closely spaced deep acceptor states.

Neugebauer and Van de Walle [143] have calculated the equilibrium concentrations of defects in n-GaN in a Si-doped material in the presence of oxygen. They found a significant concentration of \(V_{Ga}-O_N\) complex acceptor centres, about one order of magnitude less than the shallow donor concentration. The concentration of \(V_{Ga}\) was also significant. The association of YL with Ga vacancies either isolated or in complexes can explain why the YL is observed only in n-GaN. This is because the equilibrium concentration of \(V_{Ga}\)-related defects decreases rapidly as the Fermi level moves away from the conduction band. Likewise, in Ga-rich growth conditions the Ga vacancies are less likely to form, leading to a reduced YL intensity.

The works by Saarinen et al [148,149] and Mattila and Nieminen [150] give further evidence that cation vacancies and/or their complexes are common in n-type samples. The concentration of these defects increases with increasing \(V/III\) molar ratio. The concentration of gallium vacancies is related closely to the intensity of the YL band. Mattila and Nieminen [150] underline that complex formation between cation vacancies and substitutional oxygen donors is a very likely process. The dominant charge-state is doubly negative and its energy state in the gap is dominated by the vacancy level.

The nature of shallow donors in GaN was discussed by many authors, and results of earlier doping studies are somewhat contradictory. For example Ogino and Aoki [32] showed that Si and O doping did not affect the relative intensity of YL to band edge emission, while C doping clearly enhanced it.
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According to Nakamura et al. [151] an increased doping with Si and Ge produced a moderate decrease of the YL to band edge emission ratio. These results are very surprising, since oxygen [143, 152, 153] and silicon [146, 154] are the two most common shallow donors in GaN and in GaN epilayers and oxygen was shown to be involved in both YL and BL emissions in bulk GaN samples [123]. It is often forgotten that silicon at a nitrogen site acts as a deep acceptor in the GaN lattice. Its energy position is predicted to be about 1.2 eV above the valence band edge [146], i.e., at or very near the position of the deep acceptor active in the YL. The formation energy of Si_N is, however, relatively high [146] and thus Si prefentially occupies gallium site and acts as a shallow donor only.

The direct support of the role of oxygen in the YL was furnished by Toth et al. [155]. In this original experiment, cathodoluminescence kinetics was used to study electron-beam-induced impurity diffusion. These studies were supplemented by cathodoluminescence imaging and wavelength-dispersive X-ray spectrometry.

The issue of oxygen-related donor in GaN was recently revisited by Chen et al. [156]. These authors reported a striking similarity between the local vibrational spectra of the deep oxygen donor in GaP and oxygen in GaN. They also argue that the 0.88 eV PL of GaN is, in analogy to GaP, due to capture of an electron by an excited shallow state of the oxygen donor (substituting nitrogen) followed by radiative recombination to a deep ground state of the oxygen donor. This model requires further experimental support to be fully verified.

A study of YL in Se-doped GaN films has been reported by Chen et al. [157]. Unlike Si, selenium substitutes on N site. An equivalent of the yellow band was observed in the photoconductivity spectra. The persistent photoconductivity effect was found for photon energies down to 2.3 eV, that is within the range of yellow emission. It should be emphasised that GaN films without the YL do not show the persistent photoconductivity effects [158].

Spectral signatures of defects associated with the yellow emission have been also observed in Raman spectroscopy measurements [159], and several low energy peaks with a Raman shift between 10 meV and 30 meV were identified. These peaks are enhanced in resonance with the YL transitions and are being attributed to electronic excitations of donors, while the lowest peak is identified as a quasi-local vibrational mode. This study indicates that all shallow donors in GaN may be involved in the YL emission.
3.2 Blue emission in acceptor doped GaN

The blue photoluminescence (BL) band is present in acceptor doped GaN layers. In heavily Mg-doped samples an asymmetric PL band can be observed with a maximum at approximately 3 eV and a low energy wing extending down to about 2 eV. This PL gradually replaces the YL, as shown in Figure 3.6 where we present the PL spectra of bulk GaN samples compensated with different acceptors. The decrease of the YL intensity with p-type doping was explained earlier, and is related to the Ga vacancy generation rate being correlated with the Fermi level position.

In GaN layers grown on sapphire the peak position of the BL varies with the doping level and shifts to lower energies with increasing Mg concentration [22, 160]. Such a shift was attributed to either large potential fluctuations in heavily doped samples [21, 115, 160] or to deep donors in the GaN lattice created during doping with acceptors [23, 160, 161] by the self-compensation process [22, 160]. By self-compensation we understand here the process of spontaneous generation of donor or acceptor defects, which counteracts the attempt to increase the intentional p- or n-type doping level. The simple explanation of the process is that the energy required to promote one or several electrons (holes) from the Fermi level to the impurity level may become smaller than the formation energy of a given intrinsic defect. If so, the formation of a native defect results in compensation of the sample and in lowering of the system energy. Since intrinsic defects (vacancies, interstitials, antisites) are created as a consequence of doping, the doping process may result in a change of film stoichiometry, as discussed by Boguslawski et al. [136].

The model of strong potential fluctuations was recently supported by the results of Oh et al. [115]. They observed that the BL strongly shifts to higher energies with increasing excitation density, similarly to the reports by Eckey et al. [160]. The BL at low excitation intensities has a maximum at about 2.85 eV and progressively shifts to about 3.2 eV at high excitation conditions. The authors also claim that the observed temperature dependence of the BL is consistent with free to bound (electron to acceptor) recombination transitions. Such assignment of the BL agrees with the results of the PL kinetics investigations of Smith et al. [21].

The model of potential fluctuations was earlier proposed to explain the emission properties in heavily doped GaAs [162, 163]. These potential fluctuations are due to charge compensation effects and large concentration of ionised impurities. We point out, however, that the results of Oh et al. can also be explained within the model of donor-acceptor pair transitions. The reported strong blue-shift of the PL maximum with increasing excitation
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Density is also expected for the donor-acceptor pair process. The blue-shift itself does not provide distinction between these two models of the BL.

The ODMR investigations of Glaser et al [164] also do not confirm the importance of self-compensation processes in their samples. The red-shift of BL is observed in samples with high Mg concentration. The BL in the sample with Mg concentration below $10^{19}$ cm$^{-3}$ is due to shallow donor-shallow acceptor pair recombination and has a structured form with a well-resolved zero-phonon line and three LO-phonon replicas. With increasing acceptor concentration, the PL broadens, while the fine structure is not resolved at the Mg concentration above $10^{19}$ cm$^{-3}$. Such broadening can be explained by potential fluctuations in the structure caused by nonuniform distribution of charged impurities. In addition to broadening, the PL red-shifts from its initial position with the band maximum moving to 2.7 eV at the Mg concentration of $5 \times 10^{19}$ cm$^{-3}$. The ODMR studies indicate the same origin of the BL in lightly and in heavily Mg-doped samples. The magnetic resonances of shallow donors and Mg acceptors were detected through the change in intensity of the BL emission indicating the donor-acceptor origin of the PL. Thus the shift of the PL maximum cannot be explained by the change of defects active in the PL process, but it is consistent with the potential fluctuation model. The same authors report that the $g$-factors of shallow donor and Mg-acceptor vary from sample to sample. The latter observation was also confirmed in other works [165]. It was reported that the $g$-factor of the Mg acceptor in GaN epilayers varies between 2.102 and 2.005 for $g_{||}$ and 1.94 and 2.00 for $g_{\perp}$. This result is not yet fully explained. In other materials the electron spin resonance and ODMR measurements are commonly used for defect identification, since the $g$-factor and its anisotropy are treated as a unique feature of a given defect. Apparently this is not the case in GaN epilayers, with large potential fluctuations in films, large nonuniformities of the material and fluctuations of strain and/or electric field.

