Optical properties and degradation of deep ultraviolet AlGaN-based light-emitting diodes

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Abstract

AlGaN alloys have enabled electroluminescence in the deep ultraviolet owing to their large and direct bandgap. AlGaN is part of the III-nitride material system and it shares several properties and technological issues with the more researched GaN and InGaN. AlGaN layers are usually grown on lattice mismatched substrates and contain a relatively high density of extended defects. Strong polarization fields are present in AlGaN-based heterostructures. The problem of low free carrier concentrations in the doped layers becomes more severe in AlGaN, where even the n-type conductivity strongly decreases as the Al molar fraction is increased. All these properties influence the performance of AlGaN-based light emitters. Although deep ultraviolet light-emitting diodes are commercially available and are finding numerous applications, they still suffer from low luminous efficiency and limited operation lifetime.

This thesis addresses three main topics that are related to the technology of AlGaN-based deep ultraviolet emitters: (a) the polarization fields in AlGaN-based quantum wells, (b) the homogeneity of the epitaxial layers and quantum well structures and (c) the aging mechanism of deep ultraviolet light-emitting diodes. AlGaN epitaxial layers and quantum well structures grown by migration-enhanced metalorganic vapor phase epitaxy on sapphire have been studied by time-resolved photoluminescence, degenerate differential transmission pump-probe and near-field spectroscopy techniques.

It was found that the polarization charge in AlGaN-based heterostructures is lower than the predicted value from first principle calculations. It was proposed that the presence of excitons enhances the carrier confinement within AlGaN-quantum wells. A double-scale composition inhomogeneity was measured in epitaxial layers by near-field measurements and dominant nonradiative recombination at the location of the potential minima was observed at some compositions. Moreover, the carrier localization in deep potential minima was measured in quantum well structures. Lastly, alloy fluctuations, dislocations and nitrogen vacancies were found to determine the aging mechanism and operation lifetime of AlGaN-based deep ultraviolet light-emitting diodes.

Keywords: AlGaN, deep-UV LEDs, polarization fields, screening, exciton binding energy, alloy fluctuations, near-field microscopy, carrier dynamics, LED aging.
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List of publications

The thesis is based on the following publications:


The following journal publications are related to the thesis but have not been included in it:


The research results have been presented at the following conferences:


## List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>Al</td>
<td>aluminum</td>
</tr>
<tr>
<td>AlGaN</td>
<td>aluminum gallium nitride</td>
</tr>
<tr>
<td>AlInGaP</td>
<td>aluminum indium gallium phosphide</td>
</tr>
<tr>
<td>BBO</td>
<td>barium borate</td>
</tr>
<tr>
<td>BN</td>
<td>boron nitride</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CH</td>
<td>crystal-field split-off hole</td>
</tr>
<tr>
<td>CL</td>
<td>cathodoluminescence</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>DTPP</td>
<td>differential transmission pump-probe</td>
</tr>
<tr>
<td>EBL</td>
<td>electron blocking layer</td>
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<tr>
<td>EL</td>
<td>electroluminescence</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>far-field</td>
</tr>
<tr>
<td>Ga</td>
<td>gallium</td>
</tr>
<tr>
<td>GaN</td>
<td>gallium nitride</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
</tr>
<tr>
<td>HH</td>
<td>heavy hole</td>
</tr>
<tr>
<td>IC</td>
<td>illumination/collection</td>
</tr>
<tr>
<td>InGaN</td>
<td>indium gallium nitride</td>
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</table>
InN  indium nitride
IR   infrared
LBO  lithium triborate
LED  light-emitting diode
LH   light hole
MEMOCVD  migration-enhanced metalorganic chemical vapor deposition
Mg   magnesium
MOVPE  metalorganic vapor phase epitaxy
MQW  multi quantum well
N    nitrogen
NA   numerical aperture
Nd:YAG  neodymium-doped yttrium aluminum garnet
NF   near-field
NL   nucleation layer
PL   photoluminescence
QB   quantum barrier
QCSE  quantum confined Stark effect
QW   quantum well
SEM  secondary electron microscope
Si   silicon
SL   superlattice
TD   threading dislocation
TE   transverse electric
TEM  transmission electron microscope
Ti:Sapphire  titanium-doped sapphire
TM   transverse magnetic
TRPL  time-resolved photoluminescence
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>$V_N$</td>
<td>nitrogen vacancy</td>
</tr>
<tr>
<td>$V_{Ga}$</td>
<td>gallium vacancy</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>ZnO</td>
<td>zinc oxide</td>
</tr>
<tr>
<td>ZnSe</td>
<td>zinc selenide</td>
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Chapter 1

Introduction

The history of the light-emitting diode (LED) starts in 1907 when the first report on electroluminescence (EL) from silicon carbide crystallites was published [1]. 54 years later the infrared gallium arsenide LED became the first patented LED design [2]. In the following decades, the semiconductor growth technology steadily improved and LEDs emitting in the visible range were introduced in the 60s and 70s. For the initial decades after the first commercialization, the LEDs remained confined to low emission applications as indicators on circuit boards and dialing pads or in numeric displays. Since then, two main goals of the research on solid state light emitters have been the increase of brightness and the widening of the attainable wavelength range via EL. A new era in the history of the LED opened up at the beginning of the 90s with the introduction of high-brightness devices covering the whole visible spectrum: the aluminum indium gallium phosphide (AlInGaP) LED [3] and the indium gallium nitride (InGaN) LED [4-6], emitting in the yellow-red (590 nm<λ<625 nm) and green-blue (470 nm<λ<525 nm) spectral range, respectively. Today, AlGaInP and InGaN LEDs are widely used in traffic signals and large area displays. Furthermore, white-light LEDs based on the InGaN technology have acquired a competitive position in the lighting market [7]. Devices emitting at even shorter wavelengths, in the deep-ultraviolet (UV) spectral range, are the topic of one of the latest chapters in the history of the LED. These new devices are based on the aluminum gallium nitride (AlGaN) ternary alloys, which, like InGaN, belong to the III-nitride material system.

A commonly used classification distinguishes the near-UV (320-390 nm) from the deep-UV (320-200 nm) spectral range. InGaN-based LEDs can be engineered to emit in the near-UV range. The minimum attainable emission wavelength from InGaN-based LEDs is limited by the gallium nitride (GaN) bandgap to about 300 nm. AlGaN was immediately employed to achieve shorter emission wavelengths, initially as barrier material in multi quantum well (MQW) structures with GaN as well material and later in both quantum barriers (QBs) and quantum wells...
(QWs) [8]. The AlGaN-based LEDs are to date the only commercial solid state device capable of providing EL in the deep-UV range between 240 nm and 400 nm [9]. Similar devices with even shorter wavelengths reaching 210 nm have been demonstrated [10, 11].

At present, the most common source of UV light is the mercury lamp. Mercury lamps are used for the curing of polymeric materials and in the process of screen printing. They find application as disinfection tool for water, air and medical equipment. In the lighting industry, they are the excitation source in fluorescent lamps. Mercury vapors emit narrow lines at fixed wavelengths, mostly between 254 nm and 365 nm, which can be converted to visible light using appropriate phosphors. Mercury lamps require a high voltage source to initiate the discharge and they have an expected lifetime of 1000 hours. Other shortcomings include size, weight and, above all, environmental pollution [12]. Compared to UV lamps, UV LEDs have lower power consumption, are more compact and emit a narrower spectrum [13]. Moreover, the emission from UV LEDs can be tuned continuously by alloying, differently from the fixed emission lines from mercury vapor. Table 1.1 shows a comparison between UV LEDs and UV lamps.

<table>
<thead>
<tr>
<th></th>
<th>Mercury lamp</th>
<th>UV LED</th>
</tr>
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<tbody>
<tr>
<td>Form factor</td>
<td>Bulky</td>
<td>Compact, flexible</td>
</tr>
<tr>
<td>Emission spectrum</td>
<td>Fixed, broad, limited available wavelengths</td>
<td>Tunable from 210 nm and up, narrow bandwidth</td>
</tr>
<tr>
<td>Power consumption</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Operation lifetime</td>
<td>1000 hrs</td>
<td>5000 hrs* (predicted value, 40000 hrs†)</td>
</tr>
<tr>
<td>On/off switching speed</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td>Environmental impact</td>
<td>Toxic</td>
<td>Benign</td>
</tr>
</tbody>
</table>

*Value for commercial LEDs by SET, inc. [9] with λ > 300 nm operated in continuous mode at 20 mA. For shorter wavelength devices, the lifetime decreases exponentially down to 300 hrs for 255 nm devices.
†Predicted value from comparison with the more mature InGaN-based LED technology [14].

Additionally, UV LEDs are advantageous as part of spectroscopy instrumentation owing to the low noise of the radiant flux, the possibility of high-frequency modulation and sub-nanosecond pulse generation. Other possible applications include biochemical detection, optical remote sensing and covert communications [12, 15].
Although a steady improvement of the performances of the deep-UV LEDs is taking place, there remains a considerable gap between the achieved external quantum efficiency (EQE) of the InGaN-based blue emitters and the AlGaN-based UV emitters. Fig. 1.1 shows a summarized plot of the reported maximum EQE of III-nitride-based LEDs by different research groups. The obtained values drop as the aluminum (Al) molar fraction is increased in the active region of the devices. Besides, one of the foreseen benefits of the UV LEDs is the longer durability with respect to mercury-based sources. However, the measured operation lifetime of the AlGaN-based devices reaches values largely inferior to the more mature InGaN-based LED technology and, to date, it is only marginally superior to conventional UV lamps. Therefore, the full deployment of AlGaN-based LEDs is hindered by an insufficient wall-plug efficiency and operation lifetime.

Figure 1.1: EQE of UV LEDs for continuous wave (blue circles) and pulsed (red triangles) operation. The closed symbols are from Ref. [16] and the open symbols are more recent data from Ref. [11]. The subdivision of the UV spectral range into the UV-A (400 nm - 315 nm), UV-B (315 nm - 280 nm) and UV-C (280 nm - 100 nm) windows is also indicated.
1.1 Motivation and overview of the original work

In these thesis, several issues that determine the efficiency and durability of deep-UV LEDs have been studied:

(i) III-nitride layers grown on the c-plane exhibit fixed polarization charges located at each side of the layer surface [18]. As a result, an internal electric field is present within the QWs. The internal field separates electrons from holes, decreasing the probability of recombination [19]. Furthermore, the polarization fields may impede the carrier transport to the active region of III-nitride-based LEDs [20, 21] by forming potential barriers. On the other hand, the field-induced band bending is sometimes exploited to achieve higher electrical activation of the dopant impurities [8, 22]. Hence, the characterization of the polarization properties of AlGaN layers is fundamental for the design of efficient devices. The magnitude of the polarization field in AlGaN layers is the subject matter of Paper I and Paper II.

(ii) The polarization fields strongly modify the confinement energy and the barrier potential profile for free carriers in MQW structures. These modifications are likely to have significant consequences on the carrier capture and escape processes in the active region. Furthermore, the internal field in the QWs reduces the exciton binding energy by separating the opposite sign carriers. Excitons have large binding energies in AlGaN alloys and may significantly contribute to the luminescence of AlGaN-based devices. Thus, the effect of the polarization fields on the free carrier and exciton lifetimes needs to be accounted for. Paper III contains a study of the exciton escape probability from the QWs of a deep-UV LED at different bias regimes.

(iii) The insensitivity to dislocation density of the EQE in blue InGaN-based LEDs has been associated with carrier localization at potential fluctuations [23]. Although a similar mechanism may occur in AlGaN-based LEDs [24], the achieved EQE is still much lower than for blue InGaN LEDs (see Fig. 1.1). In order to understand what is really limiting the efficiency of AlGaN-based devices, it is important to examine the carrier localization in AlGaN alloys. The issue of carrier localization in MQW structures with different well thicknesses and AlGaN epitaxial layers with different Al molar fractions has been studied in Paper VI and Paper VIII, respectively.

(iv) High Al molar fraction AlGaN-based LEDs suffer from an increased resistivity of the n-type and particularly of the p-type cladding layers. Higher resistivity of the cladding layers causes an increased device self-heating and current crowding effects. Besides, current leakage and crowding around threading dislocations (TDs) [25] was observed in GaN-based devices. As a result, the wall plug efficiency and the device operation lifetime decrease. Interestingly, the increase of nonradiative recombination in the active region during aging...
1.2. OUTLINE OF THE THESIS

is under debate [26] and it is not clear which defect species is responsible for
the device failure. Paper IV contains a preliminary study of the influence
of point defects on the luminescence decay time in GaN epitaxial layers. Paper V
and Paper VII present studies of the aging and failure modes in
deep-UV AlGaN-based LEDs.

1.2 Outline of the thesis

The rest of the thesis is organized as follows: Chapter 2 summarizes the basic
principles behind the light emission from semiconductors. Furthermore, it describes
the carrier dynamics after ultrafast optical excitation. Chapter 3 describes the
experimental techniques and instruments used in this thesis. The concept of near-
field (NF) and the technology of near-field microscopy are discussed in some detail.
Chapter 4 contains an introduction to the basic properties of the III-nitride material
system. The nature of the spontaneous and piezoelectric polarizations in III-nitride
layers and the used techniques to measure the polarization values are exposed
in this chapter. The growth technology and the structure of deep-UV LEDs are
presented in Chapter 5. Additionally, some issues that affect the efficiency and
durability of deep-UV LEDs are summarized. The issue of inhomogeneities in
AlGaN layers and the aging mechanisms of deep-UV LEDs are treated in separated
sections. Conclusions and suggestions for future work follow in Chapter 6. The
Appendix contains a list of material parameters that were used in the calculations.
Moreover, it contains a brief description of the numerical models for the calculation
of the screening-induced PL energy peak shift and the exciton binding energy in III-
nitride QWs. A description of the original work and the appended articles conclude
the thesis.
Chapter 2

Optical transitions and carrier dynamics

In a LED, an electric current flows through a semiconductor material and is converted into light. Alternatively, semiconductors may emit light via photoluminescence (PL) when excited with an external light source. Short pulse excitation is routinely employed in time-resolved PL (TRPL) and pump-probe measurements, as described in Chapter 3. Solid state theory and semiconductor optics explain the circumstances under which EL and PL occur. In this chapter, some fundamental concepts that are connected with the thesis work are stated. Their derivation can be found in the cited literature.

2.1 Electrons in semiconductors

EL and PL involve the transition of electrons between energy levels inside a semiconductor crystal. Hence, an appropriate description of the energy distribution of the electrons inside the crystal is a prerequisite to explain the luminescence processes. According to the Bloch’s theorem, the electronic wavefunctions in a perfectly periodic potential in thermodynamic equilibrium can be written in the form of propagating waves, or Bloch waves, with associated wave vector $k$ [27]. The electronic band structure $E(k)$ is a representation of the energy levels of the electronic states as a function of $k$. The light-matter interaction is accounted for by means of transitions between equilibrium states [28].

The electronic energy levels are grouped in bands separated by gaps. Within each band, the adjacent energy levels are finely spaced so that the bands can be considered as a continuum of levels. In an intrinsic semiconductor in equilibrium at 0 K, the completely occupied band with highest energy is the valence band (VB), $E_v(k)$, and the next completely empty band is conduction band (CB), $E_c(k)$. The energy difference between the top of the VB and the bottom of the CB is the
energy bandgap, $E_g$. At higher temperatures, the equilibrium carrier concentration in CB and VB depends on the presence of doping impurities and defects. If the electrons are in thermodynamic equilibrium with the crystal at a temperature $T$, the electrons fill up the bands following the Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp\left[\frac{(E - E_F)}{k_B T}\right] + 1},$$  \hspace{1cm} (2.1)

where $E_F$ is the Fermi energy. $f(E)$ quantifies the fraction of occupied states in every energy interval $dE$ around $E$.

In a semiconductor, optical transitions involve states in the VB and in the CB. Near-bandgap optical transitions are much more likely in direct bandgap semiconductors, where the top of the VB and the bottom of the CB occur at the same $k$ value. The absorption of a photon with energy larger than the bandgap causes the transition of an electron from the VB to an empty state in the CB. The transition leaves an empty state or hole in the VB. Holes can be considered as virtual particles in the VB carrying a positive charge. Their energy distribution is also characterized via a Fermi-Dirac distribution. In the following, $f_e(E)$ will be used to indicate the the Fermi-Dirac distribution for electrons in the CB and $f_h(E)$ for the holes in the VB.

Near the top of the VB and the bottom of the CB it is sometimes possible to approximate the shape of the $E(k)$ extrema as parabolas. In this case, it is convenient to define the electron and hole effective masses as

$$m_e = \frac{\hbar^2}{d^2 E_e / dk^2}, \hspace{1cm} (2.2a)$$

$$m_h = -\frac{\hbar^2}{d^2 E_h / dk^2}. \hspace{1cm} (2.2b)$$

Using this approximation, known as the effective mass approximation, the electrons and holes in the parabolic regions of CB and VB, respectively, can be treated as free propagating particles with mass $m_e$ and $m_h$, respectively. Furthermore, the use of the parabolic band approximation yields analytic expressions for the density of states (DOS) in CB and VB, in other words, the number of available states per unit of volume and energy. The derivation can be found in Ref. [29].

