Luminescence of group-III-V nanowires containing heterostructures

The role of polytypism, polarization fields and carrier localization

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Abstract

In this thesis, the spectral and spatial luminescence distribution of heterostructures in self-induced nanowires (NWs) is investigated by cathodoluminescence spectroscopy in a scanning electron microscope. This method is complemented by data from both continuous and time-resolved micro-photoluminescence measurements. Three different structures are considered: (i) GaAs NWs containing segments of the wurtzite (WZ) and zincblende (ZB) polytypes, (ii) GaN microcrystals overgrown on GaN NWs, and (iii) (In,Ga)N insertions embedded in GaN NWs.

The polytypism of GaAs NWs results in complex emission spectra. The observation of luminescence either exclusively at energies below the ZB band gap or also at higher energies is explained by differences in the distribution of ZB and WZ segment thicknesses. Measurements at room temperature suggest that the band gap of WZ GaAs is at least 55 meV larger than that of the ZB phase.

The luminescence spectra of the GaN microcrystals contain distinct emission lines associated with stacking faults (SFs). SFs essentially constitute ZB quantum wells of varying thickness in a WZ matrix and it is shown that their emission energy is dominated by the spontaneous polarization. Through a detailed statistical analysis of the emission energies of the different SF types, emission energies of 3.42, 3.35 and 3.29 eV are determined for the intrinsic (I₁ and I₂) as well as the extrinsic SFs, respectively. From the corresponding energy differences, an experimental value of -0.022 C/m^2 is derived for the spontaneous polarization of GaN.

The importance of both carrier localization and the quantum confined Stark effect induced by the piezoelectric polarization is shown for the luminescence of (In,Ga)N insertions in GaN NWs. Not only localized excitons, but also electrons and holes individually localized at different potential minima contribute to the observed emission.

Keywords: GaN, (In,Ga)N, GaAs, nanowire, cathodoluminescence, stacking fault, spontaneous polarization, polytypism, wurtzite, zincblende

Zusammenfassung

In dieser Dissertation wird die spektrale und örtliche Verteilung der Lumineszenz von Heterostrukturen in selbstorganisierten Nanodrähten (ND) mit Hilfe von Kathodolumineszenz-Spektroskopie (KL) im Rasterelektronenmikroskop untersucht. Diese Methode wird ergänzt durch Messungen der kontinuierlichen und zeitaufgelösten Mikro-Photolumineszenz. Drei verschiedene Strukturen werden behandelt: (i) GaAs-ND bestehend aus Segmenten der Wurtzit (WZ) bzw. Zinkblende (ZB) Kristallstrukturen, (ii) auf GaN-ND überwachsene GaN-Mikrokristalle und (iii) (In,Ga)N Einschlüsse in GaN-ND.

Die gemischte Kristallstruktur der GaAs-ND führt zu komplexen Emissionsspektren. Dabei wird entweder ausschließlich Lumineszenz bei Energien unterhalb der ZB Bandlücke, oder aber zusätzlich bei höheren Energien, gemessen. Diese Differenz wird durch unterschiedliche Dicken der ZB und WZ Segmente erklärt. Messungen bei Raumtemperatur zeigen, dass die Bandlücke von WZ-GaAs mindestens 55 meV größer als die von ZB-GaAs ist.

Die Lumineszenz-Spektren der GaN-Mikrokristalle enthalten verschiedene Emissionslinien, die auf Stapelfehler (SF) zurückzuführen sind. SF sind ZB Quantentöpfe verschiedener Dicke in einem WZ-Kristall und es wird gezeigt, dass ihre Emissionsenergie durch die spontane Polarisation bestimmt wird. Aus einer detaillierten statistischen Analyse der Emissionsenergien der verschiedenen SF-Typen werden Emissionsenergien von 3.42, 3.35 und 3.29 eV für die intrinsischen (I₁ und I₂) sowie für extrinsische SF ermittelt. Aus den entsprechenden Energiedifferenzen wird -0.022 C/m^2 als experimenteller Wert für die spontane Polarisation von GaN bestimmt.