Several other groups indicate that deep donors in addition to shallow donors are involved in the BL transition. Following the PL and deep level transient spectroscopy investigations it was proposed that doping with Mg acceptors is accompanied by generation of at least three deep donors [22, 160, 162]. Thus, the term "Mg-related deep donors" was coined [160]. The energies of these donors were estimated to be 240 meV, 350 meV and 850 meV [160], or 265 meV, 400 meV and 615 meV [162]. We point out, however, that similar deep donor levels were also observed in samples not doped with acceptors. For example, the 234 meV, 578 meV and 657 meV donors were recently observed in n-type MBE-grown GaN samples, which were not Mg doped [166].

The multi-band character of the BL and involvement of deep donors in the emission is confirmed by ODMR investigations by Godlewski et al. We
PART 3. COMMON DEEP EMISSION BANDS IN GaN

studied the origin of BL in bulk GaN samples, which are metallic n-type prior to acceptor doping. In Figure 3.6 we show the 2 K PL spectra observed in the as-grown GaN sample (not compensated with acceptors), the Zn doped sample, the Ca doped sample and in two Mg doped samples, one lightly doped and the other heavily doped. The PL spectrum of the as-grown sample is dominated by the YL emission with the maximum at 2.26 eV. The acceptor doped samples either show a two-band PL with YL still well resolved or, in the case of the heavily doped film, an asymmetric and intense BL with a long, low energy tail. In the latter case, the YL is not resolved as a separate PL emission, but likely to contribute to the low-energy wing of the BL. The ODMR signals were detected via the intensity increase of either the entire BL emission band, or by selecting different spectral regions using a set of optical filters. We identified at least three slightly anisotropic and overlapping ODMR signals (D1, D2, A1), with $g$-factors of: $g_{\parallel}=1.995$ (D1), $g_{\parallel}=1.982$ (D2), and $g_{\parallel}=2.042$ (A1), as shown in Figure 3.7. All values are determined with the accuracy of ($\pm 0.005$). The first two signals (D1 and D2) are relatively narrow (10 mT (D1), 19 mT (D2)) and slightly anisotropic, with $g$-factors close to 2. They show typical features of deep donor-related ODMR signals in GaN [121, 167, 168]. The shallow donor-related signal (slightly anisotropic with $g$-factors of $g_{\parallel}=1.9514$, $g_{\perp}=1.9486$ [169]), which was reported previously [121, 164, 167, 169], is not resolved in this work. The shallow donors are however, apparent in the observed fast components of the PL decay, and can also be deduced from the temperature dependence of the PL intensity, not discussed here. We thus expect that, similarly to the situation reported by Glaser et al. [164], shallow donor-shallow acceptor pair recombination contributes to the high energy wing of the BL. The third anisotropic signal (denoted as A1) has a $g$-factor larger than 2 ($g_{\parallel}=2.042 \pm 0.005$) and shows the characteristic of an acceptor-related signal. Such value of the $g$-factor agrees with range of $g$ values reported for the Mg acceptor in the GaN lattice [165]. We thus tentatively associate the A3 resonance with Mg acceptors. The relative intensity of the D1 and D2 ODMR signals varies within the spectral region of the BL (see Figure 3.7), but the A1 signal was detected within the whole spectral region of this emission, which means that the same acceptor (Mg acceptor) participates in all PL transitions responsible for the BL. These properties of the ODMR signals confirm a multi-band nature of the BL and the contribution of donor-acceptor transitions to this PL, as both donor- and acceptor-related signals are observed.

The PL spectroscopy and PL kinetics investigations of bulk GaN samples fully support the multi-band character of the BL. We can not, however, conclude whether doping with Mg (and also with other acceptors) is accompanied by self-compensation processes, in which deep donor levels are introduced. Our studies only prove that the BL and possibly self-compensation is not a unique property of Mg doping. Doping with Ca or Zn also leads to
3.2. BLUE EMISSION IN ACCEPTOR DOPED GaN

an asymmetric PL band, in close analogy to the BL in Mg-doped crystals. We also point out that the YL emission is still observed in acceptor doped samples, but becomes weaker in Zn doped and in lightly Mg doped samples. In heavily Mg doped samples the YL is no longer resolved, but is likely to contribute to the low energy wing of the broad BL band.

The donor-acceptor contribution to the BL, as concluded from the above ODMR study, is also confirmed by our PL kinetics measurements. The PL decay curves for acceptor doped samples (see Figure 2.4) are strongly non-exponential and show that the slow components of the decay are energy dependent. As already mentioned, such properties of the PL kinetics are characteristic for donor-acceptor pair recombination.

The origin of deep donors active in the BL emission and their relation to Mg doping are still not fully explained. But if created as a consequence of doping (self-compensation) these donors are most likely to be related to native point defects either directly or indirectly, for example as a complex with an intrinsic defect [170, 171]. The formation energy of a given intrinsic defect strongly depends on the Fermi energy and thus a particular defect formation can be stimulated by p-type doping. The theoretical calculations [136, 144, 145, 152] indicate that depending on doping conditions nitrogen or gallium vacancies or Ga interstitials can be formed. The antisite defects, so important in other III-V semiconductors, are also formed in the GaN lattice. For example, in Ga-rich conditions self-interstitials and antisites are favoured. In both Ga-rich and N-rich conditions the most important defects are vacancies [135]. Recent theoretical calculations indicate that upon doping with Mg the Fermi level is pushed down, which can considerably increase the formation rate of nitrogen vacancies [172, 173]. Thus nitrogen vacancies, which can occur in the $3^+$ and $1^+$ charge states, can act as compensating defects in p-type doped GaN [126]. The vacancies can also form complex centres with impurities. Mg-$V_N$ complexes are thus good candidates for deep donors created by Mg doping [174].

Intrinsic defects can also form complexes with hydrogen, present in large quantities in MOCVD-grown samples. The role of hydrogen complexes in YL and BL emissions and the influence of annealing processes related to acceptor activation in MOCVD films on the stability of Mg-H and $V_N$-H complexes remains unclear but is being pursued with increasing interest [152, 174, 175]. It is too early to make definite statements about the origin and efficiency of self-compensation processes and on the role played by hydrogen in these phenomena.