### Heterostructures

Efficient III-nitride-based LEDs employ QWs in the active region [13]. The confinement of the carriers in the direction of the QW stack introduces substantial changes in the band structure. The energy levels for the carriers in a QW have the following form:

$$E = E_i + E(k_t), \hspace{1cm} (2.3)$$

where $E_i$ is one of the discrete energy levels associated with motion in the direction of the confinement, and $E(k_t)$ and $k_t$ are the energy and the wave vector component
associated with the motion in the plane of the well, respectively. Moreover, it is convenient to write the electron and hole wavefunctions \( \psi(r) \) as the product of an in-plane plane wave component, function of the in-plane coordinate \( r_t \), and an out-of-plane component, function of \( z \) \cite{30}, as follows:

\[
\psi(r) = F_i(z) e^{i k_r r_t} \sqrt{A},
\]  

(2.4)

The wavefunction is normalized with respect to the QW surface area \( A \) and \( F(z) \) and \( E_i \) are found by solving the time-independent Schrödinger equation:

\[
\hat{H} \psi(z) = E \psi(z),
\]  

(2.5a)

\[
\hat{H} = -\hbar^2 \frac{d}{d z} \left( \frac{1}{m_{e,h}(z)} \frac{d}{d z} \right) + U(z).
\]  

(2.5b)

In the effective mass approximation, position dependent effective masses \( m_e(z) \) and \( m_h(z) \) for electrons and holes, respectively, are considered. The potential energy profile \( U(z) \) is determined by the CB and VB offsets, \( \Delta E_c(k = 0) \) and \( \Delta E_v(k = 0) \).

Figure 2.1: Free carrier distribution in CB and VB: (a) Fermi-Dirac distributions for electrons (blue) and holes (red), (b) free electron (blue) and hole (red) energy distributions in a bulk semiconductor, (c) free carrier energy distributions in a QW. In (b) and (c), the DOS for electrons, \( \rho_e \), and holes, \( \rho_h \), are also indicated with blue and red lines, respectively.
CHAPTER 2. OPTICAL TRANSITIONS AND CARRIER DYNAMICS

respectively, between the barrier and well layers. Finally, the two boundary conditions

\begin{align*}
\psi(z_0^-) & = \psi(z_0^+), \quad (2.6a) \\
\frac{1}{m(z_0^-)} \frac{d\psi}{dz}(z_0^-) & = \frac{1}{m(z_0^+)} \frac{d\psi}{dz}(z_0^+), \quad (2.6b)
\end{align*}

where \( z_0^- \) and \( z_0^+ \) are the two sides of each interface in the heterostructure, must be enforced to ensure the continuity of the Bloch waves and the conservation of the probability current, respectively [31].

In Fig. 2.1, the Fermi-Dirac distributions for electrons and holes \( (a) \), the DOS in the parabolic band approximation and the corresponding carrier distributions for the bulk \( (b) \) and QW \( (c) \) cases are schematically represented. The carrier confinement in QWs produces an increase of the bandgap energy and a reduction of the DOS.

### 2.2 Interband optical transitions

Given the electron and hole energy distributions in CB and VB, \( n(E) \) and \( p(E) \), respectively, the spontaneous emission spectrum, \( R_{sp}(E) \), is calculated invoking the Fermi’s golden rule. \( R_{sp}(E) \) quantifies the transitions rate between occupied levels in CB, \( E_1 \), and empty levels in VB, \( E_2 = E_1 - E \) in the unit of volume and in the energy interval \( dE \) around \( E \) (in units of \( \text{cm}^{-3}\text{s}^{-1}\text{eV}^{-1} \)). The relevant formulas for the bulk and QW cases in the parabolic bands and effective mass approximations are as follows [29]:

\begin{align*}
R_{sp-bulk}(E, \hat{e}) & = \beta_{r1}(\hat{e}) n_r E \sqrt{E - E_g} \cdot f_1 f_2 \quad (2.7a) \\
R_{sp-well}(E, \hat{e}) & = \beta_{r2}(\hat{e}) n_r \frac{E}{L_w} \sum_{c,v} |I_{cv}|^2 H(E - \Delta E_{v,c}) \cdot f_1 f_2, \quad (2.7b)
\end{align*}

where \( f_1 = f_e(E_1) \) and \( f_2 = f_h(E_2) \) and it is assumed that there is quasi-equilibrium within the electron and hole populations. \( \beta_{r1} \) and \( \beta_{r2} \) are material constants that may assume different values depending on the direction of polarization \( \hat{e} \) of the emitted light with respect to the crystallographic orientation and the plane of the QW. \( n_r \) is the refractive index, \( L_w \) is the well width, \( \Delta E_{v,c} \) are energy differences between confined electron and hole energy levels in the QW and \( I_{cv} \) is the overlap integral between the component of the wavefunctions along the confinement direction in the QW. The initial and final states have the form in Eq. (2.4) and the overlap integral is calculated as follows:

\[ I_{cv} = \int F_c(z) F_v^*(z) dz. \quad (2.8) \]

The polarization field in polar III-nitride QWs pushes electrons and holes towards opposite directions reducing the overlap integral \( I_{cv} \) and the spontaneous emission rate.
2.3. EXCITON LINES AND BROADENING MECHANISMS

Similar expressions for the absorption coefficients of bulk and QW semiconductors can be directly derived from the spontaneous emission spectra \([32]\). The resulting formulas in units of \(\text{cm}^{-1}\) are as follows:

\[
\alpha_{\text{bulk}}(E, \hat{e}) = \frac{\beta_{\alpha_1}(\hat{e})}{n_r E} \sqrt{E - E_g} \cdot (1 - f_1)(1 - f_2) \quad (2.9a)
\]

\[
\alpha_{\text{well}}(E, \hat{e}) = \frac{\beta_{\alpha_2}(\hat{e})}{n_r L_w E} \sum_{\nu, \ell} |I_{\nu \ell}|^2 H(E - \Delta E_{\nu \ell}) \cdot (1 - f_1)(1 - f_2), \quad (2.9b)
\]

were \(\beta_{\alpha_1}\) and \(\beta_{\alpha_2}\) are similar constants as in Eqs \((2.7)\). Under low excitation in lightly doped samples, \(f_e\) and \(f_h\) are much smaller than one within the CB and VB, respectively. In this case, the factors containing \(f_1\) and \(f_2\) can be simplified as

\[
(1 - f_1)(1 - f_2) \approx 1 - (f_1 + f_2). \quad (2.10)
\]

In Eqs. \((2.7)\) and \((2.9)\), only \(f_1\) and \(f_2\) are dependent on the carrier density if the many-body effects are neglected. In polar nitride QWs, also the overlap integral \(I_{\nu \ell}\) and the transition energies \(\Delta E_{\nu \ell}\) become dependent on the carrier density via the screening effect (see Section \(4.2\)).

2.3 Exciton lines and broadening mechanisms

A more accurate version of the spontaneous emission and absorption spectra must include spectral broadening and exciton lines. Many sources of spectral broadening affect measured spectra. Inhomogeneous broadening is caused by inhomogeneities in the crystal structure such as defects, compositional variations, inhomogeneous strain and, in QWs, thickness variations. Homogeneous broadening is due to electron interaction with phonons. When the mentioned sources of broadening are minimized, exciton recombination can be observed in the luminescence spectra as emission lines at energies below the bandgap. Ultimately, the linewidth of free carrier and exciton transitions are limited by carrier scattering mechanisms. Scattering limits the electron lifetime in a particular energy level and determines a broadening of the energy levels. A few aspects of the mentioned phenomena that were explicitly considered in the thesis work are treated in this section.

Density of state tails

Real crystals often present deviations from a completely ordered structure that induce localization of the electron and hole wavefunctions. Typical examples of inhomogeneities in semiconductor crystals are compositional fluctuations in ternary alloys and well width fluctuations in QW structures. It was shown that in the weak disorder regime as defined in the Anderson’s model, disorder introduces localized states at the band edges. However, extended states in the CB and VB retain their Bloch-type character \([33]\). Presence of localization of this kind can be taken into
account by modifying the ideal DOS. A possible approach is to convolve the ideal DOS with a Gaussian distribution, \( \rho(E) \), with the following expression \[34\]:

\[
\rho_{e,h} = \rho_{0e,h} \exp \left[ -\frac{(E - E_{0e,h})^2}{2\sigma_{0e,h}^2} \right].
\] (2.11)

\( \rho_{0e}, \rho_{0h}, \sigma_{0e}, \sigma_{0h}, E_{0e} \) and \( E_{0h} \) are parameters for band-tails in CB and VB. In particular, \( \sigma_{0e} \) and \( \sigma_{0h} \) are related to the average localization depth of the potential minima. The localized states are represented by a low energy tail in the DOS diagram in Fig. 2.2.

\[ \sigma_L = \sqrt{\sigma_{0e}^2 + \sigma_{0h}^2} \]

compared to the ideal spectrum. \( \sigma_L \) contributes to the total temperature-independent spectral broadening, known as inhomogeneous broadening.

**Excitons**

Excitons are a form of crystal excitation in which electron-hole pairs form hydrogen-like systems with the opposite sign charges orbiting around each other. The Bohr radius \( a_B \) is the exciton radius in the ground state. Excitons are free if they can move within the crystal or bound if the electron-hole pair orbits around a lattice site or defect. Similarly to the case of impurity bound excitons, excitons can be localized at potential fluctuations. In the case of free excitons with larger \( a_B \) than the crystal unit cell, known as Wannier excitons, there exist simple formulas to calculate an approximate value of the electron-hole binding energy. The binding energy of a free exciton in the n-th excited state is calculated as

\[
E(n) = -\frac{\mu}{m_0} \frac{R_H}{\epsilon^2} \frac{1}{n^2}.
\] (2.12)
where $R_H$ is the Rydberg constant of the hydrogen atom (13.6 eV), $\epsilon_r$ is the static relative permittivity and $\mu$ is the reduced mass of the electron-hole pair,

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h},$$  

(2.13)

Excitons are more stable in confined structures. In the ideal bidimensional case, the binding energy increases up to four times the exciton binding energy in bulk semiconductors [30]. Stable excitons form if the binding energy is larger than $\sim k_B T$. Furthermore, the screening of the Coulomb potential by the presence of neighboring excitons determines the exciton ionization at high carrier densities. An approximate value for the critical ionization density, known as Mott density, is equal to $n^{3D}_M \approx 1/a_B^3$ for a bulk material and $n^{2D}_M \approx 1/a_B^2$ for a QW, where $n^{3D}_M$ and $n^{2D}_M$ are volume density and surface density of charges, respectively [33]. The presence of excitons can be directly detected in PL experiments on homogeneous samples at cryogenic temperatures. Under these circumstances, exciton generation and recombination introduce sharp absorption and emission lines, respectively, at energies $E(n)$ below the bandgap.

The free exciton wavefunction in the effective mass approximation, $\psi(r_e, r_h, R)$, can be written as [30]

$$\psi(r_e, r_h, R) = \frac{1}{\sqrt{A}} e^{iK \cdot R} \phi(r_e, r_h).$$  

(2.14)

In this expression, $\phi(r_e, r_h)$ is the wavefunction in the center of mass reference system and $r_e$ and $r_h$ identify the electron and hole position with respect the center of mass. The variable $R$ identifies the center of mass of the exciton and $K$ is the exciton momentum. The emission of discrete lines depends on the selection rule for the conservation of $K$. Only the “bright states” [35] with $K = 0$ can be optically excited and recombine radiatively. The identification of exciton transition lines in AlGaN alloys is complicated by alloy disorder and compositional fluctuations (see Section 5.4). Moreover, the interaction of excitons with phonons at room temperature further increases the broadening of the exciton lines. Therefore, exciton lines are often indistinguishable from the free carrier emission/absorption.

**Phonon broadening**

Energy transfer between carriers and the lattice is made possible by phonon absorption or emission. Phonons are the quanta of the lattice vibration. A polar crystal can sustain acoustic and optical phonons. The vibrations can in turn propagate as transverse or longitudinal waves. In general, the emission or absorption of phonons produces a spectral broadening of the luminescence. In the case of the exciton recombination, the luminescence broadening was calculated as [36]

$$\Gamma(T) = \Gamma_0 + \sigma T + \frac{\gamma}{\exp(\hbar\omega_{LO}/k_B T) - 1},$$  

(2.15)
On the right-hand side, $\Gamma_0$ is the inhomogeneous broadening, $\sigma$ is the exciton coupling strength with acoustic phonons, $\gamma$ is the exciton coupling strength with longitudinal optical phonons and $\hbar\omega_{LO}$ is the longitudinal optical phonon energy. At low temperatures, carrier interaction with acoustic phonons dominates the linewidth broadening with temperature [37]. The longitudinal optical phonon interaction becomes dominant above 200 K in both AlN and GaN.

### 2.4 Carrier dynamics

In this section, the relaxation processes that occur in a semiconductor after carrier excitation with ultrafast laser pulses are briefly reviewed.

#### Carrier thermalisation

Right after ultrafast pulse excitation, an excess of carriers with respect to the thermodynamic equilibrium is produced in the sample. The carrier energy distribution evolves through different regimes that may partially overlap in time [38]. These are (i) the coherent regime, (ii) the non-thermal regime, (iii) the hot-carrier regime and (iv) the isothermal regime.

(i) Initially, the exciting electromagnetic field generates a macroscopic polarization in the semiconductor. Carrier wavefunctions have well-defined phase relationships with each other and with the external field. This coherency is lost through several scattering mechanisms within few hundreds of femtoseconds.

(ii) For a few picoseconds after the excitation, the energy distribution of the carriers cannot be described by the Fermi-Dirac distribution. This time domain is typically too short to be observed in PL experiments. Pump-probe measurements (see Chapter 3) can provide information on this time scale.

(iii) During the hot-carrier regime, equilibrium is first reached within the electron and hole populations separately by means of carrier-carrier scattering. During this process, called thermalisation, the electrons move toward the bottom of the CB and the holes toward the top of the VB. This regime has a typical duration of the order of hundreds of picoseconds and can be observed in the PL spectra. The high energy tail of the PL spectra reveals the effective carrier temperature $T = (1/T_e + 1/T_h)^{-1}$, where $T_e$ and $T_h$ are the electron and hole temperatures, respectively.

(iv) In the isothermal regime, equilibrium between free carriers and the lattice is reached via carrier-phonon scattering. This regime can be observed in PL measurements if the thermalisation time is shorter than the carrier lifetime.

Fig. 2.3 schematically represents the carrier thermalisation.
2.4. CARRIER DYNAMICS

Figure 2.3: Interband transitions and carrier thermalisation: (a) carrier excitation and transfer to the band edges ($h\nu_E$ is the energy of the exciting photons and $h\nu_L$ is the energy of the emitted photons), (b) formation of a thermal distribution (reproduced from Ref. [39]).

Radiative and nonradiative recombination

After thermalisation, the system still contains an excess of electron-hole pairs, free or bound in excitons, compared to the thermodynamic equilibrium. Several possible recombination paths are schematically represented in Fig. 2.4. Radiative recombination has been discussed in Section 2.2. When deriving a rate equation

Figure 2.4: Carrier recombination: (a) radiative recombination, (b) intraband Auger recombination and (c) nonradiative recombination at defect states.
model for the carrier recombination in a LED, a simple expression for the spontaneous recombination is derived from Eqs. (2.7) [40]. Far from degeneracy, the Fermi-Dirac distributions for electrons and holes evaluated near the band edges are approximately proportional to the total density of electrons and holes, \( n \) and \( p \), respectively [41]:

\[ f_1 \propto n \quad \text{and} \quad f_2 \propto p. \]

Exploiting this simplification, the expressions for the spontaneous emission rate in Eqs. (2.7) can be integrated on the photon energy to obtain

\[
\int_{E_g}^{\infty} R_{sp} dE \approx Bnp, \quad (2.16)
\]

where \( B \) is the bimolecular recombination coefficient.

As for the nonradiative recombination, it can occur via Auger recombination and recombination at defects or surface states. In the Auger recombination, the recombination energy is transferred to a third particle, electron or hole, that is excited to a higher energy level. The higher energy level may be within the same band as for an intraband Auger recombination or within a higher energy subband as in the case of an interband Auger recombination. The rate of Auger recombination can be expressed as

\[
R_{Auger} = c_{ech}n^2p + c_{ehh}np^2, \quad (2.17)
\]

where \( c_{ech} \) and \( c_{ehh} \) are usually considered as material constants. Auger processes require the interaction of three particles and become important only at high carrier densities.

Defect states are associated with deviations from a perfectly periodic crystal structure such as point defects, dislocations, stacking faults, inversion domains and the external surface of the crystal. Crystal imperfections often introduce localized electronic states within the forbidden gap. Typically, localized states deep within the bandgap are more efficient as nonradiative recombination centers than shallow defects. This derives from the reduced probability of thermal escape of the trapped carrier in a deep level and the increased probability of trapping a carrier with the opposite sign [42]. The energy from a nonradiative recombination is transferred to the lattice as heat. Therefore, strong nonradiative recombination in LEDs, besides reducing the IQE, causes self-heating and a reduction of the device operation lifetime [17].

The evolution of the electron and hole carrier densities, \( n \) and \( p \) respectively, after short pulse excitation can be described by means of a rate equation model. The Auger recombination and diffusion effects can be neglected to a first approximation in semiconductors with relatively short carrier lifetimes and under moderate excitation regime. A simple version that also excludes drift currents can be written as follows:

\[
\frac{dn}{dt} = -Bnp - c_nNn \quad \text{(2.18a)}
\]

\[
\frac{dp}{dt} = -Bnp - c_p(N_t - N)p. \quad \text{(2.18b)}
\]
2.5 TUNNELING AND THERMIONIC EMISSION

In these equations, $B$ is the bimolecular recombination coefficient and a single defect level has been considered. Electron and hole trapping rates at defect states are proportional to the total densities of electrons and holes and to the density of empty, $N$, and occupied, $N_t - N$, trap states, respectively. The proportionality constants are the electron and hole capture rates, $c_n$ and $c_p$. Typically, the nonradiative recombination is a temperature-activated process and temperature dependent capture rates must be considered. When the nonradiative recombination is dominant and the saturation of the trap states is negligible, $n$ and $p$ evolve with single exponential decays with time constants $\tau_e$ and $\tau_h$, respectively. $\tau_e$ and $\tau_h$ can be associated with the parameters in Eqs. (2.18) as follows:

$$\frac{1}{\tau_e} = c_n N$$

$$\frac{1}{\tau_h} = c_p (N_t - N).$$

From the expression for the total spontaneous recombination in Eq. (2.16), the PL signal follows an exponential decay with time constant $\tau_{PL}=(1/\tau_e+1/\tau_h)^{-1}$. Sometimes multiple decay constants are observed. Additional effects that may explain multiple decay constants are: multiple defect levels, saturation of the trap states and descreening of internal fields in polar QW structures.