Die Bedeutung sowohl der piezoelektrischen Polarisation als auch die der Lokalisierung von Ladungsträgern wird für (In,Ga)N-Einschlüsse in GaN-ND gezeigt. Hierbei spielt nicht nur die Lokalisierung von Exzitonen, sondern auch die individueller Elektronen und Löcher an unterschiedlichen Potentialminima eine Rolle.

Stichwörter: GaN, (In,Ga)N, GaAs, Nanodraht, Kathodolumineszenz, Stapelfehler, Spontane Polarisation, Polytypismus, Wurtzit, Zinkblende

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Abbreviations

CL	cathodoluminescence
cw(-PL)	continuous-wave (photoluminescence)
DAP	donor-acceptor pair
DFT	density functional theory
DX	donor-bound exciton
EBIC	electron beam-induced current
EDX	energy dispersive x-ray spectroscopy
$E_g^{WZ,ZB}$	band gap energy of the wurtzite or zinc-blende phase
EĽ	electroluminescence
EM	effective mass
FEM	finite element
FX	free exciton
FWHM	full width at half maximum
LED	light-emitting diode
LO	longitudinal optical
MBE	molecular beam epitaxy
μPL	micro-photoluminescence
NBE	near-band edge (luminescence)
NW	nanowire
PL	photoluminescence
$P_{\rm sp}$	spontaneous polarization
P_{pz}	piezoelectric polarization
PSF	prismatic stacking fault
QCSE	quantum-confined Stark effect
QW	quantum well
SEM	scanning electron microscopy
SF	(basal plane) stacking fault
TEM	transmission electron microscopy
ТО	transverse optical
TRPL	time-resolved photoluminescence
WZ	wurtzite
XRD	x-ray diffractometry
ZB	zincblende

List of basic symbols

Symbol	Name	Unit
a	lattice parameter (along the $[11\overline{2}0]$ direction in WZ)	Å
a_0	Bohr radius (0.529×10^{-10})	m
С	lattice parameter along the [0001] direction in WZ	Å
CO	speed of light (299 792 458)	${ m m~s^{-1}}$
C_{ij}	stiffness tensor / elastic coefficients	GPa
$d, \Delta d$	thickness, thickness difference	nm
е	elementary charge ($1.602 imes 10^{-19}$)	С
e _{ij}	piezoelectric tensor	$C m^{-2}$
$\dot{E_F}$	Fermi energy	eV
E_g	band gap energy	eV
$E_{\varphi}^{WZ,ZB}$	band gap energy of wurtzite / zinc-blende phase	eV
$\vec{E_{C,V}}$	conduction band minimum / valence band maximum energy	eV
ΔE	energy difference	eV
$\Delta E_{C,V}$	conduction / valence band offset	eV
E_t	transition energy	eV
3	electric field strength	$MV cm^{-1}$
ϵ	dielectric constant	
ϵ_0	vacuum permittivity (8.854 $ imes 10^{-12}$)	$\mathrm{F}\mathrm{m}^{-1}$
ϵ_{ii}	strain tensor	
h	Planck constant (6.626×10^{-34})	Js
ħ	Planck constant divided by 2π (1.054 $ imes$ 10 ⁻³⁴)	Js
k_B	Boltzmann constant (1.381×10^{-23})	$J K^{-1}$
L	carrier diffusion length	nm
m_0	electron rest mass (9.109×10^{-31})	kg
m^*_{ehlhhh}	effective mass of electrons / holes / light holes / heavy holes	m_0
m_r^*	reduced effective mass	m_0
N _{d.a}	donor / acceptor concentration	cm^{-3}
Р	polarization	$\mathrm{C}\mathrm{m}^{-2}$
$P_{sp,pz}$	spontaneous / piezoelectric polarization	$\mathrm{C}~\mathrm{m}^{-2}$
R_G	electron beam penetration depth	nm
σ	sheet charge density	$C m^{-2}$
σ_{ij}	stress tensor	GPa
t _{ZB}	thickness of ZB segment	bilayers
$ au_{\mathrm{eff},\mathrm{r,nr}}$	effective / radiative / non-radiative lifetimes	s
Т	temperature	Κ
и	internal cell parameter of the wurtzite structure	
ΔV	potential difference	eV
Vacc	acceleration voltage (SEM)	kV
ω	angular frequency	rad/s