The recent theoretical calculation of Reboredo and Pantelides [174] indicate that compensation processes in Mg-doped GaN can include self-compensation
of the Mg acceptor by the Mg donor (interstitial magnesium). The authors conclude that complexes involving self-interstitials and interstitial impurities can play a major role in compensation processes responsible for low p-type doping efficiency. This point requires further experimental evidence.
Figure 3.1: The configurational coordinate diagram of the transitions responsible for the YL after Ref. [32]
Figure 3.2: Anisotropic spin triplet resonance detected in the spectral region of the YL emission in a heavily Mg compensated bulk GaN sample.
Figure 3.3: The PL spectra accumulated at selected delay times, between 0 and 0.2 µs and between 100 µs and 140 µs in undoped cubic GaN. After Ref [33].
Figure 3.4: The PL kinetics of the YL emission observed at 2K in undoped and in Mg-compensated bulk GaN sample. Nonexponential and energy dependent decay is observed in the latter case.
Figure 3.5: Atomic geometry of the Ga vacancy and of the $\text{V}_{\text{Ga}}$-$\text{O}_N$ complex in the 3$^-$ and 2$^-$ charge state where all defect levels are fully occupied. The numbers give the increase of the bond length in %. The bulk bond length is 1.94 Angstrom. Adopted from Ref. [143]
Figure 3.6: The 2K PL emission of undoped (a) and acceptor compensated with Ca (b), Zn (c) and Mg (d, e) (lightly doped (d) and heavily doped (e)) bulk GaN samples.
Figure 3.7: Optically detected magnetic resonance spectra detected via broad and asymmetric BL emission of heavily Mg compensated bulk GaN crystal. The spectra were detected by selecting different spectral regions with low-pass (LP) filters.
Part 4

Piezoelectric effect in GaN and its influence on emission

It has recently been realised that strong piezoelectric effects in GaN and related compounds may have a significant impact on a range of material and device properties. The area is developing rapidly, and many issues have only provisionally been addressed. First reviews of the piezoelectric effects in the nitrides, and GaN in particular, have appeared in the last few years, see for example Ref. [176] and Ref. [177].

4.1 Fundamentals of piezoelectric effects in perfect crystalline GaN

GaN typically crystallises in wurtzite structure. Its basic unit cell is defined by the edge length $a$ of the basal hexagon, the height $c$ of the hexagonal prism and the parameter $u$, the anion-cation bond length along the (0001) axis in units of $c$; in GaN $a = 6.040$ bohr, $c/a = 1.6336$ and $u = 0.376$. The wurtzite structure lacks inversion symmetry and thus yields spontaneous polarisation. Therefore, a complete description of polarisation effects in GaN needs to include both the spontaneous and piezoelectric contribution, that is additional polarisation induced by variations of strain. The wurtzite crystal structure has the hexagonal $6mm$ symmetry, and, consequently, the piezoelectric tensor of wurtzite crystals $d_{ij}$ has three different nonzero components (piezoelectric strain coefficients): $d_{33}, d_{31} (= d_{32})$, and $d_{15}(= d_{24})$ [178]. The first two are relevant for extensional strain and the third component for shear strain. We have recently determined their values using interferometric methods [179–181]. Sometimes the piezoelectric stress coefficients $e_{ij}$ are used, these are related to $d_{ij}$ through a tensor relationship [182]:

$$e_{ip} = \Sigma_q d_{iq} E_q,$$  \hspace{1cm} (4.1)
where $e_{qp}^E$ is the elastic stiffness tensor at constant electric field. $d_{15}$ for GaN has been measured to be $3.1 \pm 0.2 \text{ pm V}^{-1}$ [183]. The values of $d_{31}$ and $d_{33}$ are given in Table 4.1, other coefficients are given in Table 4.2.

The GaN films have two faces: a Ga face and a N face. They correspond to polarities where the bonds along the $c$ direction are from Ga cations to N anions and N anions to Ga cations, respectively (see Figure 4.1). Most GaN structures are grown along $c$ or (0001) direction, which is also the direction of spontaneous polarisation $P_{eq}$. The piezoelectric polarisation along the $c$ axis is expressed through the piezoelectric coefficients as:

$$P_{\text{piezo}} = e_{33} \varepsilon_3 + e_{31} (\varepsilon_1 + \varepsilon_2).$$  (4.2)

Here, $\varepsilon_3$ is the strain along the $c$-axis, $\varepsilon_3 = (c-c_0)/c_0$ and the in-plane strain $\varepsilon_1 = \varepsilon_2 = (a-a_0)/a_0$ is assumed to be isotropic. Spontaneous polarisation has only recently been understood [184-186]. In general, spontaneous polarisation manifests itself as polarisation charge at hetero-interfaces and it can be observed in unstrained structures [187]. While the consensus on the magnitude and the relevance of spontaneous polarisation has not yet been reached, certain optical effects such as large red spectral shifts in otherwise unstrained GaN quantum well structures have been attributed to spontaneous polarisation effects [187]. It is quite likely, although not yet proven, that the magnitude of spontaneous polarisation can be controlled by appropriate growth procedures.

The spontaneous polarisation and piezoelectric coefficients were recently calculated by Bernardini et al [186] using the Berry phase approach and the relevant values are given in Table 4.3. For comparison, the same authors show the piezoelectric constants for a number of III-V and II-VI compounds, also including those crystallising in a cubic structure. It is known that in polytypical materials the values of the piezoelectric constants agree to within a few percent. Interestingly, the values in all three nitrides appear to be close to those in II-VI oxides. The absolute value of the piezoelectric constants $e_{33}$ and $e_{31}$ are about ten times larger than in the III-V and II-VI compounds, and only about three times smaller than in ferroelectric perovskites. The spontaneous polarisation, that is the polarisation at zero strain is also very large, and that of AlN is only 3-5 times smaller to that in ferroelectric perovskites.

The values given in Table 4.3 allow us to evaluate the importance of spontaneous polarisation compared to the piezoelectric polarisation [177]. For a biaxially strained layer the effective piezoelectric polarisation is given by:

$$P_{\text{piezo}} = [e_{31} - (e_{31}/e_{33}) e_{33}] (\varepsilon_1 + \varepsilon_2),$$  (4.3)
where the last term in brackets is the in-plane strain, $c_{31}$ and $c_{33}$ are the elastic constants. As an example, in the Al$_p$Ga$_{1-p}$N film deposited on GaN [177], the values of $P_{\text{piezo}} = -4.26 \times 10^{-2}$ C/m$^2$ and the spontaneous polarisation, $P_{\text{sp}} = -5.2 \times 10^{-2}$ C/m$^2$ are calculated. The piezoelectric and spontaneous polarisation contributions are thus comparable in size. This observation was confirmed in recent PL kinetics studies of unstrained GaN quantum wells in GaN/AlGaN heterostructures [187]. The piezoelectric and spontaneous polarisation in films with Ga polarity and tensile strain in the alloy have the same sign and point in the [0001] direction. The sign of polarisation is such that it produces a potential energy of electrons decreasing from the Ga face towards the N face (see Figure 4.2). An important consequence of this feature of spontaneous polarisation is that the relative direction of the two polarisation components depends on growth conditions [188]. The structures grown directly on sapphire GaN film have N-phase polarity, but if an AlGaN buffer is grown on sapphire prior to GaN deposition, then the GaN film has Ga-face polarity. In the latter case, and for films under tensile stress, both polarisations are directed towards the substrate. However, in conditions of a compressive stress, the two fields point in the opposite directions. Further consequences of this effect on GaN device behaviour and on material parameters are discussed below. The two contributions can also be easily evaluated in structures, such as InGaN/GaN, where the piezoelectric contribution is opposite in direction to the spontaneous contribution, but even larger in absolute magnitude [177].