### 2.5 Tunneling and thermionic emission

Besides radiative and nonradiative recombination, the electron and hole lifetimes in a QW LED may be determined by escape processes. Carrier escape out of shallow wells and/or in case of thin barriers may occur via thermionic emission [43] and carrier tunneling [44]. The tunneling and thermionic emission of carriers are represented in Fig. 2.5. The escape mechanisms are influenced by the presence of an electric field in the QW region. In this case, the potential profiles in the well and barrier regions assume a triangular shape. As a consequence, the energy level for carriers within the QW moves toward the top of the well and the effective barrier thickness decreases. Thus the probabilities of tunneling and thermionic emission increase. The probabilities of tunneling and thermionic emission are characterized in terms of tunneling and thermionic emission lifetimes, $\tau_t$ and $\tau_{th}$, respectively. The tunneling lifetime is calculated as [45]

$$\tau_t = \tau_p \exp \left[ 2 \int_{\text{barrier}} \left( \frac{2 m_b}{\hbar^2} [E_{c,v}(z) - E_0] \right)^{1/2} \, dz \right],$$

$$\tau_p = \int_{\text{well}} \left( \frac{2 m_w}{E_0 - E_{c,v}(z)} \right)^{1/2} \, dz,$$

where $E_{c,v}(z)$ is the CB (VB) edge, $E_0$ is the carrier energy level and $m_b$ is the effective mass in the barrier layers.
CHAPTER 2. OPTICAL TRANSITIONS AND CARRIER DYNAMICS

Thermionic emission occurs for the electrons and holes in the high energy tails of the carrier energy distributions. The sum of potential and kinetic energy for these electrons and holes is larger than the confinement potential. Therefore, they are free to diffuse outside the well region. The thermionic emission lifetime can be calculated as [43]

\[ \tau_{th} = L_w \left( \frac{2\pi m_w}{k_B T} \right)^{1/2} \exp \left( \frac{E_b - E_0}{k_B T} \right), \]  

(2.21)

where \( E_b \) is the barrier height for the carrier escape, \( L_w \) is the well width and \( m_w \) is the effective mass in the well layer.

Figure 2.5: Schematic of the electron escape mechanisms from a QW: \( E_0 \) is the carrier energy level and \( E_b \) is the height of the confining barrier.
Chapter 3

Experimental techniques

In the experimental part of the thesis work, far-field (FF) EL and PL spectra were measured to reveal the general emission properties of the samples such as radiative transition energy, spectral width and effective carrier temperature. TRPL was employed to study the recombination dynamics and the screening dynamics of the internal field in QWs. Degenerate differential transmission pump-probe (DTPP) measurements were used to reveal the presence of localization and measure the localization depth in MQW structures. Additionally, the spatial distribution of the EL in AlGaN-based QW LEDs and of the PL in epitaxial layers was analyzed by means of NF spectroscopy. In this chapter, the general principles of the used experimental techniques are outlined and the specific setups briefly described.

3.1 Laser system

The DTPP setup and the TRPL setup at KTH use the third harmonic pulses of a mode-locked titanium-doped sapphire (Ti:Sapphire) laser (model Mira 900 by Coherent Inc.) as the excitation source. The third harmonic pulses were obtained using a setup that is schematically shown Fig. 3.1. The central wavelength of the Ti:Sapphire laser pulses is tunable in the near-IR between 700 nm and 980 nm. The pulse duration is around 150 fs and the repetition rate is 76 MHz. The third harmonic of the Ti:Sapphire pulses is needed to excite band-to-band transitions in AlGaN alloys. The third harmonic is obtained in two stages [46]. Firstly, the second harmonic generation is obtained focusing the near-IR pulses onto a lithium triborate (LBO) crystal. The near-IR and blue pulses are separated by a dichroic mirror that is highly reflective in the blue region. The polarization of the blue pulses is rotated to be parallel with the one of the near-IR pulses. Moreover, the temporal delay between near-IR and blue pulses is adjusted so that they perfectly overlap onto a barium borate (BBO) crystal. The third harmonic of the near-IR
Figure 3.1: Third harmonic generation: second harmonic pulses are generated inside the LBO crystal, dichroic mirrors (B-DM) are used to separate the blue from IR pulses after the LBO crystal and to mix them again after polarization rotation and delay adjustment. Blue and IR pulses overlap inside the BBO crystal where UV pulses are generated by sum-frequency. Lastly, the UV pulses are separated by another dichroic mirror (UV-DM).

pulses is obtained by sum-frequency generation in the BBO crystal. The UV pulses are separated by a dichroic mirror that is highly reflective for the UV pulses. Thin crystals have to be used to minimize dispersion and pulse stretching inside the crystals. To maximize conversion efficiency, the beams have to be tightly focused onto the crystals whose orientation must be adjusted to fulfill the phase matching condition. Typical achieved average power of the third harmonic pulses with central wavelength around 266 nm is about 30 mW, which corresponds to $5.3 \times 10^8$ photons per pulse.
3.2. FAR-FIELD TECHNIQUES

3.2 Far-field techniques

Time-resolved photoluminescence

TRPL is a contactless and non-destructive technique that is used to characterize the carrier dynamics in semiconductors. Electron and hole pairs are generated in the sample by means of short laser pulses that are tuned above the semiconductor bandgap. The excited carriers can be separated if a sufficiently strong electric field is present in the excited region as in the active region of a photodiode. Otherwise, they recombine via radiative or nonradiative recombination. Radiative recombination gives rise to luminescence from the sample. Under the same conditions as in the derivation of Eq. (2.16), the wavelength-integrated instantaneous luminescence intensity is proportional to the instantaneous total electron and hole densities $n(t)$ and $p(t)$, respectively:

$$I(t) \propto n(t)p(t).$$

(3.1)

Therefore, the luminescence transient provides information on the recombination dynamics such as the carrier lifetimes.

Figure 3.2: Operating principle of the streak camera (reproduced from Ref. [47]).
The streak camera is often used to obtain the temporal resolution in TRPL experiments. Fig. 3.2 shows a schematic representation of the streak camera main components and operation principle [47]. Often the luminescence is spectrally resolved by coupling a spectrograph to the streak camera input. The wavelength components of the light entering the instrument are separated along the direction of the streak camera entrance slit, which defines the direction of wavelength axis in the final image. The amount of light entering the instrument can be modified by adjusting the entrance slit width. A lens assembly inside the camera forms an image of the slit onto the surface of a photocathode inside a vacuum tube. A number of electrons proportional to the photon flux is emitted at every point of the photocathode surface. Inside the vacuum tube, the electrons are accelerated toward a pair of deflection plates with parallel orientation to the entrance slit of the instrument. A high-speed sweep voltage is applied to the plates as the electrons stream between them. The experienced deflection by the electrons passing through the electrodes depends on their arrival time. The direction of deflection, that is normal to the direction of the wavelength axis, defines the direction of the temporal axis in the final image. The deflected electrons pass through a microchannel plate where their number is multiplied. Finally, they hit a phosphor screen exciting fluorescence. The fluorescence image on the screen is read by a charge-coupled device camera. The fluorescence intensity at every point of the image is proportional to the photon flux at the corresponding wavelength and arrival time. The synchroscan mode allows accumulating multiple luminescence transients. Their correct synchronization is accomplished by detecting a replica of the excitation pulses that triggers the voltage sweep. Fig. 3.3 shows a typical streak camera image. Wavelength and temporal axes are also indicated for clarity. Two different streak camera setups have been used in the thesis experimental work. The streak camera at KTH is a

![Streak Camera Image](image-url)

**Figure 3.3:** Example of streak camera image. Wavelength and temporal axes are also indicated.
Hamamatsu Universal Streak camera C5680 Series with time resolution of 2 ps. The duration of the measured dynamics is limited in this setup by the laser repetition rate to below 13 ns. The setup at Rensselaer Polytechnic Institute employs a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. The pulse central wavelength, duration and repetition rate are 1064 nm, 20 ps and 10 Hz, respectively. The harmonics up to the fifth at 213 nm are obtained with the use of multiple non-linear crystals. Moreover, the achievable pulse energy is of the order of µJ for pulses with central wavelength at around 266 nm and corresponds to a four orders of magnitude larger photon flux per pulse than for the setup at KTH. The streak camera is in this case a Hamamatsu single shot streak camera with enhanced sensitivity in the UV. In this setup, the time resolution is limited by the excitation pulse length. The slow laser repetition rate allows measuring longer luminescent transients.

**Pump-probe setup**

The DTPP setup allows measuring carrier dynamics with higher temporal resolution than with a streak-camera-based setup. In the DTPP experiment, the time resolution is limited by the pulse duration. Fig. 3.4 (a) shows a schematic representation of the used setup for measuring the results in Paper VI. In the experiment, the third harmonic pulse train from the Ti:Sapphire laser is split into two beams - pump and probe - and separately focused on the same spot on the sample surface. The pump pulses are more intense and excite the electron and hole densities \( n_0 \) and \( p_0 \), respectively, at the reference time \( t_0 \). The presence of free carriers near the band edge modifies the absorption coefficient and the refractive index of the material from the unexcited values. If the temporal evolution of the many-body effects can be neglected, the change of absorption coefficient at photon energy \( h\nu \) can be expressed as [48]

\[
\Delta \alpha(h\nu,t) = -\alpha_0(h\nu)(c_1 n(t) + c_2 p(t)),
\]

where \( \Delta \alpha(h\nu) \) is the absorption coefficient of the unexcited semiconductor and \( E_e \) and \( E_h \) are the electron and hole levels, respectively, that are directly excited by photons with energy \( h\nu \). As mentioned in Section 2.4, the Fermi-Dirac distributions \( f_e(E_e) \) and \( f_h(E_h) \) are proportional to the total electron and hole densities \( n \) and \( p \), respectively. Therefore, Eq. (3.2) can be expressed in terms of \( n \) and \( p \) as

\[
\Delta \alpha(h\nu,t) = -\alpha_0(h\nu)(c_1 n(t) + c_2 p(t)),
\]

where \( c_1 \) and \( c_2 \) are two constants.

The probe pulses are weaker and reach the sample with an adjustable temporal delay \( t \) after \( t_0 \). If the sample has a low optical density, the transmitted part of the probe pulse train can be reliably measured. Because of the carrier recombination, the carrier densities \( n(t) \) and \( p(t) \) at the time \( t \) are reduced from the initial values \( n_0 \) and \( p_0 \) at time \( t_0 \). As a consequence, the transmittivity usually decreases for
increasing delay time $t$ between the pump and the probe. Referring to Eq. (3.3), the change of transmittivity is proportional to a weighted sum of electron and hole densities. In Fig. 3.4 (b), a typical pump-probe trace is shown. The maximum relative change of transmittivity for the probe pulse is often fairly weak and lock-in detection is used to increase the sensitivity of the experiment. The pump signal is mechanically chopped at a lower frequency than the repetition rate of the laser pulses. The changes in the probe signal that have the same periodicity as the chopping frequency are filtered from the total signal by means of lock-in detection.

### 3.3 Near-field microscopy

The optical transitions and carrier dynamics in III-nitride layers are strongly influenced by crystal inhomogeneities. As a result of their presence, variations of the peak wavelength, spectral width and luminescence intensity occur over the layer surface. Spatially resolved spectral measurements are of fundamental interest to
characterize the transport and luminescence properties of III-nitride-based light emitters. On the other hand, the length scale at which the relevant phenomena occur is small and often beyond the resolution limit of conventional FF techniques. For this reason, NF spectroscopy has emerged as an important tool for semiconductor characterization. This chapter provides a short introduction to the concept of optical NF and the related experimental techniques.

The diffraction limit

The resolution of conventional optical microscopes is limited by the diffraction limit to \( \lambda/NA \), where \( \lambda \) is the illuminating wavelength and \( NA \) is the numerical aperture of the objective lens. The NA is defined by \( NA = n_r \sin \theta_M \), where \( n_r \) is the refractive index of the medium between the object and the objective lens and \( \theta_M \) defines the half angle of the acceptance cone of the objective lens. Diffraction causes the spreading of the wavefront during propagation. The effect of diffraction is evident observing the emerging light from a narrow aperture, as shown in Fig. 3.5.

![Figure 3.5: Illustration of the diffraction by a small circular aperture with diameter \( d \). A lens can capture only a finite portion, depending on the NA, of the diffraction pattern formed at the focal distance. The Airy disk from a circular aperture diffraction has a diameter \( 1.22 \frac{\lambda}{d} \) and tends to exceed the limit imposed by the lens NA as \( d \) is reduced.](image)

The cone angle of the emerging light increases as the aperture size is reduced to values comparable or smaller than the wavelength. As a consequence, only a certain fraction of the wavefront can be collected by the limited acceptance cone of the objective lens. As a result, the formed image is blurred. More insight on the connection between limited NA and blurring of the image can be gained by
means of the angular momentum representation which is introduced in the next subsection.

As in the case of the emerging light from a small aperture, all the fine features of the object under observation generate widely diverging wave components whose partial collection is responsible for the blurring of the obtained image. There are practical limitations to the maximum achievable NA that limit the resolution of standard microscopes to values larger than \( \lambda/2 \) [49]. It can be shown that diffraction is intrinsically associated with the propagation of electromagnetic waves. On the other hand, the field in the proximity of the source contains localized, non-propagating components. The non-propagating field components are evanescent, that is, they decay exponentially with the distance from the source. The region of space where the evanescent components are stronger than the propagating ones is called the NF [50]. The extent of the NF region does not depend on the wavelength but only on the source dimension [49]. This is an important difference between NF and the evanescent field produced by total internal reflection. The NF microscope circumvents the limitation of a finite NA by moving an electric field probe in close proximity of the source, where the evanescent components can be detected, thereby realizing a high effective NA.

The angular momentum representation

In this section, a more quantitative description of the NF is given in terms of the angular momentum representation. The connection between diffraction and momentum representation is clarified by means of a two-dimensional electromagnetic simulation. The simulations were performed with the commercial software COMSOL Multiphysics 3.5. Let us consider a dielectric flat rod aligned along the \( x \) axis with the longer side equal to \( L \) and subwavelength thickness. A plane wave that is polarized in the plane of the image impinges on the long side along the negative \( z \) direction. In Fig. 3.6 the scattered field patterns for two values of the rod length are shown. The color scale represents the module of the scattered electric field that are parallel in every point to the field vector. In Fig. 3.6(a), the side of the rod is much longer than the incident wavelength and the scattered field along \( z \) propagates with approximately plane waves. The length \( L \) of the rod can be determined to a good accuracy from the size of the wavefront in the FF. As the rod dimension \( L \) is reduced, the scattered field tends to diverge laterally while propagating away from the rod. As the lateral dimension of the rod is reduced below the wavelength of the incident light as in Fig. 3.6(b), the scattered field pattern resembles the one from an electric dipole. At this point, the information on the lateral dimension of the rod cannot be retrieved from a FF measurement. The module of the scattered field across two sections at distance \( z_1 = \lambda/100 \) and \( z_2 = 4 \lambda \) are shown in Fig. 3.7(a) and (b), respectively. The field pattern in close proximity of the rod retains the information on the rod dimension. This simple observation justifies the use of NF detection to break though the diffraction limit.
The angular momentum representation of the scattered electric field provides a more quantitative description of the different information content in the NF and FF regions. In the angular momentum representation, the optical NF is represented as a superposition of plane and evanescent waves [51]. The decomposition of the electric field along a section \( z_1 \) is obtained by means of the spatial Fourier transform:

\[
\hat{E}(k_x; z_1) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} E(x, z_1)e^{-ik_x x} dx,
\]

(3.4)

where \( k_x^2 = k^2 - k_z^2 \). The field components at different sections \( z \) can be obtained with the following relationship:

\[
\hat{E}(k_x; z) = \hat{E}(k_x; z_1)e^{ik_x(z-z_1)}.
\]

(3.5)

Strongly diverging field components are characterized by large \( k_x \) components.

**Figure 3.6:** Simulation of the light scattering from a dielectric rod. The basic parameters of the simulation are indicated in the figure. \( E_{inc} \) and \( E_{sc} \) are the incident field and the scattered field, respectively.
Figure 3.7: Scattered field magnitude at a distance $z_1 = \lambda/100$ (a) and $z_2 = 4\lambda$ (b) from a rod of length $L$. Several rod lengths $L$ are considered. (c) and (d) show the angular momentum representation of the $y$-polarized component of the scattered field at the same positions.

There is no limitation to $k_x < k$, thus $k_z$ is free to become imaginary. The components for which this happens become evanescent and constitute the NF.

In Fig. 3.7 (c) and (d), the Fourier transform of the $y$-component of the electric field along the sections $z_1$ and $z_2$ is shown. There is an evident loss of spectral components as the field propagates away from the scattering source. The source geometry determines the $k_x$ bandwidth of the optical signal in the NF. In fact,
the field in close proximity of the source reproduces the surface geometry. Hence, the high $k_x$ components are associated with the small features of the surface. The loss of high spatial frequency components corresponds to a low pass filtering of the object geometry and generates the blurring effect in the reconstructed image. In particular, sub-wavelength features generate evanescent field components that, by definition, do not reach the FF. This establishes an intrinsic limit to the resolution of FF microscopes.