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1. Introduction

Information and communication technology enabled by the semiconductor industry has become an integral part not only of modern economies, but also of our personal life. At the same time, we need to find sustainable ways to harvest and utilize energy given the ongoing worldwide development, especially concerning the imminent climate change.^[1] New solid-state technologies based on compound semiconductors are suitable for applications in energy efficient lighting and displays, power electronics, and solar energy conversion.^[2] These technologies promise vast savings in global energy consumption and are thus expected to have profound economic and ecological consequences.

For many of these applications, compound III-V semiconductors, combining elements from the third and fifth group of the periodic table, have gained in technological relevance over the past decades. As most of them exhibit a direct band gap and therefore provide a superior electron–photon coupling compared with the indirect semiconductor silicon, the III-V compounds are predestined for optoelectronic devices. For example, high efficiency multi-junction solar cells are based on group-III arsenides and phosphides,^[3] whereas the materials of choice for solid state lighting are a combination of GaN and (In,Ga)N.^[4] For a variety of other fields, among them laser diodes, high power electronics, sensor applications, solar water splitting and solid-state memory, III-V semiconductors do already or may in the future play a significant role.

A prerequisite for the production of devices is the direct integration of different semiconductor layers during crystal growth. However, this heteroepitaxy faces some fundamental challenges. The mismatch of lattice constants and thermal expansion coefficients results in strained layers. Passing a certain threshold in strain energy, plastic relaxation of this strain leads to the formation of dislocations and other structural defects detrimental to the performance of semiconductor devices. An elegant solution to overcome this mismatch is the reduction of the interface area. Therefore, in recent years, three-dimensional semiconductor nanostructures have become a prime research subject. Nanowires, columns of crystal material with a high aspect ratio and sub-µm diameters, offer the desired small cross-sections, and elastic strain relaxation at the side surfaces becomes possible.^[5,6]

Taking the example of (In,Ga)N/GaN structures for light emitting diodes (LEDs), the lattice mismatch in the quantum well structures providing the light emission increases with the indium content. For planar devices, the efficiency drops significantly when increasing the indium content to achieve longer wavelengths. To obtain white light, blue LEDs have to be combined with a yellow emitting phosphor for light conversion. However, this approach suffers from a decrease in luminous efficacy when "warm white" emission (lower color temperature) or a higher color rendering index are required.^[4] Quantum wells integrated along the axis of nanowires could enable a superior color tunability throughout the entire visible spectral range, because for this geometry a higher indium content does not necessarily result in plastic relaxation. Furthermore, the elastic strain relaxation should be associated with a reduction of the piezoelectric polarization, which could increase the electron–hole overlap in the quantum well leading to an improved internal quantum efficiency.^[7] As a consequence, emitters for all three primary

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colors (red-green-blue) can be realized with the same material system. By tuning the emission wavelength of subsets of the nanowire ensemble, it would be possible to realize white light emitting diodes based on the integration of red, green and blue emitters on a single chip.^[8] Additionally, the nanowire geometry may provide an improved light extraction efficiency.^[9]

The small basis of the nanowires also plays a role concerning the choice of the substrate. Substrates of the same material (for homoepitaxial growth) are very costly in the case of most III-V semiconductors. Taking foreign substrates, lattice mismatch and differences in thermal expansion coefficients again limit the available choices in planar epitaxy. In contrast, nanowires can be grown on essentially any substrate without the selection affecting the crystal quality,^[9–11] because mismatch induced dislocations are confined to the interface region and residual strain declines exponentially along the nanowire axis. The combination of compound semiconductors with the well established silicon technology is particularly attractive. To date, sapphire is the substrate typically used for the growth of GaN. Not only would silicon be an economically attractive alternative, but also more elaborate device schemes can be envisaged. For example, the structures emitting different colors for white LEDs could be directly grown on the silicon electronics necessary to individually control such a set of devices.^[12]