### 4.2 Film surface polarity

The epitaxial growth of nitrides takes place along a the polar axis of the material and thus the surface can be expected to have a certain polarity. However so far this aspect of the films, difficult to determine experimentally has been mostly overlooked (for a comprehensive review of experimental methods see Hellman [189]). Two relatively simple methods include measurements of the sign of the piezoelectric effect - difficult due to high conductivity, but feasible in interferometric measurements [179, 190] and chemical studies through etching in KOH and NaOH, where it was found that smooth films etch more slowly. More advanced techniques used include coaxial impact collision ion scattering spectroscopy used by Sumiya et al [191]. While the problem has not been conclusively resolved, Hellman has presented a "standard framework" to describe the polar faces of GaN. Selected characteristics include surface morphology of the films with the smooth side of the as-grown GaN being identified as the N face and the rough side as the Ga face. The films with hexagonal pyramidal morphology grown on sapphire are considered to have the top N face, and in the smooth films grown by MOCVD the top surface is thought to have Ga face. The Ga face of GaN
is chemically more stable than the N face. KOH and NaOH solutions will etch the N face but not the Ga face. At the same time, methods of growth of single face GaN films have been explored. For example Bridger et al. [192] report growth of Ga-polar GaN films by radio-frequency plasma assisted MBE on AlN buffers, while N-polar films were nucleated using GaN buffer layers by the same technique. These different polarities affect the relative orientation of piezoelectric and spontaneous polarisation components.

4.3 Piezoelectric phenomena in real structures

Theoretical predictions of a significant magnitude of piezoelectric effects in GaN and related heterostructures is often poorly supported by experimental results. Many factors in real heterostructures conspire to reduce their relative significance. For example, in partially relaxed heterostructures with misfit dislocations, the piezoelectric effect is reduced, but the spontaneous polarisation should remain unchanged. This effect is manifested through high internal electric field as recently reported in unstrained GaN QWs [187]. In films grown with domains of inverted polarity, the overall polarisation effects may even be effectively eliminated, as shown in Ref. [193, 194]. This prompted many groups to pursue growth strategies that would lead to single domain GaN films. Single-domain growth is additionally important because films with different polarities respond differently to various chemical procedures, such as wet or dry etching. Any intermixing of the interfaces between the two types of domains would reduce the effect of differences in spontaneous polarisation, as the charge would be effectively distributed over a certain volume. Therefore, in order to fully exploit all the potential of the piezoelectric effects in GaN and related structures, growth technologies are being developed to yield good domain control and, ultimately, single domain films. The calculations presented in the preceding section (Equation 4.3) indicate that the effect of spontaneous polarisation is significant, and therefore intense electric fields should appear and band edge energies be strongly affected. However, it needs to be noted that the overall magnitude of the effect depends on screening of the internal electric fields in the bulk and at heterointerfaces and on the extent of strain relaxation. Improvements in structural quality of GaN (AlGaN) epilayers are not related to the magnitude of spontaneous polarisation in a straightforward way. To illustrate this effect in Figure 4.3 we compare the PL emissions from two GaN/AlGaN multiple QW structures grown by MBE on sapphire with a thick MOCVD-grown GaN buffer layer. Two MBE growth methods were used: one sample was grown by MBE using the electron cyclotron resonance (ECR-MBE) nitrogen plasma cell, and the other was grown using a new generation radio frequency (rf-MBE) nitrogen plasma cell. The first structure has poor structural quality and relatively high surface roughness,
with granular film morphology as shown in Figure 4.4. The comparison of the PL spectra indicates large differences in optical properties of the two structures. The relatively weak PL emission from the 8 nm wide QWs in the ECR sample partially overlaps with the PL emission from the underlying MOCVD film, whereas the emission from the 6 nm wide QWs in the rf-MBE sample is strong and its spectral position strongly red-shifted compared to predictions based on quantum confinement effects. In this sample the PL from the underlying GaN MOCVD film is practically not observed. The observed red-shift of the PL in the 6 nm QW is due to strong built-in electric fields in GaN QWs, as further supported by the time-resolved PL measurements. Due to a strong built-in electric field in GaN QWs in the rf-MBE structures, the PL decay time is significantly larger compared to about 100 ps observed for free excitons in the ECR-MBE sample and in MOCVD-grown epilayers. The decay times of excitons in wider QWs are up to 1000 times longer [187]. The effect is clearly seen in Figure 4.6 in 4 nm and 6 nm wide QWs, where we compare the PL decay times in these two QWs with those in 2 nm wide QW and in the MOCVD-grown GaN buffer layer. The built-in electric field in the 2 nm QW can not significantly separate the recombining e-h pairs and does not change the potential across the QW. In consequence, the oscillator strength of the PL transition is not affected and the PL recombination energy is unchanged.

In equilibrium, that is without external effects such as strain and also heat flow, the charge responsible for spontaneous polarisation is usually compensated by either ambient charges or internal charges forming an equal and opposite dipole moment [195]. Large densities of surface and interface states provide an additional mechanism for the reduction of interface electric fields due to spontaneous polarisation. The phenomenon is well documented in ferroelectrics, where no traces of an internal electric field have been reported so far. Similar interface states have been identified in AlGaN/GaN heterostructures [196, 197], and on the surface of GaN films [192]. In the latter report the surface state density has been directly measured to be $9.4 \pm 0.5 \times 10^{10}$ cm$^{-2}$ using the electric field force microscopy. The same technique is capable of imaging planar distribution of the domains. While the consensus on the magnitude and relevance of spontaneous polarisation has not yet been reached, certain optical effects such as large red spectral shifts in otherwise unstrained GaN quantum well structures have been attributed to spontaneous polarisation effects [187]. We believe that the data shown in Figure 4.3 demonstrate that spontaneous polarisation may be affected by growth conditions.
4.4 Implications of piezoelectric effects for devices

Strong lattice polarisation effects identified in GaN provide unique opportunities for GaN and related materials to be used in high temperature piezoelectric sensors and in pyroelectric detectors. Most significant applications were found, however, in devices based on two-dimensional transport, such as HEMTs. It needs to be emphasised that, independently of piezoelectric properties, GaN possesses a suite of transport properties desirable from the point of view of high frequency/high current density electronic devices, and their combined effect leads to a vastly improved power handling capability (for details see for example Ref.[177]). However, piezoelectric effects introduce additional, beneficial features. It was found, that piezoelectric effects affect the concentration of 2D electrons (2DEG) confined in the triangular potential well at the AlGaN/GaN heterointerface. The AlGaN layers grown on GaN are under strain, and the piezoelectric effect induces an electric field. Consequently, charge accumulation (or depletion) takes place at the heterointerfaces, depending on the polarity of the top surface (see Figure 4.2). If the top surface has Ga polarity, then the resulting electric field will drive any available electrons, for example from the ohmic contacts, towards the 2DEG. At some point, a balance is reached as the Fermi level, constant throughout the structure, sets the values of band bending. This effect was recently illustrated by Ramvall et al [198]. We underline here that the present mechanism makes it possible for charge carriers to be introduced from very remote sources, so that donor centres causing additional scattering are not introduced. This phenomenon has thus been termed the "piezoelectric doping". The values of the sheet carrier concentration in AlGaN/GaN heterostructure field effect transistors (HFETs) were found to be of the order of $10^{12-10^{13}}$ cm$^{-2}$ [199–201]. For such a high sheet carrier concentration, the internal electric field can be partly or even fully screened, which may help maintain the rectangular shape of GaN QWs [186]. Accurate control of the doping level is thus crucial for the size of the observed piezoelectric effects.