The angular momentum representation elucidates how the dimension of the NF depends on the dimension of the source. The decay length of the NF is determined by the relationship between $k_x$ and $k_z$, thus, by the source geometry. Another conclusion that can be drawn from the angular momentum representation is that the NF does not contribute to the propagation of energy. The base functions in the angular momentum representation in Eq. (3.4) are orthonormal. Hence, the total power emitted from the source can be computed as the sum of the power in each field component or “mode”. The evanescent components decay within the NF region. Therefore, they do not contribute to the power transmission to the FF.

Near-field probes

The detection of the evanescent components of the source field requires their transformation from evanescent to propagating [49]. This is obtained by perturbing the optical NF with a probe. Sensitive detection requires the separation of the generated waves by the probe - the secondary waves - from the rest of the signal coming from the source. The resolution of the measurement is limited by the dimension of the probe. However, it should be reminded that the presence of the probe perturbs the original NF at the source. Therefore, it is not possible to separate the original NF from the probe-sample interaction in the results of real measurements. As a consequence, measurement artifacts may occur [52].

In a common implementation of the NF microscope, a tapered optical fiber is used as a probe. Several measurement configurations are possible [51]. In the collection mode setup, a fiber probe is used to guide the scattered field from the NF region around the tip to the detector, while the illumination source is in the FF. No external light sources are required in case of EL NF measurements. In the illumination mode, the probe is used to illuminate the sample in NF and the detection occurs in the FF. Lastly, illumination and collection can be both guided through the fiber in the illumination/collection (IC) setup. The latter operation mode simplifies the NF measurements on opaque samples.

The fiber tips employed in this work were obtained with the tube etching method [53]. The etching solution that is contained inside a Teflon vessel is composed by 50 % water solution of hydrofluoric acid covered by a few millimeters thick isoctane layer. The isoctane layer prevents the evaporation of the acid from the vessel. The tip is vertically dipped in the solution at room temperature. The etching process takes a variable amount of time depending on the fiber composition and diameter; the obtained tip quality can also vary greatly [54]. The etching process
Figure 3.8: Tube etching: (a) the fiber probe is immersed in the HF solution with the jacket, (b) symmetrical thinning, (c) formation of a conical tip, (d) convection of fresh HF, indicated with dashed lines, and reaction products, indicated with dotted lines (adapted from Ref. [53]).
3.3. NEAR-FIELD MICROSCOPY

collection from the taper of the tip. Reproducible apertures can be obtained on the coated tip using a focused ion beam. However, sub-wavelength resolution with uncoated fiber probes has also been theoretically predicted [55, 56] and experimentally verified [57, 58] in the IC setup. Metal-coated probes are believed to be superior to uncoated probes with respect to spatial resolution and contrast because their small apertures represent well-defined subwavelength radiation sources or detectors [59]. However, there are some important advantages of using uncoated probes. The fabrication of uncoated probes is simpler and less time consuming. Moreover, the detected optical signal is usually stronger for uncoated probes, though sometimes at the expense of the lateral resolution. Uncoated tips can also sustain larger optical powers without the risk of melting or detaching the metal coating. Furthermore, the tip is more resistant to wearing out and to topographically induced image artifacts due to formation of metallic protrusions. Lastly, the larger throughput enables a simpler implementation of the IC setup.

Two different UV transparent multimode fibers were used to manufacture the used probes in the thesis experimental work. UV transparent fibers usually have a pure silica core and a fluorine doped cladding. Besides the low attenuation in the UV range, the noise from self-luminescence in pure silica core fibers is much smaller than in germanium doped fibers [60]. One of the used fibers was a 20 µm diameter core manufactured by Acreo AB and the other was a 50 µm diameter core manufactured by CeramOptec. The etching time was about 2.5 and 3 hours, respectively. Typical etched probes are shown in the secondary electron microscope (SEM) scans reproduced in Fig. 3.9. The tip diameter is smaller than 100 nm in both cases and the cone angle in the tapered section is around 31° and 63°, respectively. The fiber with the smaller cone angle was used to measure the EL from UV-LEDs in collection-mode. The experimental results are presented in Paper V. The smaller cone angle probably contributed to the rejection of the FF signal from

![SEM images of UV fiber probes: (a) small cone angle probe from Acreo AB fiber and (b) large cone angle probe from CeramOptec fiber.](image_url)

**Figure 3.9:** SEM images of UV fiber probes: (a) small cone angle probe from Acreo AB fiber and (b) large cone angle probe from CeramOptec fiber.
the tapered part of the probe. In this operation mode, it is hardly possible to make claims on subwavelength resolution from a theoretical standpoint. However, the \textit{a posteriori} inspection of the measurements recorded with a photomultiplier tube (see Fig. 3.10) reveals the presence of well defined features which do not seem to be induced by the sample morphology.

![Image of photomultiplier-tube scans of a UV LED surface](image)

\textbf{Figure 3.10:} Photomultiplier-tube scans of a UV LED surface. Panels (a) and (c) show the topography and panels (b) and (d) spectrally integrated EL intensity from the corresponding regions.

Furthermore, the published spectral measurements are not affected by topographical artifacts. The results show sub-micrometer-sized regions emitting at a different wavelength from the FF background.

In the case of IC NF spectroscopy, the signal level is critical. The excitation intensity that is coupled into the fiber is limited by the damage threshold and the noise generation in the fiber. Moreover, the excitation intensity is further decreased by the reflection and losses during propagation in the tapered part of the fiber. On the other hand, the IC setup was found to improve the spatial resolution of the measurement with respect to the collection-mode setup with uncoated probes. The larger cone angle and lower noise generation of the probes that were manufactured from the CeramOptec fiber was well-suited for the IC measurements presented in \textbf{Paper VIII}. 
3.3. NEAR-FIELD MICROSCOPY

The near-field microscope

A scheme of the used NF microscope is presented in Fig. 3.11.

The NF signal is collected by a fiber probe. The other end of the probe is coupled to a detector. In the thesis work, a UV-sensitive photomultiplier tube was used for preliminary intensity measurements. NF spectra were measured with a 0.5 m focal length spectrograph coupled to a liquid nitrogen-cooled silicon charge-coupled device detector. The light from the fiber was collimated with an objective lens and focused on the entrance slit of the instrument with a second lens. Maximum light collection is obtained when the f-number of the coupling optics matches the f-number of the spectrograph, equal to 6.5.

In the SNOM setup, the tip of the fiber probe is glued with epoxy resin along one arm of a commercial quartz tuning fork with resonance frequency at 32.768 KHz [61]. The fiber probe can be detached from the fork using acetone and the same fork can be reused with a fresh tip. The tuning fork is magnetically attached to a small segmented piezoelectric tube - the dither piezo - and the electrical contacts are connected to a current amplifier. During operation, the dither piezo vibrates the
tuning fork-fiber probe assembly. The oscillation frequency of the dither is set by a function generator at the resonance frequency. The mechanical vibration of the fork generates a current which is amplified and fed to a lock-in amplifier. Interestingly, a subnanometer vibration of the center of mass of the tuning fork at resonance is sufficient to generate a measurable current [62]. Therefore, the lateral vibration of the tip above the sample does not affect the resolution of the experiment.

The principle of the probe-to-sample distance control is based on the detection of the shear force between the tip and the sample. In the setup, a proportional-integral controller uses the amplitude signal to adjust the probe-to-sample distance by driving a second piezoelectric tube. While scanning the sample surface, the friction forces between the sample and the tip tend to damp the amplitude of the tip oscillations. The probe-to-sample distance is adjusted as to keep the oscillation amplitude constant. Thus, the use of the shear force as the feedback implies a constant gapwidth between the tip and the sample. In general, the use of the optical signal as feedback is possible as well. However, it produces a less accurate distance control [51] because the collected signal is neither short-ranged nor monotonously dependent on the probe-sample distance. The nature of the friction forces is most probably related to mechanical damping that is mediated through adsorbate filling in the tip sample gap [62], particularly in the case of atmospheric pressure experiments.
Chapter 4

Basic properties of III-nitrides

This chapter provides an introduction to the basic properties of the wurtzite III-nitrides with particular emphasis on the AlGaN alloys.

4.1 Nitrides for light emitters

The group III-nitrides include indium nitride (InN), GaN, AlN and their ternary and quaternary alloys. Although other alloys belong to the same family, for example those containing boron nitride (BN), they have attracted significantly less attention so far and they will not be considered in the following. In the wurtzite polype, III-nitride alloys exhibit direct bandgaps for all compositions. Their bandgap can be tuned by alloying in the range from 0.7 eV for InN, through 3.42 eV for GaN, up to 6.25 eV for AlN, as shown in Fig. 4.1. The breadth of this interval, which spans from the IR through all the visible range up to deep-UV, makes the III-nitrides highly attractive for the production of light emitters.

As light-emitting materials, GaN-based alloys are superior at present to the other available wide bandgap materials - SiC, zinc selenide (ZnSe) and zinc oxide (ZnO). The indirect bandgap of SiC limits the luminescence efficiency of this material. The poor electronic properties, low thermal conductivity and weak bond strength in ZnSe-based alloys determine a very short operation lifetime for ZnSe-based devices [64]. Although ZnO-based alloys may eventually become competitive with III-nitride alloys, they still suffer from low luminescence efficiency and unstable and non-reproducible p-type doping [65]. The IQE of InGaN-based LEDs can be as high as 70% [66, 67] and there are indications that comparable values may be achieved in AlGaN-based devices as well [13]. In principle, III-nitride-based devices are able to operate in high-temperature environments due to their high bond strength. Additionally, the III-nitrides exhibit good thermal conductivity, which allows efficient heat dissipation from devices operating in high-current conditions.
such as high-brightness LEDs [68]. Unfortunately, these advantageous properties have been only partially harnessed by the deep-UV technology so far. The poor thermal conductivity of the normally employed sapphire substrates [16] and the high density of native extended defects are among the limiting factors. The extended defects are thought to reduce the operation lifetime of AlGaN-base devices at high current/temperature operating conditions [69, 70] (see Section 5.5). Some important properties of the AlN and GaN binary compounds are summarized in Appendix A.1.

Crystal structure

The thermodynamically most stable phase of the III-nitrides is the wurtzite structure [71]. In Fig. 4.2, the GaN wurtzite crystal structure is shown and the lattice constants $c$ and $a$ are defined. The projection on the c-plane (0001) in Fig. 4.2 (b) evidences the hexagonal symmetry. The wurtzite group-III nitrides lack an inversion symmetry plane perpendicular to the $c$-axis (the $c$-axis is indicated in Fig. 4.2).
Figure 4.2: Ga-face wurtzite crystal structure of GaN: (a) projection on the a-plane (11\overline{2}0), (b) projection on the c-plane (0001). The violet parallelepiped contains the primitive unit cell. The lattice constants $c$ and $a$ are indicated with black arrows. The green dashed arrow represents the electrostatic interaction between non-bonded anion-cation pairs aligned along the $c$-axis (the structure was drawn with the software VESTA).

with its Bravais-Miller index [0001]). As a consequence, two possible stacking orders can be distinguished. If the bonds along the $c$-axis in the direction of growth go from a metal atom to a nitrogen (N) atom, the layer has a (Ga,In,Al)-polarity – otherwise a N-polarity. The polarity of nitride epitaxial layers determines the sign of the polarization charge in heterostructures (see Section 4.2).

AlGaN band structure

In Fig. 4.3 (a), a portion of the bulk GaN VB structure near $k = 0$ is represented [72]. The considered direction of the $k$-vector are within the $c$-plane, $k_t$, and along the $c$-axis, $k_z$. In the represented region, the VB is split into three subbands, denominated heavy hole (HH), light hole (LH) and crystal-field split-off hole (CH) bands. The energy difference between the top of the HH and LH bands is only around 10 meV, thus, holes from both the bands contribute to the luminescence at room temperature. The dashed lines represent the effect of an in-plane biaxial compressive strain. This case is of particular interest because the well layers of deep-UV AlGaN-based LEDs are often under compressive strain. In general, strain
Figure 4.3: GaN and AlN bandstructure around $k=0$. (a) GaN band structure near the top of the VB. The dashed lines represent the effect of an in-plane biaxial compressive strain equal to $\epsilon_{xx} = \epsilon_{yy} = -0.4\%$ (adapted from Ref. [72]). In (b) and (c), a schematic representation of the band arrangement in GaN and AlN is shown (reproduced from Ref. [73]).

shifts the bands and modifies the values of the effective masses. A downward shift of the CH band and a reduction of the LH effective mass are the most significant strain-induced effects. In Fig. 4.3 (b) and (c), the band structures for bulk GaN and AlN are compared. In AlN, the CH band emerges at the top of the VB [75]. However, strain and confinement in a QW layer produce a downward shift of the CH band and move the VB crossing to higher Al content [73, 76].

The VB crossing has important consequences on the emission properties of high Al molar fraction AlGaN-based QWs. Transitions between the CB and the HH bands emit mainly transverse electric (TE) waves with polarization on the c-plane. On the contrary, transitions between the CB and the CH band emit mainly transverse magnetic (TM) waves with polarization along the c-axis [77]. The polarization of the emitted light in a near-band-edge radiative recombination in GaN and AlN is indicated in Fig. 4.3 (b) and (c). In a QW structure grown on the c-plane (see Fig. 4.3 for the definition of some relevant planes of the wurtzite III-nitrides), only TE-polarized photons can propagate along the c-axis and are emitted from the QW surface. Significant emission with TM polarization may contribute to the measured low extraction efficiency in high Al molar fraction c-plane deep-UV LEDs [13]. Evidence that supports this hypothesis is found in a TRPL study of a set of epitaxial
layers with different Al molar fractions [78]. Comparable values of PL decay time were measured among the samples. This indicates that there were not significant differences of nonradiative recombination rate. However, the samples with higher Al molar fractions exhibited reduced values of total PL intensity.

A precise calculation of the carrier distribution in the bands requires the knowledge of the band splitting and effective mass for each band. However, these values are affected by considerable uncertainty in the relaxed materials. Additionally, the uncertainty on the extent of the strain-induced modifications is even larger. The situation is greatly complicated in AlGaN heterostructures where extended defects and alloy fluctuations may induce partial strain relaxation [13]. In the approach that was followed in the calculations of Paper II and Paper III, only the holes in the HH band were considered and the linear interpolations of the effective masses in relaxed GaN and AlN was used (see Appendix A.1). Similar calculations for AlGaN/GaN QWs have confirmed that holes occupy mainly the first HH subband for a wide range of excitation levels [79].

### Excitons in nitrides

The binding energy of excitons is large in III-nitrides [80, 81]. Table 4.1 reports the binding energy and Bohr radius for bulk Wannier type excitons in GaN and AlN. The exciton binding energy is further enhanced in confined structures [82].

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>AlN</th>
</tr>
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<tbody>
<tr>
<td>Binding energy (meV)</td>
<td>28</td>
<td>44</td>
</tr>
<tr>
<td>Bohr radius (Å)</td>
<td>30</td>
<td>19</td>
</tr>
</tbody>
</table>

*Table 4.1: Exciton properties of GaN and AlN [80, 81]*

In GaN, excitons may form with holes in the HH, LH and CH bands and are known as excitons A, B and C, respectively. All three exciton types were observed up to room temperature [83]. The spectral broadening of the exciton absorption and emission lines in AlGaN alloys makes their direct observation more difficult. However, the presence of fairly deep localization minima in AlGaN epitaxial layers [84] and QWs (see Paper VI) increases the stability of the excitons against thermal and electric field ionization. The radiative lifetime of localized excitons in potential minima increases with the localization depth [24]. Additionally, localization prevents nonradiative recombination at dislocations [85], thereby increasing the exciton lifetime.

In order to establish the role of exciton recombination in light-emitting devices, it is necessary to evaluate the stability of excitons at the carrier densities typical for device operation. In a 4 nm GaN/AlGaN QW, the Mott density was calculated as \(1.9 \times 10^{12} \text{ cm}^{-2} \) [86, 87] and around \(1 \times 10^{19} \text{ cm}^{-3} \) in bulk GaN [88]. These densities may be reached in high-brightness InGaN-based LEDs [89]. Much lower
carrier densities are typically reached in AlGaN/AlGaN LEDs that are usually driven at lower currents [90]. Actually, considering the transparency carrier density of $4.5 \times 10^{12}$ cm$^{-2}$ in InGaN-based QWs [91], excitonic effects may be relevant even in laser diodes [92].

4.2 Polarization fields

Strong polarization fields in III-nitride heterostructures have important consequences on the luminescence and carrier transport in nitride-based LEDs. The existence of a macroscopic polarization in III-nitride layers was first predicted from ab initio calculations by Bernardini and Fiorentini [93]. The experimental confirmation followed shortly after [94]. Typically, the polarization of QW structures is experimentally determined from PL measurements. In this section, the polarization properties of AlGaN heterostructures are reviewed and PL-based measurements of the polarization constants are described.

The origin of the polarization charge

Fig. 4.4 shows the disposition of the bonds around a Ga atom in the wurtzite, Ga-face GaN crystal.