Nanowires can be synthesized by different methods. Structures obtained by the "topdown" approach, based on the post–growth processing of layers via lithography and etching, do not offer the desired reduction in defect densities. The "bottom-up" approach is the direct epitaxial growth of nanowires. Either lithographic pre–processing is used for selective area growth, or strategies for a self-induced formation of nanowires are pursued. The former provides a higher degree of growth control resulting in more uniform structures, whereas the latter avoids the additional processing steps. For the epitaxy of nanowires, the best growth control is attained either by metal-organic chemical vapor deposition or by molecular beam epitaxy.

Especially for self-induced growth, more or less significant variations between the nanowires are inevitable. The inhomogeneity may concern properties such as diameter, composition or doping levels. For the analysis of these structures by luminescence spectroscopy, already slight differences in the emission properties of individual nanowires lead to broadened peaks in the ensemble spectra.^[9] It is therefore essential to investigate individual nanowires, in order to truly elucidate the origin of spectral features. Due to the inherent technical difficulties of single nanowire spectroscopy, many groups investigate only the luminescence of nanowire ensembles. For the example of (In,Ga)N/GaN heterostructures in nanowires, only few reports look at the micro-photoluminescence of single nanowires.^[13,14] To address the luminescence of embedded heterostructures, an additional spatial resolution along the nanowire axis would be advantageous. Thereby, not only fluctuations of the In content between nanowires, but also within a single nanowire might be resolved. For such a high spatial resolution, cathodoluminescence spectroscopy in a scanning electron microscope is the method of choice.

As already pointed out, the free surfaces at the side walls are an essential characteristic of nanowires. Another consequence of the free surfaces available during the growth of nanowires concerns the crystal structure. III-V semiconductors exist in different polytypes with a closely related structure but different band gap energies,^[15] only one of which is usually stable during planar growth.^[16,17] In nanowires, the crystallization of metastable polytypes can become energetically favorable.^[6] The presence of different polytypes in a single nanowire constitutes an unintentional heterostructure, which is also

reflected in the luminescence spectra.^[18] The spatial resolution of cathodoluminescence spectroscopy can elucidate where in a nanowire, and thus during which growth stage, such polytypes are formed.

Naturally, the large surface-to-volume ratio entails an augmented role of surface effects also concerning the optoelectronic properties of nanowires. Among other things, it has been shown that the depletion region may span the entire cross-section of the nanowires,^[19] and the emission energy of donor bound excitons in nanowires will change with proximity to the surface.^[9] Therefore, knowledge from planar semiconductor structures may not be directly transferable to nanostructures, and dedicated spectroscopic investigations are needed.

In this thesis, nanowires grown by molecular beam epitaxy in a self-induced approach are investigated. The aim is to spatially resolve different contributions to the luminescence spectra within single nanowires. The materials in focus are GaAs, often considered as prototype of the III-V compounds,^[20] and GaN as potential basis for nanowire LEDs.^[12] Both unintentionally grown quantum wells of different polytypes in GaAs nanowires and GaN microcrystals as well as intentionally grown (In,Ga)N insertions embedded in GaN nanowires are studied. The state of the art scanning electron microscope used in this work is equipped with a field-emission electron gun to facilitate the necessary imaging resolution and is operated at acceleration voltages of only a few kV to ensure a good spatial resolution for the cathodoluminescence measurements. The setup employs a parabolic mirror for an efficient collection of the emitted light and can be operated both at room temperature and at cryogenic temperatures.

The aim of this thesis is not only to learn more on the luminescence of quantum well structures in nanowires, but also to exploit this emission in order to derive fundamental material parameters. In particular, the band gap energy of wurtzite GaAs and the spontaneous polarization of wurtzite GaN are addressed. The former parameter is still controversially discussed in the literature, while for the latter theoretical predictions were so far awaiting a verification from experiments.