The second, important aspect of piezoelectric phenomena arises from the influence of polarisation charge on the properties of heterointerfaces. It was found that the static potential at the GaN/AlN interface is different from that at the AlN/GaN interface, and this effect was attributed to spontaneous polarisation differences in GaN and in AlN. As a result, band gap discontinuities could not be conclusively established. This effect has its useful implications for devices, as it may allow to vary the Schottky barrier height and to significantly reduce the operating voltage of the nitride field emitters.

The third effect is related to optical properties of quantum well structures. It was found that the observed transition energies in nitride quantum wells
4.4. IMPLICATIONS OF PIEZOELECTRIC EFFECTS FOR DEVICES

Generally show large red shifts compared to simple calculations (see Figure 4.3 and Figure 4.5). This red shift is attributed to electric fields due to piezoelectric effects [68, 187, 202, 203]. We emphasise that a careful analysis may be necessary to eliminate red-shifted transitions that are simply defect-related and not intrinsic. Such identification can be done using two-photon spectroscopy. The electric field in an alternating sequence of wells $F_{\text{well}}$ and barriers $F_{\text{barrier}}$ can be calculated as:

$$F_{\text{well}} = -\frac{4\pi L_{\text{barrier}} (P_{\text{well}} - P_{\text{barrier}})}{L_{\text{well}} \epsilon_{\text{barrier}} + L_{\text{barrier}} \epsilon_{\text{well}}},$$

$$F_{\text{barrier}} = -\frac{4\pi L_{\text{well}} (P_{\text{barrier}} - P_{\text{well}})}{L_{\text{barrier}} \epsilon_{\text{well}} + L_{\text{well}} \epsilon_{\text{barrier}}},$$

Here, $L$ and $\epsilon$ and $P$ are widths, dielectric constants and polarisations in wells and barriers, respectively. Using these expressions, the values of electric field in the range of $1 \cdot 3 \times 10^6$ V/cm were found. Such high values lead to a significant red shift through a quadratic Stark effect.

The magnitude of the PL red shift can be directly determined experimentally in time-resolved experiments under intense excitation [68, 202, 203]. Immediately after an intense laser pulse the free carrier concentration can be large enough to screen an internal electric field. Figure 4.5 shows that at an early stage after the excitation pulse, the PL is blue-shifted from its final spectral position. At longer delay times after the excitation pulse, the PL red shifts, with a time scale characteristic of the decay of free carriers population.

A range of related consequences of piezoelectric effects have also been observed, such as for example the increased exciton lifetimes observed in time-resolved spectroscopy in GaN quantum wells, as presented in Figure 4.6. The effect is due to reduction of the oscillator strength in GaN/AlGaN quantum wells [68, 187, 202, 203] because of an increased separation of electrons and holes in a quantum well subjected to piezoelectric fields.

The recent studies of piezoelectric effects in the nitrides have considerably advanced our knowledge, but many issues have not been conclusively resolved yet. For example, the effects of domain inversion on the current transport in FET structures have not been established. It is anticipated that the domains might cause the electric field to vary, causing variations in the sheet carrier concentration. These nonuniformities should have a significant effect on the carrier scattering and on device performance.
Table 4.1: Values of extensional piezoelectric coefficients in wurtzite GaN.

<table>
<thead>
<tr>
<th></th>
<th>$d_{33}$ [pmV$^{-1}$]</th>
<th>$d_{33}$ [pmV$^{-1}$]</th>
<th>$e_{33}$ [Cm$^{-2}$]</th>
<th>$e_{31}$ [Cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN bulk</td>
<td>3.7$^b$</td>
<td>-1.9$^b$</td>
<td>1.12$^b$</td>
<td>-0.55$^b$</td>
</tr>
<tr>
<td>clamped single crystal</td>
<td>2.8 ± 0.1$^b$</td>
<td>-1.4 ± 0.1$^b$</td>
<td>0.85$^b$</td>
<td>-0.41$^b$</td>
</tr>
<tr>
<td>clamped polycrystalline</td>
<td>2.0 ± 0.1$^{b,c}$</td>
<td>-1.0 ± 0.1$^{b,c}$</td>
<td>0.60$^b$</td>
<td>-0.30$^b$</td>
</tr>
</tbody>
</table>

$^a$ Reference [186]
$^b$ Reference [190]
4.4. IMPLICATIONS OF PIEZOELECTRIC EFFECTS FOR DEVICES

Table 4.2: Values of the extensional piezoelectric coefficients in cubic GaN obtained in [190].

<table>
<thead>
<tr>
<th></th>
<th>(d_{14} \text{ [pmV}^{-1}])</th>
<th>(e_{14} \text{ [Cm}^{-2}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN, bulk</td>
<td>6.4 ± 0.2</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Table 4.3: Calculated spontaneous polarization and piezoelectric constants in units of C/m².

<table>
<thead>
<tr>
<th></th>
<th>(P_{eq})</th>
<th>(e_{33})</th>
<th>(e_{31})</th>
</tr>
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<tbody>
<tr>
<td>GaN</td>
<td>0.029</td>
<td>0.73</td>
<td>-0.49</td>
</tr>
<tr>
<td>AlN</td>
<td>-0.081</td>
<td>1.46</td>
<td>-0.6</td>
</tr>
<tr>
<td>InN</td>
<td>-0.032</td>
<td>0.97</td>
<td>-0.57</td>
</tr>
</tbody>
</table>
Figure 4.1: The wurtzite crystal structure of GaN. The size of spheres indicates the ionic radii (Ga is smaller than N). After Ref. [189].
Figure 4.2: Band diagrams for standard framework Ga face heterostructures. The charge accumulation (or depletion) takes place at the heterointerfaces, depending on the polarity of the top surface. After Ref. [189].
Figure 4.3: PL emission of two multiple quantum well structures grown by ECR-MBE and rf-MBE. The samples were grown on sapphire substrate covered with 1.5 \( \mu \text{m} \) thick MOCVD-grown GaN epilayer. The PL from the 6 nm QW in the structure grown with radio frequency (rf) nitrogen plasma cell is strong and considerably red-shifted from its expected spectral position. The PL from the 8 nm QWs in the sample grown with electron cyclotron resonance (ECR) nitrogen plasma cell is weak and overlaps with a strong PL emission from the MOCVD-grown buffer layer.
Figure 4.4: Surface morphology of GaN epilayers grown by MBE studied with atomic force microscopy.
Figure 4.5: Comparison of cw and pulsed PL spectra measured in an MBE-grown GaN/AlGaN QW structure with three (2nm, 4nm and 6nm wide) GaN QWs. The top spectrum was recorded with a high intensity 10 ns exciting laser pulse. A dramatic modification of the PL emission is observed with PL spectra from wider QWs significantly blue-shifted compared to their cw spectral positions.
4.4. IMPLICATIONS OF PIEZOELECTRIC EFFECTS FOR DEVICES