![Figure 4.4: Bond distribution around a Ga atom in the wurtzite, Ga-face GaN (reproduced from Ref. [71]).](image)

A similar arrangement, where four N atoms surround every group-III metal atom, occurs in all III-nitride crystals. N is more electronegative than group III atoms. As a result, a fractional negative charge accumulates close to the N atom in every covalent bond of the crystal. Hence, every bond in the crystal is associated with a permanent dipole moment, $p_0$, in units of Cm. $p_0$ is represented in Fig. 4.4 with a green arrow pointing from the negative charge around the N atom to the
positive charge around the Ga atom. The sum of the four dipole moments around every group-III atom would add to zero in the ideal wurtzite structure, where the bonds are arranged as a perfect tetrahedron. However, the electrostatic interaction between non-bonded anion-cation pairs, represented with a green dashed arrow in Fig. 4.2, compresses the ideal tetrahedral structure along the \( c \)-axis [95]. As a result, the dipole moment along the \( c \)-axis is not compensated by those off the axis. The red arrow in Fig. 4.4 represents the net dipole moment, \( \mathbf{p}_{\text{TOT}} \), around every Ga atom. The density of \( \mathbf{p}_{\text{TOT}} \) constitutes the spontaneous polarization, \( \mathbf{P}_{\text{sp}} \), in units of Cm\(^{-2}\). The alignment of \( \mathbf{p}_{\text{TOT}} \) along the \( c \)-axis explains why the planes that are parallel to the \( c \)-axis are not polar, as shown in Fig. 4.5.

![Figure 4.5](image-url)

**Figure 4.5:** Some wurtzite crystallographic planes: (a) conventional unit cell displaying a \( c \)-plane (polar), \( a \)-plane (non-polar) and \( m \)-plane (non-polar); (b) projection on the \( c \)-plane (0001). The direction of the \( c \)-axis and \( \mathbf{P}_{\text{sp}} \) for a Ga-face crystal are also indicated (adapted from Ref. [13]).

Strain contributes to the total deformation of the crystal from the ideal wurtzite structure as well and it alters the value of \( \mathbf{p}_{\text{TOT}} \). The strain-induced contribution to the total polarization is known as piezoelectric polarization, \( \mathbf{P}_{\text{pz}} \). The total polarization \( \mathbf{P} = \mathbf{P}_{\text{sp}} + \mathbf{P}_{\text{pz}} \) within each lattice \( c \)-plane corresponds to fixed polarization charge densities \( +\sigma_b \) and \( -\sigma_b \) at the two interfaces of the plane. \( \mathbf{P} \) is related to the surface bound charge density as

\[
\mathbf{P} \cdot \hat{n} = \sigma_b, \quad (4.1)
\]

where \( \hat{n} \) is the unit vector normal to the surface. Within the material, the contributions from adjacent planes cancel each other. However, in correspondence of the external boundaries or at the interface between layers with different compositions, a net surface charge remains uncompensated. The presence of a fixed charge sheet at the interface between nitride layers gives rise to intense polarization fields inside QW structures. The actual sign of the net surface charge densities and the direction of the electric fields in a heterostructure depend on the difference of total polarization \( \mathbf{P} \) between adjacent layers.
**Polarization constants in AlGaN**

The spontaneous polarization in (Al,Ga)-face AlN and GaN points towards the substrate, and its value is larger in Al-rich alloys than in Al-poor ones. When an AlGaN film is under a biaxial tensile strain, the piezoelectric polarization component points towards the substrate, and vice versa in case of biaxial compressive strain. Moreover, in AlGaN layers the spontaneous polarization is larger than the piezoelectric polarization in the absolute value. Fig. 4.6 shows the direction of the spontaneous and piezoelectric polarizations in a typical layer stack that is contained in AlGaN-based LEDs.

![Diagram](image)

**Figure 4.6:** Direction of the polarization and electric fields inside a typical layer stack as used in MQWs LEDs. The layers are (Al,Ga)-face, the buffer is relaxed and the overlapping layers are under compressive strain. The sign of the polarization sheet charge is also indicated (adapted from Ref. [96]).

The sign of the resulting interface charge and the direction of the associated electric fields are also shown. Typical values of polarization for (Al,Ga)-face, coherently strained AlGaN epitaxial layers grown on AlN and GaN are shown in Fig. 4.7 (see also Appendix A.1 for the relevant formulas). Interestingly, both the spontaneous and the piezoelectric polarizations exhibit a significant nonlinear dependence with the alloy composition.

The experimental determination of the polarization fields in QW structures typically involves the comparison of the measured PL peak energy with the calculated transition energies. The transition energies for recombination in the wells are redshifted by the quantum confined Stark effect (QCSE) [30]. Thus, the polarization value is used as a fitting parameter to match the calculated and measured transition energies. To increase the reliability of the fitting procedure, measurements are typically performed on structures with different compositions and well widths [97]. Alternatively, if the the QWs are embedded in a p-i-n structure, the field in the QWs can be modified applying an external bias [88].

The calculation of the transition energies involves solving the Schrödinger equation (Eqs. [2.3]) for free carriers in the active region in the effective mass approximation [88]. The transition energy is obtained as the sum of the ground state energy levels for electrons, $E_{1e}$, and holes, $E_{1h}$, inside the QWs. The polarization
Figure 4.7: Polarization of AlGaN layers (calculated values using the constants in Ref. [63]). The $P_{pz}$ is calculated for coherently strained layers on GaN (in red) and on AlN (in blue).

charges enter in the Schrödinger equation via the polarization-induced modification of the potential profile in CB and VB. A term equal to $\Delta U(z) = qV(z)$ must be added to the potential energy in Eq. (2.5b), where $V(z)$ is calculated according to the Poisson equation [32]:

$$
\frac{d}{dz} \left( \epsilon(z) \frac{dV(z)}{dz} + P(z) \right) = -\rho(z).
$$

In the Poisson equation, $P(z)$ is the total internal polarization as given by the sum of the spontaneous and piezoelectric polarizations (in C/m$^{-2}$) and $\rho(z)$ is the charge density (in C/m$^{-3}$) that is associated with free carriers. $\rho(z)$ is usually set to zero in the calculation of the PL peak energy under low excitation. Sometimes, the Schrödinger equation is modified to account for the presence of excitons [97].

A different approach makes use of the screening of the electric field by free-carrier injection [79]. Screening occurs when a high density of free carriers in the active region counterbalances the polarization field. In this case, the PL peak energy shift rather than its absolute value is compared with calculated values. In case of short pulse excitation, dynamic descreening of the internal field can also be observed [79].

In Paper I, the value of polarization charge in QWs within a p-i-n structure was determined making use of the linear relationship between the electric field and the
PL peak shift in the high field regime [30]. Fig. 4.8 shows a schematic representation of the band profiles during the experiment.

![Diagram of band profiles](image)

**Figure 4.8:** Band profiles in a p-i-n structure: at zero bias (a) the field in the wells is given by the polarization field plus the built-in field of the p-i-n structure; the built-in field is compensated at flat-band (b); the remaining polarization fields are compensated by free-carrier screening under optical excitation (c).

The comparison of the induced PL peak shift by an external bias (b) and by free-carrier screening (c) allows calculating the polarization field in the wells. Once the field value is known, the difference between the polarization in the barriers, $P_b$, and in the wells, $P_w$, in a MQW structure can be derived according to the following formulas [99]:

$$F_w = L_b(P_b - P_w)/(L_b\epsilon_w + L_w\epsilon_b), \quad (4.3a)$$

$$F_b = L_w(P_w - P_b)/(L_b\epsilon_w + L_w\epsilon_b), \quad (4.3b)$$

where $F_w$ and $F_b$ are the fields, $L_w$ and $L_b$ are the thicknesses and $\epsilon_w$ and $\epsilon_b$ are the static permittivities of the well and barrier layers, respectively.

In Paper [11] the value of PL peak shift under free-carrier screening was compared with the calculated value from Eqs. (2.5). In this case, the charge density term $\rho(z)$ in the Eq. (4.2) is determined by the spatial distribution of the free carriers in the QW structure as given by the solution of the Schrödinger equation. Thus, a self-consistent solution of Eqs. (2.5) and (4.2) must be found through iteration. A short introduction to the used numerical model is given in Appendix A.2.

The interpretation of the data from this experiment is complicated by high carrier...
density effects. Specifically, the filling of the band tail states and localized states within the bandgap causes a blueshift while many-body effects induce a redshift [79]. Comparison of the results from QWs with various thicknesses helps to single out the field screening contribution to the spectral shift. Also, the presence of free carriers in the QWs at equilibrium may affect the experimental results. Free carriers at equilibrium may come from adjacent doped regions. Moreover, if the field in the wells is so intense that the Fermi level becomes close to the band edges, carrier accumulation may spontaneously take place [100].

Fig. 4.9 shows a calculation example of free-carrier screening in a MQW. The MQW has 2.5 nm thick wells and 11.5 nm thick barriers with composition $x=0.35$ in the QWs and $x=0.48$ in the QBs.
The structure is coherently strained on a relaxed $x=0.5$ AlGaN buffer layer. The upper panels show the band profiles and the ground state wavefunctions for electrons and holes. In Fig. 4.9 (a), the internal field is not screened while in Fig. 4.9 (b) the field is screened by a high density of free carriers. In the unscreened case, electron and hole wavefunctions are pushed toward the opposite sides of the well. As the potential inside the QW levels out, the wavefunctions increasingly overlap. In Fig. 4.9 (c), the screening-induced blueshift of the ground state transition energy and the increase of the overlap integral are shown as a function of the carrier density. The overlap integral is calculated as in Eq. (2.8). Fig. 4.10 shows the total screening-induced blueshift as a function of the well width for structures with the same composition as in the previous example. The dependence of the PL peak shift on the polarization charge is presented in Fig. 4.10 (b) for the reference case of a 2.5 nm thick QW. The electric field in the barriers and wells changes linearly with the polarization charge in Eqs. (4.3). Therefore, the initial quadratic relationship between polarization and PL peak shift and the linear relationship at higher field values reproduce the dependence of the QCSE on the electric field value.

**Figure 4.10:** Screening-induced shift of the transition energy as a function of well width (a) and polarization charge (b). In (a), $P_{TH}$ is the theoretical value of the difference $P_b-P_w$ in Eqs. (4.3). In (b), the used values of polarization constants are reduced by a factor equal to $k$ compared to the theoretical values.
4.2. POLARIZATION FIELDS

Excitons in presence of an electric field

The internal field in nitride QWs has an important influence on the exciton binding energy. In an ideal QW structure with narrower well width than the bulk exciton Bohr radius, the binding energy of the confined excitons increases up to four times the bulk value and their radius decreases to a half of the bulk exciton Bohr radius [30]. The presence of an internal field represents a major deviation from the ideal model. By pushing electrons and holes toward the opposite sides of the well, the internal field reduces the exciton binding energy. This phenomenon was first discovered by Miller and co-workers [101].

A numerical calculation of the exciton binding energy in QWs under the influence of an electric field is presented in Appendix A.3. The same numerical method was applied to the study of excitons in a ZnSe/Zn$_{1-x}$Mn$_x$Se QW structure [45]. Despite the reduced binding energy compared to the zero field case, it was found that excitons are more confined in the QWs than free carriers, and the probability of tunneling under an external field is significantly lower. In Paper III the same procedure is applied to a structure composed by 2.5 nm QWs and 11.5 nm QBs with composition equal to $x=0.35$ and $x=0.50$, respectively. The confinement potentials along the $z$ direction and the energy levels for the electron and hole forming the exciton are represented in Fig. 4.11 at flat-band (a) and zero bias (b).

![Figure 4.11: Band profiles for free carriers (a) and excitons (b) in a 2.5 nm Al$_{0.35}$Ga$_{0.65}$N/Al$_{0.50}$Ga$_{0.50}$N QW.](image-url)

The simulated structure is the same as in one of the studied LEDs in Paper I. The LED shows a long PL decay time for excitation in the wells that is weakly dependent on bias. The direction of the polarization fields was found to be inverted compared to the predicted direction for (Al,Ga)-face layers in this device which was probably
composed by N-face layers. The calculated tunneling- and thermionic emission-limited lifetimes as in Eqs. (2.20) and (2.21) in the free-carrier model are much shorter than the measured PL decay time. Following Ref. [45], the calculations in Paper III show that electron-hole Coulomb interaction enhances the carrier confinement within the wells and reduces the probability of carrier escape from the wells. As a consequence, the obtained tunneling- and thermionic emission-limited lifetimes in the exciton recombination model are comparable with the measured PL decay time. Another possible explanation for the low tunneling and thermionic emission may be free carrier and/or exciton confinement in potential minima. The presence of potential fluctuations in AlGaN QWs is discussed in Section 5.4.
Chapter 5

AlGaN-based light-emitting diodes

Beside the fundamental properties of the AlGaN alloys that have been presented in the previous chapter, there are several other important aspects originating from the typical material growth and processing techniques. This chapter treats the technology, the structure and some issues related to the performance and reliability of deep-UV LEDs.

5.1 AlGaN epitaxial growth

The studied devices in this thesis were grown by the migration-enhanced metalorganic chemical vapor deposition (MEMOCVD). The MEMOCVD is a modified version of the metalorganic vapor phase epitaxy (MOVPE) that was specifically introduced to enhance the crystal quality of the AlGaN layers. In this section, an introduction to the MOVPE and MEMOCVD growth of AlGaN layers on sapphire are given, as described in Ref. [71]. The description is not intended to be comprehensive but only to highlight a few critical steps in the manufacturing of deep-UV light-emitting devices.

All the commercially available devices and the vast majority of the research prototypes are grown on lattice mismatched sapphire substrates [13, 16]. The equilibrium melt growth of III-nitride single crystals is complicated by the high equilibrium nitrogen pressure on the binary III-nitrides at their melting temperature [102] (see Appendix A.1). This determines the scarce availability of native substrates on the market to date. Sapphire substrates are widely available with good quality and relatively low cost. Moreover, sapphire exhibits hexagonal symmetry and is compatible with high temperature growth and ammonia environment.

MOVPE is usually employed for the growth of III-nitride-based devices because it allows the creation of abrupt interfaces and supplies a sufficiently high growth rate. N and group-III atoms are brought close to the growing surface as part of
larger precursor compounds: ammonia for N, trimethylgallium for gallium (Ga), trimethylaluminum for Al. Molecular hydrogen and nitrogen are used as carrier gases. For the growth of doped layers, bis(cyclopentadienyl)magnesium and silane are also flown into the chamber. The deposition occurs via pyrolysis of the precursors on the heated surface.

Among the substrate preparation steps, the exposure to ammonia at 600 °C, called nitridation, is critical to fix the (Al,Ga)-face polarity of the following layers \[103\]. One of the major breakthroughs in the III-nitride technology was the introduction of the nucleation layer (NL) by Amano in 1986 \[4\], which resulted in a drastic reduction of the dislocation density. This growth step consists in the deposition of a thin (∼ 50 nm) GaN or AlN amorphous layer at low temperature followed by a temperature ramp-up. At high temperatures, the NL assumes a columnar structure \[104\]. The columns are tilted and twisted with respect to each other to accommodate the lattice mismatch with the substrate and provide a high nucleation density for the following high temperature growth. Initially, nearly dislocation-free trapezoid III-nitride crystals grow on the top of the columns and eventually coalescence. The boundaries of coalescence are likely to be the most defect-rich regions of the epilayer. The TD density decreases with thickness \[105\] due to dislocation self-annealing. Although the NL is still widely employed for the growth of AlN, the necessity of a NL in the AlN growth on sapphire is currently under debate \[106\] as good quality AlN layers were directly grown on sapphire at high temperatures \[107\]. The growth temperature for AlGaN epitaxial layers is higher than the one for GaN, typically between 1100 °C and 1220 °C \[108\].

The choice of the growth parameters, particularly growth temperature, total precursor flow rate and III/V precursor flow ratio, is dictated by several trade-offs. The thermal stability of ammonia requires high substrate temperatures to dissociate the molecule. Besides, high growth temperatures are needed to mobilize TDs and promote their self-annealing during growth. However, the high nitrogen vapor pressure over the III-nitrides at the growth temperature leads to the inevitable nitrogen loss from the film. Therefore, N vacancies (V\(_N\)) and voids may form at high growth temperatures \[71\]. Besides, the mismatch of thermal expansion coefficient for sapphire and the III-nitrides induces a high mechanical stress when cooling from high temperatures that may cause the cracking of the layer. Finally, the growth temperature and the III/V precursor flow ratio influence the uniformity of incorporation of the metallic species on the surface via their diffusion length. The diffusion length of the adatoms on the surface quantifies the average length that the adatoms cover on the surface between adsorption and incorporation into the crystal or desorption. The limited diffusion length of Al adatoms is particularly critical for the growth of high quality AlGaN layers. Ideally, the growth proceeds layer by layer. For this to happen, the diffusion length of the metallic adatoms must be sufficient to reach the boundaries of the lateral expansion of the growing layer. The diffusion length of the group-III adatoms can be enhanced to some extent by increasing the growth temperature, adjusting the total precursor flow rate and the III/V flow ratio. Usually, slight Ga-rich conditions, for which the growth rate is
5.2. Structure of the AlGaN-based LEDs

The studied devices in this thesis were provided by Sensor Electronic Technology, Inc. [9]. In this section, the structure of a commercial UVTOP® deep-UV LED is described. The flip-chip design of a typical AlGaN-based LED is reproduced in Fig. 5.1.

As a substrate for UV emitters, sapphire provides a transparent window through which emission can take place. This is highly desirable because, for reasons explained in the following, the top p-type layer is composed of a GaN layer that is highly absorbing for the UV radiation. Therefore, light emission can only take place through the substrate and all the layers between the substrate and the active region must be transparent to the UV radiation. As a consequence, deep-UV LEDs are usually grown on thick AlN layers rather than on thick GaN layers as the InGaN-based LEDs. Besides, AlGaN layers grown on relaxed GaN are under...
tensile strain and are prone to crack \cite{71, 112}. On the contrary, cracking is inhibited for compressively strained AlGaN layers grown on relaxed AlN \cite{113, 114}. In general, while the epitaxial growth of GaN on sapphire has reached a considerable level of maturity, intense research is still under way to improve the quality of the AlN growth on sapphire. This is one of the reasons for the lower efficiency of the deep-UV emitters as compared to the visible InGaN-based emitters.