This thesis is structured as follows. To begin with, the fundamental physical concepts underlying this work are introduced in Chapter 2. Namely, the discussion encompasses crystal structures and polytypism of III-V semiconductors, spontaneous and piezoelectric polarization fields, as well as the localization of carriers in ternary alloys. The focus of Chapter 3 are the recombination mechanisms underlying luminescence spectroscopy and the experimental setups used. Special emphasis is put on cathodoluminescence with a digression concerning the possible reasons behind the observation of a quenching of the near-band edge emission in GaN nanowires. To complete the introductory part, Chapter 4 briefly introduces the growth of the investigated nanostructures by molecular beam epitaxy, some aspects concerning the preparation of samples, as well as additional experimental methods used to complement the spectroscopic analysis.

The main experimental part of this thesis starts in Chapter 5 with the discussion of quantum well structures formed by segments of the wurtzite and zincblende polytypes in GaAs nanowires. The resulting complex luminescence spectra are analyzed and discussed, and specifically the controversy concerning the band gap energy of wurtzite GaAs is addressed. Afterwards, zincblende/wurtzite heterostructures in GaN are investigated in Chapter 6. To this end, microcrystals grown on top of nanowires turn out to be ideal samples. A special emphasis is put on stacking faults as the thinnest possible zincblende quantum wells in a wurtzite matrix. Furthermore, an experimental value for the spontaneous polarization of wurtzite GaN is derived from the luminescence of

1. Introduction

these stacking faults. Shifting to ternary heterostructures, (In,Ga)N insertions in GaN nanowires are studied in Chapter 7. The influence of both piezoelectric polarization fields and carrier localization on the luminescence are examined.

Finally, Chapter 8 summarizes the conclusions from this thesis and gives an outlook beyond this work. In addition, Appendix A presents cathodoluminescence and electron beam-induced current measurements on an (In,Ga)N/GaN nanowire-based light emitting diode. This investigation of an actual device structure is moved to the appendix, because it departs from the more fundamental considerations concerning the luminescence of heterostructures in nanowires, which make up the main part of this work.

This chapter gives an introduction to some of the basic physical aspects underlying the work presented in this thesis. Starting from the crystal structures commonly observed for III-V semiconductors, physical properties directly arising from the crystal symmetry, such as the spontaneous and piezoelectric polarization, are introduced. In heterostructures, discontinuities of the polarization lead to electric fields, which manifest themselves in the quantum-confined Stark effect. Next, the coexistence of different polytypes and the specific case of stacking faults are discussed. The consequence are homomaterial quantum well structures. As a foundation for later chapters, the route to derive the spontaneous polarization from the luminescence energy associated with stacking faults is sketched, and a summary of the dispute concerning the band gap of the wurtzite phase of GaAs is given. Finally, a brief review of carrier localization in (In,Ga)N heterostructures is presented.

2.1. Crystal structures of III-V semiconductors

At ambient conditions, all binary III-V semiconductors except BN adopt either of two tetrahedrally coordinated close-packed crystal structures: the hexagonal wurtzite (WZ) or the cubic zincblende (ZB) structures; the preference of one of the two is controlled by the ionicity of the crystal.^[16] Their names are derived from the corresponding minerals wurtzite and zincblende (sphalerite), two varieties of ZnS crystals. Only under high-pressure, these semiconductors might adopt other crystal structures such as the rocksalt structure.^[21]