Figure 4.6: The PL decay spectra measured under 2 ps pulse excitation at 2 K. The PL kinetics of free excitons is shown in the underlying MOCVD-grown GaN buffer layer and in three (2nm, 4nm and 6nm wide) GaN QWs grown by rf-MBE.
Part 5

Dislocations and their effects on emission

Most GaN epilayers are grown on lattice mismatched substrates. This fact has important consequences as lattice mismatch results in strained epilayers and leads to generation of high concentration of dislocations. Both these effects are important for optical and electrical properties of GaN. The values the lattice mismatch are given in the Table 5.1 which shows that both tensile and compressive (consile) stress is possible in GaN films grown on different substrates. In the latter case stress can induce changes of the sequence of hole states, where light hole states can be shifted in energy below the heavy hole states. In strained epilayers the position of PL peaks can be red- or blue-shifted from their expected positions in unstrained layers [204]. The shift should be directly related to the strength and character (tensile or consile strain) of the stress. However, the experimentally documented situation is not so simple. Shifts of the PL spectra often do not follow changes in the lattice constants, and, likewise, differences in the thermal expansion coefficient, growth temperature, cooling rate etc. can be equally important.

The large lattice mismatch between GaN films and substrate materials and between GaN, InN and AlN leads to generation of a large density of dislocations in the epilayers. In a good quality optoelectronic material designed to work as a light emitter the density of dislocations should be below $10^5$ cm$^{-2}$ [205]. In this context, bright light emission from GaN-based light emitting diodes, with dislocation density as high as $10^{10}$ cm$^{-2}$ was very surprising. This observation prompted a continuing discussion on the role of dislocations in radiative and nonradiative recombination processes in GaN and in InGaN. Overall, the quantum efficiency in many nitride devices is surprisingly high, about 12 % in blue and green LEDs, and 5 % in amber LEDs, and thus comparable to 11 % in high quality lattice matched AlInGaP-based LEDs [206].
We discuss several works clearly showing that dislocations are centres of nonradiative recombination in GaN and InGaN. If so, a dramatic reduction of dislocation density in a new generation of InGaN-based structures using the concept of epitaxial layer overgrowth (ELOG) [207–209]) should result in a large increase of efficiency of light emission. However, despite the decrease of dislocation density by about 4 orders in magnitude, the quantum efficiency of the emission from ELOG structures remained nearly the same [210, 211]. The reason for this surprising observation is still discussed. ELOG grown InGaN-based LEDs show quite homogeneous light emission, while cathodoluminescence (CL) emission from ELOG-grown InGaN and GaN films is strongly affected by dislocations [212]. Such results suggest that dislocations act as centres of nonradiative recombination in InGaN and GaN and that an alternative explanation is required of a relatively low impact of dislocations on light emission processes in InGaN-based optoelectronic devices.

Nakamura [205] and Chichibu et al [211] proposed that nonradiative recombination of excitons at dislocations does not contradict high quantum efficiency of InGaN-based devices, which can be explained by strong localisation effects in the InGaN QW plane. These localisation effects are caused by fluctuations of In fraction in InGaN QW plane and not by high dislocation density in these films [211]. Such large composition fluctuations in a QW plane lead to carrier/exciton localisation and to uncommonly large Stokes shift values between the PL and PL excitation peaks, often as large as 600 meV in green LEDs, 200 meV in blue LEDs and 100 meV in laser diodes [213], or respectively 70 meV, 200 meV and 450 meV for \( x=0.13, 0.35 \) and 0.45 in \( \text{In}_x\text{Ga}_{1-x}\text{N} \) [214].

Concluding, it is believed now that dislocations are efficient centres of nonradiative recombination in InGaN and that localisation effects are crucial to explain high quantum efficiency of InGaN-based LEDs. This explanation of the link between the sample morphology or In composition fluctuations and its optical properties has one weak point. A very homogeneous emission is observed in InGaN-based LED devices, where In fluctuations in a QW plane are rather random. A possible explanation of this contradiction was recently proposed by Bellaiche et al [215]. These authors postulate that alloying of GaN with In leads to strong localisation of the hole states near the valence band edge. If so, strong localisation can also occur in InGaN epilayers with the homogeneous In composition. Recently Narukawa et al [216] proposed that their PL kinetics studies at temperatures above 70 K can be explained by recombination of delocalised excitons. An important role of localisation effects in InGaN QWs was also questioned by Kollmer et al [217]. These authors explained the properties of excitons by strong built-in electric field...
in strained InGaN QWs and not by strong localisation effect. If confirmed, these observations would call for another explanation of the low recombination rate at dislocations and the origin of large inhomogeneous PL line widths, commonly attributed to localisation of excitons.

5.1 Spatially-resolved studies

The relationship between the density of dislocations, PL emission intensity, spectral shape of emission bands, and the rate of radiative recombination was recently explored by Domen et al [218] and Holst et al [219]. The first authors show that the etch pits density (or the density of dislocations) correlates well with density of dark spots observed in the CL mapping investigations and confirm that dislocations are centres of nonradiative recombination in InGaN epilayers. They also show that their emission shares some common features with the emission of quantum dots. This effect results from a combined effect of granular structure of the films and from large In composition fluctuations. Using the spot mode option available in the CL technique they were able to excite the emission from grain centres and from grain boundaries and compare the properties of these two emissions. The radiation decay time from bright spots is relatively long, of about 2 ns, the CL decay time observed from the from the dark spots in the sample is ten times smaller. Similar results are reported by Holst et al [219]. These authors show that the PL kinetics is strongly nonexponential, a typical feature of the PL emission in strongly disordered systems.