Narrow QWs with thickness between 2 and 3 nm are typically used to maximize the probability of electron-hole recombination. Because the sapphire substrate is insulating, electrical access to the n-type cladding layer cannot take place through the substrate. Instead, the MQW region is located within a mesa-like structure, and the contacts to p-type and n-type cladding are located on the same side of the device. The side walls of the mesa are covered with a silicon nitride layer that reduces the interface density of states \cite{115} and decreases the surface leakage current.

A thick n-type layer is necessary to minimize the resistance of the n-type cladding and improve the current spreading. The need for a thick conductive layer exacerbates the cracking issue in deep-UV LEDs. Recently, the introduction of a superlattice (SL) of AlGaN/AlN has accomplished a reduction of the residual strain \cite{116, 117}. Additionally, the SL acts as dislocation filter \cite{112}. Transmission electron microscope (TEM) images have shown that TD lines bend in the region of the SL, increasing the probability of their self-annealing \cite{118}. Dislocations are associated with nonradiative recombination in AlGaN layers \cite{78, 119}. Moreover, they are responsible for vertical current leakage \cite{25, 120}. Therefore, the reduction of dislocation density is essential for increasing the device efficiency.

An AlGaN layer with larger bandgap than the cladding layers, known as the electron blocking layer (EBL), is usually inserted between the active region and the p-type cladding of III-nitride LEDs. The EBL improves the electron confinement in the active region and increases the EQE efficiency at high carrier regimes.

The p-type cladding contains a p-GaN/p-AlGaN junction. The piezoelectric field at the heterointerface produces a hole accumulation layer that increases the conductivity of the p-type cladding \cite{22}. Under forward-bias, holes move from the accumulation layer to the active region via the field assisted tunneling and thermionic emission. The composition of the p-AlGaN layer is graded to optimize the potential profile of the p-type cladding.

A considerable increase in the output power has been obtained with the use of a H-shaped metal contact on the p-side, as shown in Fig. 5.2. The advantage of the contact layout is associated with an increased heat dissipation \cite{13}.

### 5.3 Efficiency issues of deep-UV LEDs

In this section, the main issues that influence the efficiency of deep-UV LEDs are summarized. Among them, some derive from fundamental properties of the AlGaN alloys, others are consequences of the employed technology.
5.3. EFFICIENCY ISSUES OF DEEP-UV LEDS

Figure 5.2: H-shaped pad layout of deep-UV LEDs. The right-hand side of the figure shows a micrograph of the EL from a device emitting at 310 nm. The observed shape reproduces the layout of the top p-type contact.

(i) The polarization fields in devices that are grown on polar surfaces separate the opposite sign carriers in the wells decreasing the probability of radiative recombination. This negative effect can be overcome to large extent by using thin QWs. However, the polarization fields impact the wall-plug efficiency in other ways. The band profiles in CB and VB across a typical LED structure are shown in Fig. 5.3 (the parameters of the simulated structure are the same as for the calculations presented in Fig. 4.10). The polarization sheet charge at the interface between layers produces potential barriers that impede the carrier transport [20, 21]. The presence of polarization-induced barriers was associated with the high ideality factor that is usually measured in III-nitride-based LEDs [20].

(ii) The low conductivity of p-type and n-type cladding layers is a major issue that affects the wall-plug efficiency and durability of deep-UV LEDs. The conductivity of AlGaN layers is impaired by compensating and scattering centers [2], thus, high crystal quality layers are of primary importance. However, fundamental obstacles remain to the achievement of highly conductive AlGaN layers. At variance with unintentionally doped GaN layers that are usually n-type, unintentionally doped Al$_{x}$Ga$_{1-x}$N films with $x>0.4$ are highly resistive. Although the n- and p-type doping of GaN and InGaN are well established, the successful doping of AlGaN is much more complicated. The commonly used dopant impurities are silicon (Si) and magnesium (Mg) that introduce donor and acceptor states, respectively. With increasing Al composition, the conductivity of epilayers for both doping types rapidly decreases. This is due to the continuous increase of the donor and acceptor ionization energies. The activation energy of Si increases linearly from 20 meV in GaN to 320 meV in AlN [121]. These values correspond to 0.8k$_{B}$T and 12.5k$_{B}$T, respectively, at room temperature. The activation energy of Mg is even higher. It increases almost linearly from 160 meV in GaN to 500 meV in AlN [122], corresponding to 6.3k$_{B}$T and 19.5k$_{B}$T at room temperature. So far, the p-GaN/p-AlGaN
heterointerface and the SL doping approaches have only partially solved the problem of the low p-type conductivity.

(iii) As it was mentioned previously, significant emission in the TM polarization may occur in structures with high Al molar fraction in the active region. Although there is still little experimental evidence, it seems that this mechanism takes place at very high Al molar fractions. Therefore, it is unlikely that TM polarized emission influences significantly the efficiency of commercially available devices.

(iv) The efficiency of InGaN-based LEDs decreases under high carrier injection, a phenomenon known as efficiency droop. The origin of the efficiency droop is still under debate. Auger recombination is one of the explanations that have been put forward. The probability of Auger recombination in direct bandgap semiconductors decreases strongly with increasing bandgap energy. For the III-V semiconductors other than the III nitrides, an exponentially decreasing trend is recognizable in spite of large uncertainties. The extrapolation of the trend for GaN would lead to an upper bound of $10^{-34}$ cm$^6$s$^{-1}$. This value agrees with first principle calculations for intraband Auger recombination. However, experimental values are much larger, usually in the range between $1\times10^{-31}$ and $3\times10^{-30}$ cm$^6$s$^{-1}$ as measured in InGaN-based heterostructures. Refined models were employed to explain the experimental data. It was found
that interband Auger recombination can occur in green-emitting InGaN alloys [124]. However, this process is not likely to occur in AlGaN alloys because of the different energy gaps between the electronic bands. In a recent publication, values closer to the experimental ones were calculated including indirect Auger processes that involve electron-phonon coupling and alloy scattering [125]. The efficiency droop in AlGaN-based layers occurs at much higher current densities than in InGaN-based LEDs [89, 126]. This may hint to a smaller value of Auger coefficients in AlGaN. In any case, the effect of Auger recombination can be neglected from the interpretation of our experimental data. Although Auger recombination may limit the efficiency of high-brightness devices in the future, it appears to be of secondary importance in the performance of commercial low-current-density devices to date.

(v) The electron leakage in the p-cladding at high current densities offers an alternative explanation for the efficiency droop in GaN-based LEDs [89]. This phenomenon is common to III-nitride-based LEDs because of the larger diffusion constant of electrons compared with holes in III-V semiconductors [2]. Moreover, leakage is enhanced at high current densities by band filling in the active region and device self-heating. Electron leakage in the p-type cladding was associated with a broad red-shifted band in the EL spectra. The band is originated from the electron recombination with a deep level in the p-type cladding [127, 128]. The EBL has proven to quench the red-shifted emission band and increase the efficiency at low to medium carrier regimes although the leakage still limits the efficiency at high current densities [89].

(vi) The density of dislocations was determined to be of primary importance in AlGaN-based devices. Experiments have shown that the IQE of MQW structures can be increased from 4% to 64% in a wide range of compositions by reducing the dislocation density [129]. The strong influence of the crystal quality on the IQE of the devices was also confirmed by the increased luminescence decay time in high quality layers grown by MEMOCVD [130]. Although there is direct evidence that dislocations act as nonradiative recombination centers in III-nitrides, the specific carrier trapping mechanism may change with sample composition and doping. The study in Paper IV suggests that dislocations may be efficient nonradiative recombination centers when they are decorated with point defects. Furthermore, the influence of potential fluctuations around dislocations is discussed in Section 5.4.

(vii) The EQE of flip-chip devices is severely limited by the internal reflection at the sapphire substrate interfaces. The light extraction efficiency for flip-chip GaN-based LEDs emitting through the sapphire substrate is around 23% [131]. More over, strong absorption in the p-GaN layer does not allow recovering the emitted photons on the side of the p-type contact. However, different designs have been developed to alleviate these problems in visible and near-UV LEDs,
such as the use of patterned substrates [132]. Similar solutions may eventually be deployed in deep-UV LEDs as well.

(viii) The comparison between the EQE under pulsed and continuous operation modes reveals that device self-heating is a serious problem in AlGaN devices [13]. Self-heating is due to the low conductivity of the doped cladding regions and the low thermal conductivity of sapphire. The reduction of the radiative recombination at increasing temperatures derives from the intrinsic temperature dependence of the bimolecular radiative recombination coefficient and the reduced carrier confinement in the active region.

5.4 Crystal inhomogeneities

Three types of inhomogeneities are commonly encountered in III-nitride epitaxial layers: compositional inhomogeneity [60], strain inhomogeneity [133] and extended defects [134, 135]. Additionally, fluctuations of the well thickness may occur in QW structures [136, 137]. The simultaneous presence of different kinds of inhomogeneities is often correlated, as Fig. 5.4 schematically portrays.

As outlined in Section 5.1, the growth of III-nitride layers on lattice mismatched substrates typically proceeds via coalescence of separated trapezoid crystals with different orientations [104, 138]. The misorientation among the crystals is partially accommodated by the formation of dislocations at the boundaries of coalescence. Nonetheless, an inhomogeneous strain field remains around the dislocations.

Figure 5.4: Inhomogeneities in III-nitride epitaxial layers and their interplay.
5.4. CRYSTAL INHOMOGENEITIES

[139][140], as observed in TEM measurements. The difference in mobility between the group-III adatoms is responsible for the formation of domains with different compositions during the growth of AlGaN epilayers [141]. Differences of lattice constant within these domains give rise to an additional component of inhomogeneous strain. The formation of inhomogeneous domains is aided by dislocations and inhomogeneous strain distribution as well. In fact, the atoms in the lattice may preferentially diffuse through the dislocation cores [142] during growth and device aging. Furthermore, the adatoms locally redistribute on the growing surface as to minimize the strain in the layer [133]. Therefore, compositional changes may occur around dislocations, where the strain is partially relaxed. Lastly, TDs in QWs were linked with variations of the well thickness that result in fluctuations of the confinement potentials for electrons and holes [137].

Inhomogeneities have a profound influence on the electrical and luminescence properties of III-nitride layers. In general, all inhomogeneities of the crystal structure constitute a source of carrier scattering and impair the carrier mobility. Concerning the luminescence properties, the presence of inhomogeneities locally shifts the peak wavelength. For example, Fig. 5.5 shows an estimation of the effect of compositional variations, monolayer thickness variations and strain relaxation on the ground state transition energy of an AlGaN MQW at low carrier densities.

![Figure 5.5: Bandgap variation in a 2.5 nm QW induced by monolayer variations and strain relaxation. The bandgap values are calculated solving the Schrödinger equation in the effective mass approximation. The details of the calculation and the used material parameters are summarized in Appendix A.1 and A.2.](image)
The considered structure is composed by five 2.5 nm thick Al$_{0.35}$Ga$_{0.65}$N QWs and 11.5 nm Al$_{0.48}$Ga$_{0.52}$N QBs on a relaxed Al$_{0.5}$Ga$_{0.5}$N buffer layer. Other inhomogeneity-related effects are spectral broadening and nonradiative recombination at dislocations.

Summarizing, the spectral width, peak position and luminescence efficiency depend in different proportions on the kind of inhomogeneity and the interplay between them. The rest of this chapter reviews several kinds of compositional inhomogeneities that are found in III-nitride layers with particular emphasis on the alloy fluctuations. Firstly, the issue of alloy fluctuations in epitaxial layers and QWs is briefly reviewed in the case of InGaN alloys, that have been more thoroughly studied than AlGaN alloys. The obtained results provide insight in the AlGaN case. The available results for the AlGaN alloys follow after that.

**Compositional inhomogeneities in InGaN**

The luminescence efficiency of InGaN layers strongly depends on the relationship between dislocations and alloy fluctuations. High luminous efficiency is obtained in samples where the minority carrier diffusion length is smaller than the average dislocation distance. This suggests that carrier localization in potential minima caused by compositional fluctuations has the benign effect of confining the carriers away from the detrimental dislocations in blue-emitting InGaN layers [23, 85]. Actually, SNOM measurements in QW layers combined with high-resolution atomic force microscope scans revealed the presence of regions emitting at red-shifted wavelengths. The size of the regions was comparable with the defect distance [135] and their origin was associated with compositional inhomogeneities. The measurements were found to be well-described by the presence of a miscibility gap [143].

In another work, TEM measurements revealed that the QW thickness is smaller around the TDs that are connected to V-pits in blue-emitting InGaN QW structures [137]. A smaller QW thickness around the TDs determines a larger bandgap. Thus, a potential barrier around the TD cores isolates the carriers from the TDs.

The presence of dislocations influences the compositional homogeneity as well. In accumulation at the cores of TDs was observed in CL measurements on QW structures [144]. The In excess at the TD cores may leave In-poor regions around the TDs. NF measurements on blue-emitting InGaN layers in another study [145] confirmed that deep exciton localization occurs in the In-rich regions at the sites of TDs, where the bandgap is narrower. Furthermore, the presence of local potential maxima surrounding the TDs was observed. The local potential maxima probably correspond to the In-poor areas around the TD cores, and act as potential barriers for the carriers outside the defective regions. Such potential barriers were not observed around the TDs in green-emitting InGaN layers. In this case, the NF measurements in Ref. [146] revealed that the carriers are free to diffuse to the TD cores, where they recombine nonradiatively. Therefore, the relationship between potential fluctuations and TDs seems to change with the sample preparation and composition.
Compositional inhomogeneities in AlGaN

Contrary to InGaN alloys, AlGaN alloys do not have a miscibility gap at practical growth temperatures \[ \text{[147]} \]. Because the misfit between AlN and GaN is only 2.5\%, one would expect a stable growth of AlGaN with a good control of the composition. However, several kinds of compositional inhomogeneities are commonly observed: random alloy disorder, alloy fluctuations, alloy segregation and ordering.

Randomly distributed alloy systems always present a certain degree of disorder at the scale of the lattice cell as a result of the statistical occupancy of the lattice sites \[ \text{[148]} \]. Alloy fluctuations usually refer to average variations of the alloy composition on a larger scale than the lattice cell. Segregation is the extreme situation for which one of the atoms or binary constituents of an alloy condensates within a region of the crystal. Alloy fluctuations and segregation usually occur within irregular volumes that have limited lateral size and do not present internal structure. On the other hand, ordering refers to the formation of domains containing a SL of spontaneous QWs along the growth direction. Ordering sometimes occurs within small areas of the sample \[ \text{[149]} \], but it can also extend over the whole sample surface \[ \text{[150]} \].

In AlGaN, the degree of alloy disorder has been determined from the broadening of the exciton linewidth \[ \text{[151]} \]. Regarding the ordering, TEM measurements have revealed the presence of spontaneous QWs along the c-axis \[ \text{[149, 152, 153]} \] within a wide range of compositions. Ordering occurs because there are several ordered configurations of atoms with formation energies that are close to each other and to the perfectly random configuration \[ \text{[147]} \]. The formation of ordered structures seems to be favored by the kinetics of the adatoms on the surface in the layer-by-layer growth mode \[ \text{[149]} \]. Ordering was identified as the cause of the uncertainty on the value of the bowing parameter. Concerning the segregation in AlGaN alloys, Al segregation has been observed in TEM measurements around TDs in MOVPE grown samples \[ \text{[154]} \]. Similarly to In segregation in InGaN layers, the Al surplus comes from Al-depleted regions that were observed within a few nanometers from the dislocation lines. Alloy fluctuations in AlGaN are treated in more detail in the following subsection.

Alloy fluctuations in AlGaN

Several luminescence experiments reveal the presence of alloy fluctuations in AlGaN layers. Carrier localization in domains with different compositions is evidenced by the wavelength shift between the peak of the absorption and emission spectra—the St"{o}ckes' shift. While the emission at low carrier densities is dominated by the exciton recombination in the potential minima, the absorption threshold occurs at the energy for which the density of states has a steep rise. Additionally, the same conclusion can be derived from the temperature dependence of the emission peak wavelength \[ \text{[155]} \]. The thermally activated exciton hopping between local
potential minima determines a characteristic “S” shape for the peak wavelength dependence on the temperature \[156\].

Interestingly, the measured PL decay time in AlGaN layers at 10 K increases as the Al mole fraction is increased \[24\]. This behavior is theoretically explained by the increase of the exciton radiative lifetime for increasing localization depths. Therefore, the presence of deeper localization potentials in layers with higher Al molar fraction has been suggested. Additionally, the room temperature lifetime of the nonequilibrium carriers was found to be limited by the carrier diffusion to the dislocations, where nonradiative recombination takes place \[78\]. These results seem to corroborate a similar role of potential fluctuations in Al-rich AlGaN layers as in blue-emitting InGaN layers.

In Paper \[VI\] the presence of potential minima in AlGaN-based QWs was deduced from DTPP measurements. The DTPP traces that were measured at different photon energies are shown in Fig. 5.6.

![Figure 5.6: DTPP traces from 3.3 nm thick Al\(_{0.35}\)Ga\(_{0.65}\)N QWs separated by 11.5 nm thick Al\(_{0.49}\)Ga\(_{0.51}\)N QBs.](image)

At intermediate photon energies (red curves), carriers are excited in the QW extended states above the bandgap and the induced transmission decays with a characteristic time of 80-150 ps. At lower photon energies (black curves), carriers are directly excited in the localized states with a longer lifetime, and the shape of the differential transmission transients becomes steplike with a very long decay time.
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At higher photon energies close to the barrier bandgap (green curve), the differential transmission transients change sign from induced transmission to induced absorption. For excitation in the wells and in the barriers compared to excitation just in the wells, a larger number of carriers are excited in the active region. Therefore, the field in the wells is screened shortly after the excitation and the overlap of electron and hole wavefunctions increases. Hence, the absorption increases for the probe pulse. The depth of the localization potential was estimated in 80 meV.

The direct visualization of emission inhomogeneities on the sample surface can be attained collecting the luminescence with high spatial resolution. Cathodoluminescence (CL) and NF spectroscopy are the usually employed techniques for spatially resolved spectroscopic measurements. The resolution of the CL measurement is limited by the excited volume and by the carrier diffusion within the sample. Moreover, the measurement requires conductive samples to limit the charging effect. The preparation of doped samples for CL measurements may create artifacts. In fact, the doping has a significant influence on the structural quality of GaN-related materials. Local blueshift of the emission from CL measurements was associated with relaxation of strain at cracks. Redshift was associated with Ga-rich regions at the boundaries of coalescence. Ga accumulation occurs at the beginning of the growth because of the different mobilities of Ga and Al adatoms. The inhomogeneity pattern is continued on the following layers owing to the strain inhomogeneity. This model is confirmed by the dimension of the compositionally inhomogeneous domains on the layer surface that replicates the size of the coalescence domains at the beginning of the growth.

![Figure 5.7](image)

**Figure 5.7:** Model of the growth kinetics in AlGaN on sapphire. The Ga-rich regions at the boundaries of coalescence are colored with light green and the Al-rich grains where secondary nucleation takes place in dark violet.
The same mechanisms that govern the formation of compositionally inhomogeneous domains in AlGaN and InGaN alloys strongly affect the surface morphology as well [133, 161]. Particularly in high Al molar fraction layers, the low mobility of the Al adatoms leads to secondary nucleation and increases the surface roughness [162]. The formation of compositionally inhomogeneous domains and secondary nucleation are schematically represented in Fig. 5.7.

So far, SNOM has found a limited application to the study of the homogeneity of AlGaN alloys [163]. This can be explained with the difficulties of using this technique in the UV range. On the other hand, NF measurements have some advantages with respect CL measurements. In IC mode or collection mode, NF measurements are less affected by the carrier diffusion in the sample and do not require any specific sample preparation.

In Paper VIII SNOM measurements have revealed distinctive differences among AlGaN layers with different nominal compositions. In the SNOM measurements, the presence of localization on a larger spatial scale than the experiment resolution can be detected by means of the peak wavelength shift. If the inhomogeneity occurs on a finer scale, the spectral broadening provides an estimate of the average potential depth of the fine compositional variations (see Section 2.3). The measurements have evidenced an interesting relationship between the redshift and the spectral broadening as can be seen in the NF spectra in Fig. 5.8 (b).

![Figure 5.8: NF peak energy map (a) from a 30% Al molar fraction epitaxial layer. In (b), the FF spectrum and the NF spectra from different points on the sample are compared.](image)

This is probably due to the presence of a double scale localization potential [130] with fine potential fluctuations within larger compositionally inhomogeneous domains. Fig. 5.9 shows a measurement on a sample with 42% Al molar fraction. The measurement evidences a positive correlation between the peak energy and the peak intensity. The correlation suggests that, at least in some composition range,
enhanced nonradiative recombination takes place within the potential minima, similarly as in green-emitting InGaN layers.

Figure 5.9: NF peak intensity map (a) and peak energy map (b) from a 42% Al molar fraction epitaxial layer.

5.5 LED aging

The operation lifetime of commercial deep-UV LEDs is of the order of 5000 hours for devices emitting at $\lambda>300$ nm [13] at the recommended current of 20 mA. Much shorter operation lifetimes are measured at higher currents [17] or in devices emitting at shorter wavelengths. These values are significantly lower than the operation lifetime of high-brightness InGaN-based LEDs of around 40000 hours [14]. A limited amount of work has been devoted to reliability studies of the sub-300 nm LEDs [26, 70, 164-166]. Two main failure scenarios, gradual and abrupt, have been identified [70]. The abrupt failure was associated with the presence of V-pits on the LED surface. V-pits occur at the surface termination of open-core TDs that form leakage paths through the active region. The high current density in the vicinity of these defects produces local overheating, atom migration from the contacts and formation of local electric shorting of the p-n junction [70].

The gradual output power degradation was initially linked to the formation of nonradiative recombination defects during degradation [166]. However, the comparison of the EL and PL from the active region has shown that no significant increase of the nonradiative recombination in the active region occurs after degradation [20]. Alternatively, the formation of $V_{XS}$ in the p-cladding was proposed to explain the gradual device degradation. According this interpretation, the formation of $V_{XS}$ during the device operation would be caused by electrons with high kinetic energy that traverse the junction under high current densities. Additionally, it has been shown that the device self-heating strongly reduces the operation lifetime [17].
Regardless the actual aging process, the device operation lifetime is strongly dependent on the dislocation density. Laboratory prototypes grown on patterned substrates by the MEMOCVD technique present reduced dislocation density and longer operation lifetime [167].

**Paper V** contains a NF study of a case of abrupt device failure. The results are summarized in Fig. 5.10.

![Intensity Spectra](image)

**Figure 5.10:** Failure of a 285 nm deep-UV LED. The rows from top to bottom represent successive NF measurements. In every row, the first column shows the spectrally integrated intensity, the second the peak wavelength and the third the spectra collected along a scan that is indicated by a dashed black line on the intensity maps.

Discrete regions with red-shifted emission and typical dimension of a few micrometers were observed. The magnitude of the redshift was observed to increase during aging and was explained with the migration of Al atoms out of the well region along dislocations. As mentioned before, Al segregation has been previously measured
5.5. LED AGING

at TD cores [154], leaving Al-poor regions around them. Further atom migration during aging could produce high current paths through the active region. Intense self-heating in the regions of high current density would induce a current run-away mechanism.

The gradual device failure after DC current stress is studied in Paper VII. The FF comparison of EL and PL confirms that the active region is not significantly damaged during the aging process. The device deterioration seems to be related to two phenomena: the emission of a wide, red-shifted band with respect to the main peak and the increase of conductivity at low reverse and forward bias.

**Red-shifted emission band**

The red-shifted emission band has been previously documented for AlGaN-based LEDs emitting at 325 nm [168], 285 nm [169] and 270 nm [170]. In all of these studies, the peak has been attributed to the carrier recombination in the p-cladding. The well-documented electron leakage in the p-type cladding of III-nitride-based LEDs [89] supports this interpretation. Different types of transitions have been invoked to explain the red-shifted band, such as transitions between the CB and the Mg acceptor level [109] and between the nitrogen vacancy donors $V_{N}^{4+}$'s and the Mg acceptors [122]. Furthermore, aging experiments in Ref. [170] have revealed that the weight of the red-shifted band on the total emission spectrum increases during aging, as shown in Fig. 5.11. This result suggests the emergence of an alternative recombination path during aging.

![Figure 5.11: EL from a 265 nm deep-UV LED before (solid line) and after (dashed line) aging (reproduced from Ref. [170]).](image-url)
In Paper VII, evidence is presented that indicates the origin of the red-shifted band in transitions between the $V_{3+}^N$'s and the VB. The donor-acceptor type recombination can be excluded because the measured luminescence decay time of the red-shifted band is much shorter than the typical decay time for donor-acceptor pair transitions [171]. The CB to the Mg-acceptor level transition can also be excluded because it would generate a red-shifted band in a different spectral position. Also, the increased weight of the red-shifted emission band after aging suggests that the density of $V_{3+}^N$ increases during aging.

**Vertical conduction at extended defects**

The analysis of the I-V curves in Paper VII evidences an increase of the conductivity at low reverse and forward bias and a decrease at high forward bias. An increase of the tunneling conduction at TDs was proposed to explain the aging-induced conductivity increase. In general, the results of scanning current-voltage measurements support the mechanism of tunneling conduction around dislocations [23] [20]. GaN layers contain large densities of crystallographic defects, among which TDs [172], nanopipes, inversion domains [173], and pyramidal planar defects [158] [174] can cross the whole epitaxial layer and hamper the electrical and optical properties. There is still a controversy around the electrical and optical activity of the different kinds of defects [172] [175]. However, open-core screw dislocations have been indicated as the most likely responsible for the leakage current through the active region of III-nitride-based LEDs [25] [120]. Screw dislocations in GaN exist as full-core screw dislocations, screw dislocations with a narrow opening or in the form of nanopipes, whereas the edge dislocations have filled cores [172]. Whether the screw dislocation cores in GaN are filled, depends on the growth conditions and doping. Due to the large stress field near dislocations, point defects, complexes, and impurities can be trapped at dislocations rendering them electrically active [176]. Moreover, coreless screw dislocations have been reported to start from V-shaped indentations, the density of which increases with higher concentrations of impurities or dopants [158] [174]. Therefore, there seems to be a connection between gettering of impurity at dislocation cores and formation of open-core, electrically active TDs.

In Paper IV, preliminary studies on proton implanted GaN layers sustain the presence of an interaction mechanism between the point defects and the dislocations. Proton implantation increases the density of $V_{Ga}$ without modifying the density of dislocations in the superlattice. $V_{Ga}$ and their complexes with oxygen impurities are the most common native point defects in n-type GaN [177]. PL lifetime measurements in the as-implanted and annealed samples suggest that $V_{Ga}$ are mobile at relatively low temperatures and tend to gather at extended defects.

The formation energy of point defects in GaN depend on the position of the Fermi level. In p-GaN, the $V_N$ is the point defect with minimum formation energy [178]. Moreover, in materials grown under Ga-rich conditions, the trapping of $V_{As}$ at the core of the TDs increases the stability of the dislocations [179]. Most importantly, in Ref. [25] the activation of current conduction through screw dislo-
5.5. **LED AGING**

Cations were observed by accumulation of $V_{N}$ at the dislocation cores. Therefore, formation of $V_{N}$s and electrical activation of TDs by trapping of $V_{N}$s provide a reasonable explanation for the gradual reduction of the light emission during the aging of AlGaN-based LEDs.

Fig. 5.12 is reproduced from **Paper VII** and shows the optical micrographs of two LEDs before and after aging. The devices emitted at 285 nm and 310 nm and were aged at a constant current of 100 mA for 86 and 52 hours, respectively.

![Optical micrographs from two deep-UV LEDs](image)

**Figure 5.12:** Optical micrographs from two deep-UV LEDs. The first and second rows show the optical micrographs under forward bias of the virgin and aged LEDs, respectively. In the third row, the optical micrographs of the aged devices under forward and reverse bias are superimposed (the false-color image of the EL under reverse bias is shown in red).

The images from the aged devices show a correlation between sites of strong conductivity under reverse bias (in red) and sites of weak emission under forward bias. This correlation confirms that the carriers flow through the active region via highly conductive paths without recombining.
Concerning the reduction of conductivity at high currents, hydrogen diffusion from the silicon nitride passivation layer has been suggested as a possible cause [180]. However, formation of $V_{NS}$ during aging would also lead to compensation of the p-type conductivity. An increase of resistivity of the p-type layers due to the compensation of Mg doping would cause enhanced current crowding at the tunneling sites, aggravating the increase of the ideality factor at high currents.
Chapter 6

Conclusions and future work

The development of deep-UV LEDs has begun as a natural extension of the work on blue-emitting LEDs. As it has happened before, a multitude of applications were found a posteriori for the devices. However, in order to completely fulfill the potentiality of this technology, several issues are still to be addressed. In this thesis, the characterization of AlGaN epitaxial layers and heterostructures has contributed to the understanding of some fundamental and growth-induced properties of the AlGaN layers and heterostructures. The main results are listed below.

(i) The value of polarization in high Al molar fraction AlGaN quantum wells has been studied. In particular, the dependence of the polarization on the composition (Paper I) and dimensions (Paper II) of the QW structure were considered. The obtained field values in the QWs are in the range of 1 MV/cm in low Al molar fraction structures, compatible with the derived values from first principle calculations. However, for higher Al molar fractions (x~0.35), the experimental values were smaller by a factor of two compared to the theoretically predicted values.

(ii) The carrier dynamics in presence of high polarization fields in AlGaN quantum wells was studied in Paper II and Paper III. The PL decay shortly after the excitation was found to be dominated by field descreening. Theoretical calculations of tunneling and thermionic emission limited lifetimes determined much shorter values than the measured ones and a model based on exciton recombination was proposed.

(iii) The presence of carrier localization in AlGaN QWs and epitaxial layers was evidenced by degenerate DTPP measurements (Paper VI) and NF spectroscopy (Paper VIII), respectively. The depth of the potential fluctuations was estimated to about 80 meV in the case of a QW sample. The transition from localized to extended states was evidenced by the reduction of the carrier lifetime. A double scale localization potential was measured in the epitaxial
layers. The double scale localization was explained in terms of the growth kinetics and important differences were evidenced between samples containing different Al molar fractions. The model is able to account for the correspondence of large scale localization and defect rich areas. Furthermore, it explains the origin of the spectral broadening and its characteristics in samples with different compositions.

(iv) The aging of deep-UV LEDs under high current stress was studied by means of NF spectroscopy and FF EL and PL. The abrupt LED degradation was explained with the presence of native compositional inhomogeneities [Paper V]. Furthermore, a red-shifted emission band was unambiguously identified with transitions between the $V_{3+}^N$-related states and the VB in the p-type cladding [Paper VII]. The current crowding at $V_{3+}^N$-activated screw dislocations and device self heating were revealed as the main gradual aging mechanisms in AlGaN-based deep-UV LEDs.

Suggestions for future work

To date, several questions are still open in the field of AlGaN-based light emitters. This thesis have tried to address some of them. In the process, new issues have arisen and improvement on the performed experiments are desirable.

(i) The role of potential fluctuations and their connection to dislocations need to be further studied in AlGaN alloys. It appears that potential fluctuations in AlGaN layers bring about a moderate increase of carrier lifetime but they are not as effective as in InGaN layers in increasing the EQE. In particular, we demonstrated that carrier localization may occur in the neighborhood of regions with a higher nonradiative recombination. The relationship between the large scale and the small scale potential fluctuations on one hand and the extended defects on the other needs to be further studied in samples with different compositions. To this end, low temperature time-resolved NF measurements would be highly helpful. Furthermore, the comparison of NF and high-resolution atomic force microscope scans on the same area could evidence the relationship between potential fluctuations, dislocations and nonradiative recombination.

(ii) The increase of the $V_{3+}^N$ point defect concentration in the p-cladding of the AlGaN based LEDs that occurs during aging appears as one of the fundamental aging mechanisms in the deep UV LEDs. The presence of $V_{3+}^N$ seems to be connected with the red-shifted emission band compared to the band-edge luminescence. It would be highly desirable to perform systematic FF PL studies on a set of AlGaN samples with different Al molar fractions, doping levels and, possibly, dislocation densities. Furthermore, proton implantation may allow tuning the density of $V_{3+}^N$ independently from the density of extended
defects. Additionally, annealing experiment may help understanding the stability and mobility of the point defects. Time-resolved NF studies combined with atomic force microscope measurements may also reveal the interaction of point defects and dislocations in as-grown, implanted and annealed samples. Lastly, TEM measurements on as-grown and implanted samples might shed light on the proposed process of electric activation of the TDs by modification of the dislocation cores.

(iii) Excitons have large binding energies in GaN and AlN. The binding energy in AlGaN alloys could be even larger owing to localization. The presence of excitons in AlGaN LEDs and their ionization at high temperatures or carrier densities may influence the efficiency of AlGaN-based devices. The stability of excitons in AlGaN QWs depending on temperature, carrier density and internal fields needs to be investigated. To this end, low temperature NF spectroscopy may allow distinguishing exciton lines and establish the carrier density at which the Mott transition occurs. Additionally, strip contacts on the sample surface could be used to probe the exciton stability against static electric fields.

(iv) It was claimed that AlGaN based devices have a relatively high IQE in spite of the limited EQE. There have been suggestions that low extraction efficiency is caused by the VB crossing and preferential emission of light along the well plane. The VB crossing in the well material strongly depends on the composition and strain within the well layer. So far, a very limited amount of work has been devoted to this important issue. Hence, a systematic study of the polarization properties of the emitted light from the edge of AlGaN quantum wells with different compositions and widths would provide useful information.
Appendix

A.1 Constants and parameters

Basic properties of wurtzite AlN and GaN are collected in the following table:

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å) *</td>
<td>3.189</td>
<td>3.103</td>
</tr>
<tr>
<td>c (Å) *</td>
<td>5.188</td>
<td>4.980</td>
</tr>
<tr>
<td>lattice mismatch to c-sapphire [71]</td>
<td>16.1%</td>
<td>13.3%</td>
</tr>
<tr>
<td>$E_g$ (eV) at 300 K [71]</td>
<td>3.42</td>
<td>6.25</td>
</tr>
<tr>
<td>Thermal expansion coefficient $\Delta a/(a\Delta T) (K^{-1})$ † (sapphire, 5.0×10^{-6})</td>
<td>5.59×10^{-6}</td>
<td>4.2×10^{-6}</td>
</tr>
<tr>
<td>Thermal conductivity (Wcm^{-1}K^{-1}) † (sapphire</td>
<td></td>
<td>c, 0.23)</td>
</tr>
<tr>
<td>Melting temperature (°C) (sapphire, 2000) [71]</td>
<td>2500</td>
<td>3200</td>
</tr>
<tr>
<td>$N_2$ vapor pressure at the melting temperature (bar) [102]</td>
<td>4×10^4</td>
<td>100</td>
</tr>
<tr>
<td>Average bond strength (eV) [181]</td>
<td>2.23</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Table A.1: Basic properties of wurtzite GaN and AlN.
* experimental values [63]
† near room temperature [71]

The used values of effective mass for electrons and heavy holes in the calculations were derived from the linear interpolation of the values for GaN and AlN in
Table A.2: Simulation parameters for wurtzite GaN and AlN. The effective mass values are from Ref. [182] and the static permittivities are from Ref. [63].