These observations confirm efficient nonradiative recombination at dislocations. The carrier/exciton diffusion length in InGaN films can also be estimated in the CL investigations to be about 0.3 μm [218], but other authors report much smaller values in both InGaN and GaN [220]. In other semiconducting materials a short diffusion length is due to enhanced nonradiative recombination of excitons at defect sites and efficient carrier trapping by defects. In InGaN another mechanism appears to be responsible for the observed short diffusion length. The photogenerated carriers/excitons move in the QW plane and can either approach the region of an increased In composition and be trapped or approach a dislocation and decay nonradiatively. The latter process is clearly less probable, since highly efficient light emission is observed. Short diffusion lengths, smaller than a typical distance between dislocations [220]) in InGaN can be thus attributed to numerous regions with an increased In composition rather than to carrier/exciton trapping by impurities and/or extended defects.
Similar scanning CL and electron microscopy (SEM) studies were performed by the present authors in a range of GaN epilayers [91]. We have performed detailed AFM, CL and SEM investigations to establish the link between the strength of the edge and yellow emissions and morphological quality of the samples studied. These investigations were done at room temperature, in conditions relevant for the operation of GaN-based devices. We have studied a range of different GaN epilayers grown by MBE, MOCVD or CVD methods. In Figures 5.2, 5.3 and 5.4 we show the results of these investigations. The AFM profiles of our samples show relatively rough surfaces with granular structure, similar to those shown in Figure 5.1. The granular structure is also well resolved in the SEM images (see Figure 5.2). The grains are typically of about 0.5 µm size or less. Having established the surface topography of GaN epilayers we took monochromatic, spatially-resolved CL images with the detection set either at the edge emission or at the yellow emission. A granular structure of the samples is reflected in large fluctuations of the edge CL intensity (see Figure 5.3). The CL is relatively bright at the grain centres and weak at the boundaries, i.e., in the region of increased dislocation density. We infer that excitons generated at the grain centres tend to recombine there and do not migrate to grain boundaries. This observation thus suggests that strong site localisation of excitons occurs also in GaN epilayers, in analogy to the InGaO films. Similar conclusion was also drawn by Rosner et al [221]. We anticipate the mechanism of the localisation to be different than in InGaO layers. Localisation in this material was explained by large fluctuations in In composition in the film. In GaN samples we relate the observed localisation of excitons to large potential fluctuations in GaN films resulting from their granular structure [222]. Localisation results in creation of quasi zero-dimensional excitons which can recombine practically at the location where they have been created. Thus, their recombination rate is not affected by a large concentration of dislocations, provided that the exciton wavefunction does not penetrate to the region of grain boundaries. The above tentative explanation has one weak point, as one should expect quite different localisation strength in InGaO and in GaN films. However, this is not observed. Rosner and co-workers [221] reported that diffusion length of minority carriers is very similar in both materials, despite the fact that different localisation mechanisms were proposed. This problem remains unsolved and the mechanism of strong localisation in GaN epilayers is far from being understood.

We expected that large intensity fluctuations, observed for the GaN edge emission, should also be noticeable in the YL emission. Surprisingly, the yellow CL (see Figure 5.4) is only very weakly position-dependent. In consequence, the intensity ratio of edge to yellow CL strongly fluctuates in the film plane. We have collected the CL images at varying scan times and at different excitation densities. From these investigation we conclude that the
observed in-plane homogeneity of the yellow CL could not be explained by
signal averaging or by intensity saturation in the CL experiment. We also
used the spot mode option of the CL system and measured the CL spectra
excited at different positions. The results of this experiment are shown in
Figure 5.5. The spot mode CL spectra confirm a homogeneous spatial dis-
tribution of the yellow PL intensity, whereas, the edge PL varies in intensity
by about 250 %.

We have already mentioned that strong potential fluctuations in the GaN
plane can be attributed to strain inhomogeneities, resulting from the gran-
ular structure of GaN films [111]. If so, the peak energies of the emissions
should vary across the sample, since the PL energy depends on the mag-
nitude of the built-in strain. Such shift of the PL energy was reported by
Domen et al [218] in InGaN and by Hacke et al [223] in GaN epilayers. Ap-
parently the shift is not a common property of all GaN layers studied. In
Figure 5.5 we show the CL spectra measured at room temperature at four
different positions in the sample. The peak of the edge PL in GaN is not
shifted when taken at grain centres and at grain boundaries. The spectral
shift of the edge emission is thus either very small, and smaller than the
accuracy of our experiment, or nonexistent. We thus conclude that the ob-
served localisation of excitons and also large fluctuations of intensity of the
dege emission are not always related to pronounced strain effects.

Several other groups studied the relationship of intensity of the yellow and
dge emissions and the sample morphology. Christiansen et al. [90, 224]
explained the homogenous distribution of the yellow PL by a uniform dis-
tribution of screw dislocations. If this explanation is correct, the YL should
be directly or indirectly related to the presence of dislocations in the film,
and should be enhanced at grain boundaries. The latter conclusion was
based on the assumption that dislocations or defects decorating dislocations
participate in the yellow DAP emission [225].

The spatial uniformity of the yellow emission was also examined by Ponce
et al. [226]. They examined undoped GaN MOCVD films grown on a buffer
layer. Spatial distribution of the band edge emission and of the yellow band
in MOCVD-grown GaN on sapphire showed significant nonuniformity [226].
The observed emission nonuniformities were found for both edge (λ=364
nm) and for the yellow (λ=559 nm) emissions. Their spatial variation was
correlated with the columnar structure (low-angle grain size) measured by
transmission electron microscopy. Such columns are typically observed in
wurtzite GaN films with diameters in the order of 200-500 nm. Extended
defects seem to be absent from the interior of these columns and thus the
defect distribution is spatially nonuniform. The authors hypothesise that
the sources of YL were either dislocations at low angle grain boundaries in
the material or point defects, which nucleate at the dislocations. The same authors suggest that the states responsible for the YL either arise directly from the atomic structure of the dislocations or are associated with clustering of native point defects in their proximity.

The nature of YL in undoped GaN on sapphire and in laterally overgrown GaN was investigated by Li et al. [227]. They have suggested that the states responsible for the YL are associated with extended defects. Importantly, they found that the YL could be reduced or eliminated by simply increasing the growth temperature of the buffer layer. This enlarges the hexagonal crystallites and reduces the density of extended defects. Furthermore, in laterally overgrown GaN with a very small density of extended defects, the YL intensity can be suppressed even further. Interestingly, at the same time the authors were also able to suppress the donor-acceptor emission at about 3.2-3.3 eV, which exhibited a clear correlation with YL.

Recently Li and Coleman [228] reported that the intensity ratio of the edge to yellow PL depends on the thickness of the examined epilayer, and that the ratio is smaller in regions closer to the sample/substrate interface, where the density of dislocations is the largest. This observation was questioned by Knobloch et al. [59], who underlined an important role of light reabsorption effects. Light reabsorption affects more strongly the intensity of the edge emission, since this emission overlaps with the spectral region of strong absorption. While the edge PL is strongly reabsorbed upon the passage through the GaN film, the YL band do not overlap with spectral regions of strong absorption, and thus the YL can freely pass through thick films.

The presented results combine into a rather confusing picture. All groups consistently report that the granular structure of GaN films is reflected in large intensity fluctuations of the edge emission. Information on the properties of the YL is, in turn, rather inconsistent. Recently [229] we have proposed that significant differences between the reported properties of the YL can be understood if we assume that several PL emissions are observed in the same spectral region and contribute to the YL.