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e \parallel c$</td>
<td>0.138$m_0$</td>
<td>0.231$m_0$</td>
</tr>
<tr>
<td>$m_e \perp c$</td>
<td>0.151$m_0$</td>
<td>0.242$m_0$</td>
</tr>
<tr>
<td>$m_{hh} \parallel c$</td>
<td>2.00$m_0$</td>
<td>2.38$m_0$</td>
</tr>
<tr>
<td>$m_{hh} \perp c$</td>
<td>2.255$m_0$</td>
<td>3.058$m_0$</td>
</tr>
<tr>
<td>static $\epsilon$</td>
<td>10.28$\epsilon_0$</td>
<td>10.31$\epsilon_0$</td>
</tr>
</tbody>
</table>

The used CB and VB offsets at the interface between two AlGaN alloys with bandgap difference $\Delta E_g$ is [100]:

$$\Delta E_c = 0.7\Delta E_g$$  \hspace{1cm} (A.1a)
$$\Delta E_v = 0.3\Delta E_g$$  \hspace{1cm} (A.1b)

The considered spontaneous and piezoelectric polarization constants in the simulations and in Fig. 4.7 are from Ref. [63]. The spontaneous polarization is calculated as

$$P_{SP_{\text{AlGaN}}}(x) = -0.090x - 0.034(1-x) + 0.021x(1-x), \quad (A.2a)$$
$$P_{SP_{\text{AlGaN}}}(x) = xP_{SP_{\text{AlN}}}^{PPZ}(\epsilon_{\parallel}) + (1-x)P_{SP_{\text{GaN}}}^{PPZ}(\epsilon_{\parallel}), \quad (A.2b)$$

and the piezoelectric polarization as

$$P_{\text{AlGaN}}^{PPZ}(\epsilon_{\parallel}) = -1.808\epsilon_{\parallel} + 5.624\epsilon_{\parallel}^2$$ for $\epsilon_{\parallel} < 0 \quad (A.3a)$$
$$P_{\text{AlGaN}}^{PPZ}(\epsilon_{\parallel}) = -1.808\epsilon_{\parallel} - 7.888\epsilon_{\parallel}^2$$ for $\epsilon_{\parallel} > 0 \quad (A.3b)$$
$$P_{\text{GaN}}^{PPZ}(\epsilon_{\parallel}) = -0.918\epsilon_{\parallel} + 9.541\epsilon_{\parallel}^2, \quad (A.3c)$$

where $\epsilon_{\parallel}$ is the in-plane biaxial strain:

$$\epsilon_{\parallel} = \frac{a_{\text{buffer}} - a(x)}{a(x)}. \quad (A.4)$$

A.2 Numerical solution of the Schrödinger-Poisson system

In this thesis, the Schrödinger-Poisson system is solved using the spectral element method [183]. The spectral element method is a generalization of the spectral
method. Contrary to a standard finite element method, the spectral method converts a differential equation into a full matrix problem. However, a significantly reduced number of discretization points is required to achieve comparable accuracy in case of highly regular problems. In the spectral element method, the computational domain is divided into subintervals within which the spectral method is used. The solutions in different intervals are joined using appropriate boundary conditions. This approach allows more freedom in the choice of the discretization points than for the simple spectral method and generates block matrices that are computationally lighter than full matrices. Most importantly, it allows extending the spectral method to problems presenting discontinuous properties and less regular solutions as in the case of the effective mass Schrödinger equation in a QW structure.

The numerical solution of a differential equation requires the discretization of the derivatives of the solution $u(z)$ in a set of points $\{z_j\}$, called collocation points. Let us initially assume that the values of the solution $\{u(z_j)\}$ in $N+1$ points $\{z_j\}$ are known. The basic idea of the spectral method is to use the unique polynomial $p_N$ of degree $\leq N-1$ which interpolates $u(z)$ in $\{z_j\}$ as the approximation of $u(z)$ such that

$$p_N(z_i) = u(z_i) \quad \forall z_i \in \{z_j\}.$$  

(A.5)

The first derivative, $u^{(1)}(z)$, and second derivative, $u^{(2)}(z)$, of $u(z)$ in $\{z_j\}$ can now be approximated with the derivatives of $p_N$ in $\{z_j\}$:

$$u^{(1)}(z_j) \approx p_N^{(1)}(z_j),$$  

(A.6a)

$$u^{(2)}(z_j) \approx p_N^{(2)}(z_j).$$  

(A.6b)

It can be shown that the derivatives of $p_N$ in $\{z_j\}$ can be written as linear combinations of $\{u(z_j)\}$ [184]. Thus, for every choice of collocation points $\{z_j\}$, the approximate derivatives of $u(z)$ are written as matrices that multiply the vector of $\{u(z_j)\}$ values. The original differential equation, where $\{u(z_j)\}$ are actually unknown, becomes a linear system where $\{u(z_j)\}$ is replaced by a vector $U$ of unknowns.

The explicit form of the differentiation matrices depends on the choice of the collocation points $\{z_j\}$. The calculated solution at equispaced points fails to converge to the exact solution as $N \to \infty$ because of the Runge phenomenon. Hence, unevenly spaced collocations points must be chosen. One common choice are the Chebyshev points, that are denser at the boundary of the computational interval. In the interval $[-1,1]$ they are as follows [184]:

$$z_j = -\cos \left( \frac{j\pi}{N} \right),$$

(A.7)

$$j = 0, 1, ..., N.$$

Efficient codes are available for the calculation of the differentiation matrices in the Chebyshev points [184]. The spectral method has been applied within QWs
and QBs. The boundary conditions described in Chapter 2 have been enforced to couple the subsystems [183]. The generalized eigenvalue solver contained in MATLAB R2007b has been used to solve the discretized version of the Schrödinger equation (Eqs. (2.5)) for electrons and holes.

The Poisson equation was solved considering separately the polarization charges and the free carrier densities. The potential term originating from the polarization charges was calculated by direct integration of the field distribution in wells and barriers as given by Eqs. (4.3). The other potential term from the free carrier distribution was calculated assuming charge neutrality and zero field at the boundaries of the integration domain [185]. This choice is motivated by the equal total number of electrons and holes that are optically excited in the active region.

A.3 Exciton binding energy

The exciton binding energy in a QW under an electric field was calculated following the method that is described in Ref. [101] and [186]. Firstly, the center-of-mass of the in-plane motion of the exciton is excluded from the complete excitonic Hamiltonian. Thus, the Hamiltonian can be written as

\[ H = E_g + H_{ez} + H_{hz} + K_r + U_{reh}, \]  

\[ H_e = -\frac{\hbar^2}{2} \frac{\partial}{\partial z_e} \left( \frac{1}{m_e(z_e)} \frac{\partial}{\partial z_e} \right) + U_e(z_e) + qFz_e, \]  

\[ H_h = -\frac{\hbar^2}{2} \frac{\partial}{\partial z_h} \left( \frac{1}{m_h(z_h)} \frac{\partial}{\partial z_h} \right) + U_v(z_h) - qFz_h, \]  

\[ K_r = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r_e^2} + \frac{1}{r_e} \frac{\partial}{\partial r_e} \right), \]  

\[ U_{reh} = -\frac{q^2}{4\pi\varepsilon_{eff}\sqrt{r_e^2 + (z_e - z_h)^2}}, \]

where \( z \) is the growth direction and \( r_e \) is the relative electron-hole distance in the in-plane direction \( r_e = \sqrt{(x_e - x_h)^2 + (y_e - y_h)^2}. \) \( U_e \) and \( U_v \) are the quantum well confining potential energies in \( z \) direction for the electron and the hole, respectively. In the calculation example in Section 4.2, the exciton in-plane effective static permittivity was set to \( \varepsilon_{eff} = 8.3\varepsilon_0 \). This value was derived from Eq. (2.12) using the bulk exciton binding energy in the ground state. The bulk value of binding energy for the considered alloy in the QW was obtained from a linear interpolation of the experimental values of bulk exciton binding energy in AlN and GaN in Table 4.1.

The solution of the Schrödinger equation for the exciton cannot be obtained analytically for a real QW structure. An approximated numerical solution is calculated by a self-consistent iterative method [186]. The ground state of the Hamiltonian is written as the product of functions of different coordinates as

\[ \psi(r_e, z_e, z_h) = \phi(r_e)\chi_e(z_e)\chi_h(z_h), \]
A.3. EXCITON BINDING ENERGY

where $\phi(r_e)$, $\chi_e(z_e)$ and $\chi_h(z_h)$ are approximate forms for the exciton, electron and hole wavefunctions, respectively. They are ground states of one variable Hamiltonians:

\[
\begin{align*}
(K + \bar{U}_r(r_e))\phi(r_e) &= E_\chi \phi(r_e), \quad (A.10a) \\
(H_e + \bar{U}_e(z_e))\chi_e(z_e) &= E_e \chi_e(z_e), \quad (A.10b) \\
(H_h + \bar{U}_h(z_h))\chi_h(z_h) &= E_h \chi_h(z_h), \quad (A.10c)
\end{align*}
\]

where $\bar{U}_e$, $\bar{U}_h$, $\bar{U}_r$ are the corrections due to the Coulomb potential for the electron, hole and exciton, respectively. They are evaluated as

\[
\begin{align*}
\bar{U}_e(z_e) &= \langle \phi \chi_h | U_{reh} | \phi \chi_h \rangle, \quad (A.11a) \\
\bar{U}_h(z_h) &= \langle \phi \chi_e | U_{reh} | \phi \chi_e \rangle, \quad (A.11b) \\
\bar{U}_r(r_e) &= \langle \chi_e \chi_h | U_{reh} | \chi_e \chi_h \rangle. \quad (A.11c)
\end{align*}
\]

The angle brackets notation implies the scalar product of the Coulomb potential in Eq. (A.8c) with two of three one-variable wavefunctions. The calculation of the wavefunctions in Eqs. (A.10) and the potential corrections in Eqs. (A.11) are repeated until self-consistency is reached. The corresponding value of the total energy is written as:

\[
E = E_e + E_h + E_\chi - \langle \chi_e | U_e | \chi_e \rangle - \langle \chi_h | U_h | \chi_h \rangle. \quad (A.12)
\]
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Publications
Guide to the articles

PAPER I: “Intrinsic electric fields in AlGaN quantum wells”

This article presents the first investigation of the polarization fields in high molar fraction $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$ QW structures with the same barrier and well dimensions but different compositions. A linear relationship between electric field inside the QWs and PL peak shift was assumed, approximation valid for strong fields. The polarization field value was derived from the comparison of the PL peak shift due to external p-i-n field (QCSE) and the shift induced by optically excited free carrier (screening of the field inside the QWs). In structures with lower Al content, experimental fields values around 1 MV/cm compare well with the results of first principle calculations, particularly considering partial strain relaxation.

Author contribution: calculations. The samples were grown at SET, Inc. and the measurements were carried out by S. Marcinkevičius and K. Liu.

PAPER II: “Screening dynamics of intrinsic electric field in AlGaN quantum wells”

The induced dynamic screening of the polarization field by optically excited free carriers in high molar fraction $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}/\text{Al}_{0.49}\text{Ga}_{0.51}\text{N}$ QW structures are presented. The compositions of the barrier and well layers were the same in all the examined structures but different well widths were examined. The PL peak shift was found to saturate at high optical excitation. Furthermore, the dynamic polarization field descreening was found to determine the initial luminescence decay. The PL peak shift at high intensities was compared with theoretical values computed solving self-consistently the Schrödinger-Poisson system. The comparison allowed deriving a value of the polarization field equal to 0.6 MV/cm, roughly half of the calculated value using first principle calculations.

Author contribution: modeling and data analysis. The samples were grown at SET, Inc. and the measurements were carried out by S. Marcinkevičius and K. Liu.
PAPER III: “Carrier lifetimes in AlGaN quantum wells: electric field and excitonic effects”

This article presents an experimental and theoretical study of the photoexcited carrier dynamics in a high Al molar fraction Al$_{0.35}$Ga$_{0.65}$N/Al$_{0.50}$Ga$_{0.50}$N MQW LED. The measured PL decay was biexponential, with the shortest component due to the polarization field descreening and the long to nonradiative recombination. The decay time was long, 600 ps, and slightly dependent on the applied bias below flat-band condition. The theoretical values of carrier lifetimes in the limit of dominant tunneling and thermionic emission outside the QWs were found several orders of magnitude smaller than the measured PL decay time. Much longer carrier lifetimes were obtained by including the electron-hole Coulomb interaction within the free exciton model.

Author contribution: modeling, data analysis and part of the writing. The samples were grown at SET, Inc. and the measurements were carried out by S. Martčinkovičius and K. Liu.

PAPER IV: “Time-resolved luminescence studies of proton-implanted GaN”

This article presents a study of the effect of point defect creation in unintentionally doped GaN. As-grown GaN samples were implanted with protons and annealed at several temperatures. TRPL measurement revealed that free carrier trapping time can be varied by two orders of magnitude and reach values of a few picoseconds. The reduction of carrier lifetime was attributed to $V_{Ga}$ created during implantation. Measurements on annealed samples show that carrier lifetimes can only be slightly restored by annealing at temperatures up to 750 °C. The increase of the PL decay time after annealing is attributed to annealing of free $V_{Ga}$s. Additionally, trapped vacancies at TD sites are responsible for the persistent short PL decay time in the highly implanted samples. This result sustains the role of TDs in the nonradiative recombination in III-nitrides and suggests that the widest tuning of carrier lifetime in GaN by proton implantation could be achieved in layers with a high density of TDs.

Author contribution: measurements, data analysis and writing. The samples were grown by Thomas Aggerstam and implanted by A. Hallén, the annealing was done in collaboration with M. Usman.

PAPER V: “Aging of AlGaN quantum well light emitting diode studied by scanning near-field optical spectroscopy”

In this article, NF measurements of the EL from a deep-UV LED are presented. In the flip-chip mounted device, the sapphire substrate was removed to increase
the light output. A collection mode setup is used and the emission is measured through the n-type cladding. Micrometer-sized domains emitting at lower wavelength were identified. The emission intensity from the domains was higher than the background. The EL measured from the same spot were measured during the aging of the device. As the total luminescences decreased, the peak emission wavelength progressively red-shifted to longer wavelength until the final failure of the device took place. Compositional modification of the active region during aging was suggested as failure mechanism. The migration of Al atoms along dislocation cores and current crowding were proposed.

Author contribution: measurements, data analysis and part of the writing. The device was fabricated by SET, Inc.

PAPER VI: “Dynamics of carrier recombination and localization in AlGaN quantum wells studied by time-resolved transmission spectroscopy”

In this work, DTPP measurements were performed on Al$_{0.35}$Ga$_{0.65}$N/Al$_{0.40}$Ga$_{0.51}$N QW structures with different QW widths. Pump-probe traces obtained at different wavelengths were compared with TRPL measurements. The results suggest the presence of localized states. In the case of direct excitation within the localized states, localization of one type of carrier was proposed with an estimated localization depth of around 80 meV. For excitation at higher photon energies, an increase of the absorption was related to the screening of the polarization field in the QWs. Excitation intensity measurements for excitation in the localized states evidence long lifetime of the localized carriers. Furthermore, the photon flux that was required to saturate the localized states allowed estimating the density of localized states to around $1.3 \times 10^{13}$ cm$^{-2}$.

Author contribution: preparation of the setup and preliminary measurements. The samples were grown at SET, Inc.

PAPER VII: “High current-induced degradation of AlGaN ultraviolet light emitting diodes”

The degradation under high current stress of AlGaN based deep-UV LEDs emitting at 285 and 310 nm was studied using EL, TRPL and I-V measurements. The measurements have revealed that the decrease of EL intensity during aging is accompanied by the increase of tunneling current, the increase of the $V_N$ concentration and the partial compensation of the doping in the p-type cladding. The main aging mechanism was ascribed to the electric activation of the conduction through screw dislocations, probably by $V_N^{1+}$ gettering. Carrier lifetimes in the QWs and p-type cladding were found to be unaffected by the current stress, suggesting the minor role of the nonradiative recombination.
Author contribution: measurements, data analysis and writing. The devices were fabricated by SET, Inc.

PAPER VIII: “Localization potentials in AlGaN epitaxial films studied by scanning near-field optical spectroscopy”

Scanning NF PL spectroscopy was used to study the potential fluctuations in AlGaN epitaxial layers with Al molar fraction between $x=0.30$ and $x=0.50$. The distribution of peak intensity, peak wavelength and full width at half maximum on the measured regions evidences two localization scales. The potential of the nanoscopic localization was evaluated from the inhomogeneous broadening contribution of the NF spectral width. The nanoscopic potential fluctuations were found to increase in depth and cover larger sample areas with increased Al content. They were associated with the formation of Al rich grains as a result of secondary nucleation during the samples growth. Larger scale potential fluctuations were associated with Ga-rich regions close to the boundary of columns and layer steps. The density, size and shape of these domains are composition dependent. For some compositions, stronger nonradiative recombination was observed at the sites of the carrier localization.

Author contribution: measurements, data analysis and part of the writing. The devices were fabricated by SET, Inc.