We verified the possibility that variations of the edge to yellow intensity ratio depend on the sample thickness and location of the point where the emission is excited. This was possible through depth-profiling CL investigations. In this study we used the fact that penetration depth of an electron beam depends on beam energy [91, 137]. In Figure 5.6 we show the results of the depth profile CL study of an MOCVD film. We show the CL spectra taken at two accelerating voltages at constant electrical power conditions. The study was performed using a 2.5 µm thick MOCVD epilayer. At a beam energy of 5 keV the observed CL comes from the near surface region of the
sample. At 20 keV and higher beam energies, the CL is excited close to the GaN/sapphire interface. These excitation conditions were directly confirmed experimentally by observing the infrared substrate-related emission (not shown in the figure) under appropriate conditions. Figure 5.7 confirms the observation of Li and Coleman [228] and the recent results of Fleischer et al [137] that the yellow CL becomes stronger in the interface region. We also observed that the intensity of the edge PL is reduced in the same region.

The mechanism of the observed enhancement of the yellow emission remains unclear. It can not be simply explained by an increased dislocation density in the interface region, since we do not observe an intense yellow CL coming from grain boundary regions, where the dislocation density is high. The most likely explanation relates an increased intensity of the YL to accumulation of defects in the interface region, as suggested earlier in Refs. [230,231]. To clarify this point we performed depth-profiling investigations in a range of other samples, including quasi-epitaxial GaN MBE films grown on sapphire substrate covered with thick MOCVD-grown GaN. In all the samples studied we have observed an enhancement of the YL when excited near the interface region (see Figure 5.7). The YL also red-shifts and shows an asymmetric shape, as shown in Figure 5.8. We also note that the edge emission can be enhanced in the interface region, as seen in Figure 5.7. If the bound excitons dominate the edge emission, the latter observation can also be explained by an enhanced accumulation of defects in the interface region. We must however conclude that the in-plane and in-depth properties of GaN emission are still not fully understood.

The problem of dislocations is apparently more severe in laser diodes with carrier densities larger than those in LEDs by a factor in excess of ten. At increased carrier densities the fluctuating potential and built-in electric fields are screened and the observed Stokes shifts are small [232]. In consequence, the efficiency of light output from laser diodes varies with changes in current density, as was recently reported by Nakamura [205]. Lowering of the threshold current in GaN-based laser diodes may be of advantage, as it not only helps to reduce heat dissipation but also reduces the screening efficiency and consequently the rate of nonradiative recombination at dislocations.

5.2 Recombination at dislocations

It is not fully clear what is the mechanism of carrier recombination related to the dislocations. Dislocations can affect the PL emissions in GaN
and InGaN by introducing competing paths for carrier trapping. They can also introduce short-range potentials and trap excitons by the mechanism known to form excitons at neutral centres. There is also a long list of other possible mechanisms of the PL deactivation, related to carrier trapping by dislocations. When dislocations trap carriers they become then charged and introduce large fluctuations of electric field in the samples. This fluctuating electric field can affect the rate of exciton formation and thus the PL efficiency. Another possible nonradiative recombination process is also due to carrier trapping at dislocations, namely the intensity of the edge PL can be quenched by an Auger-type energy transfer from excitons to carriers trapped at vacancy-related deep centres. Then, the excitons recombine nonradiatively, whereas carriers at dislocations are ionized by an energy transfer process. Concluding, these processes relate to either carrier trapping by dislocations or creation of fluctuations in the films. The latter process was in fact observed experimentally [233] where it was demonstrated that dislocations give rise to a spatially varying surface potential. Moreover, in edge dislocations, the polarisation charge density and electric fields are generated, but only near the interfaces. Recently, Shi et al pointed out that these effects have a rather minimal influence on electrical and optical properties of the material [234]. The most crucial issue is thus the possibility of carrier trapping by dislocations and the role of these effects on the PL emission processes.

Most of the recent studies suggest that dislocations can trap carriers, i.e., introduce deep trap centres in GaN lattice and lead to local fluctuating electric fields [221, 223, 235]. Hacke et al [223] demonstrated that the PL intensity decreases with increasing etch pit density (dislocation density) and also that the diffusion length of minority carriers directly follows changes in dislocation density. The latter effect can be understood if we consider carrier trapping by dislocations leading to the highly inhomogeneous in-plane strain and large in-plane variation of the edge PL. Similar conclusion were drawn by Rosner et al [221] from their CL mapping investigations in ELOG GaN and InGaN epilayers. They demonstrate that the ELOG procedure, which reduces the concentration of dislocations in overgrowth regions also lowers the density of electrically active centres. They report a rather surprising result that the upper limit of less than 200 nm for minority carrier diffusion is the same in InGaN and in GaN epilayers. This value is smaller than a typical inter-dislocation separation, which is significant for explanation of a relatively high light emission efficiency from GaN and InGaN films.

Several groups suggested that carrier trapping can lead to the PL emission. We already discussed the relation between the dislocation density and the YL intensity. Presently, most of the results rule out the dislocations as the microscopic centre responsible for the YL. However, few other PL tran-
sitions were tentatively related to dislocations. Radiative recombination at dislocations was considered by Shreter and Rebane [236], who attributed the PL emission at 3.404 eV to recombination of bound excitons at the c-axis screw dislocations. In turn, the 3.41 eV emission was tentatively assigned to radiative recombination of excitons bound at charged dislocations [236]. This assignment was not confirmed by later investigations of Fischer et al [237]. From the scanning CL investigations they have not observed any correlation between these two and the density of screw dislocations in GaN samples.
### Table 5.1: Lattice mismatch for thin GaN epilayers grown on various substrates.

<table>
<thead>
<tr>
<th>Material</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>+2.5</td>
</tr>
<tr>
<td>α-SiC</td>
<td>+3.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.9</td>
</tr>
<tr>
<td>Sapphire</td>
<td>+14.8</td>
</tr>
<tr>
<td>Si(111)</td>
<td>-16.9</td>
</tr>
<tr>
<td>GaAs</td>
<td>-20.2</td>
</tr>
</tbody>
</table>
Figure 5.1: Surface morphology of GaN epilayer grown by MBE studied with atomic force microscopy.
Figure 5.2: Scanning electron microscopy image of 5 by 5 μm region of MBE-grown GaN epilayer. Granular structure of the film is well resolved.
Figure 5.3: Scanning monochromatic CL image of 5 by 5 μm region of MBE-grown GaN epilayer. Granular structure of the film is well resolved as observed in large intensity fluctuations of the excitonic edge emission of GaN.
Figure 5.4: Scanning monochromatic CL image of 5 by 5 µm region of MBE-grown GaN epilayer. The granular structure of the film, resolved in SEM image, has no effect on the intensity of yellow emission of GaN.
Figure 5.5: The CL spectra measured at four different spots of MBE-grown GaN epilayer of granular structure.
Figure 5.6: The CL spectra of MOCVD-grown GaN measured at room temperature and 5 keV and 20 keV electron beam energy. For 20 keV CL comes from deeper regions of the sample, close to sapphire/GaN interface.
Figure 5.7: The CL spectra of MBE-grown GaN structure measured at room temperature and 10 keV and 25 keV electron beam energy. At 25 keV the CL comes from deeper regions of the sample, close to the sapphire/GaN interface, as confirmed by the appearance of sharp sapphire-related CL peaks.
Figure 5.8: The yellow CL observed in MBE-grown GaN epilayer grown on GaN (MOCVD)/sapphire substrate. The YL collected from the interface region (at 25 keV) is asymmetric and due to two overlapping emissions.
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