Both crystal structures exhibit tetrahedral coordination and the same nearest neighbor configuration. However, they differ in the bond angle of their third-nearest neighbor configuration. In other words, their close-packed stacking sequence differs as depicted in Figs. 2.1(a)–(c): The WZ stacking sequence along the [0001] direction is denoted as $a\alpha b\beta a\alpha b\beta \dots$, while ZB exhibits an $a\alpha b\beta c\gamma a\alpha b\beta c\gamma \dots$ stacking along the [111] direction, where the Latin and Greek letters refer to cations and anions, respectively. As a pair of cations and anions always shares the same in-plane position, the simplified terminology of an ABAB... stacking for WZ and ABCABC... for ZB is often used. The ZB structure can also be seen as a face-centered cubic (fcc) structure with a two-atom base for which the close-packed stacking is observed in the $\langle 111 \rangle$ direction [cf. Fig. 2.1(d)]. Therefore, ZB has four equivalent polar axes in the $\langle 111 \rangle$ directions and, according to the Hermann-Mauguin notation, belongs to the space group $F\overline{4}3m$ (point group $\overline{4}3m$), while WZ has a singular polar axis in the (0001) direction and belongs to the space group P6₃mc (point group 6mm). Another consequence of the difference in symmetry is that the primitive cell of ZB includes only one cation-anion pair, i.e. two atoms, while for WZ four atoms reside in the primitive cell.

While the ZB structure has a perfect tetrahedral coordination, i.e. the bond lengths are all the same, the wurtzite structure exhibits a slight deviation from the ideal structure. Therefore, the WZ unit cell is described by two basis vectors a_h and c [cf. Fig. 2.1(b)], and



Figure 2.1: Crystal structures of close-packed lattices: (a) Projection into the hexagonal *C*-plane of the three possible in-plane positions for a close-packed structure. While the WZ structure alternates only between two of the possible positions, ZB iterates through all three in-plane positions. The area of one unit cell is marked by the gray parallelogram. (b) Primitive WZ unit cell; the lattice constants a_h and *c* as well as the cation-anion spacing *uc* are marked. Filled circles denote anions, while open circles denote cations. The stacking sequence of the layers is indicated by the different colors and the letters on the side. (c) Hexagonal ZB unit cell in the [111] direction for comparison with the WZ structure. (d) Cubic ZB unit cell; the lattice constant a_c is marked.

their ratio c/a deviates from the ideal value $c/a = \sqrt{8/3}$ for a perfect tetrahedron. Another value that characterizes this deviation is the internal parameter u which is defined by the product uc being the length of the group-III to group-V (cation-anion) bond in the c-direction. The ideal value is u = 3/8 = 0.375. An approximate relation connecting these two parameters is $u = \frac{1}{3}(a/c)^2 + \frac{1}{4}$.^[22]

In equilibrium, most III-V semiconductors crystallize in the ZB phase, i.e. this phase is favored from the point of the structural energy.^[17] Among these is GaAs, which has only been reported to exhibit the metastable WZ structure as the result of a transformation from a high-pressure phase^[23] or for the growth of nanowires.^[18,24,25] In contrast, the group-III nitrides usually exhibit the WZ structure as the equilibrium phase.^a By epitaxy on suitable substrates, GaN can be obtained in the ZB structure.^[26,27] This partitioning between the equilibrium phases suggests that crystals with a high ionicity prefer the WZ structure. In fact, this link was established by Lawaetz,^[16] who has also shown that wurtzite is the stable structure for *u* larger (*c*/*a* smaller) than the ideal value. More recently, the different equilibrium phases of III-V semiconductors were reproduced by structural calculations.^[17]

The coordinate systems with the basis vectors and important crystal planes for cubic and hexagonal crystals are sketched in Fig. 2.2. The cubic lattice constant a_c denotes the interatomic distance^b along the $\langle 001 \rangle$ directions. For hexagonal crystals, a_h denotes the distance of atoms in the *C*-plane, also called basal plane, while *c* denotes the spacing of atoms of the same type (e.g. cation-cation) in the $\langle 0001 \rangle$ direction (*c*-axis). As can be seen from Fig. 2.1(b), *c* is equivalent to the thickness of two bilayers of atoms (two layers each of cations and anions). The cubic and hexagonal *a* lattice constants are related by

^aAs an exception, BN crystallizes in the graphite-like structure.^[17]

^bThe interatomic distance along a specific crystal axis should not be confused with the nearest neighbor distance.



Figure 2.2: Sketch of the coordinate systems (basis vectors) and labeling of crystal planes for cubic and hexagonal crystal structures.

 $a_c = \sqrt{2}a_h$. A summary of the lattice constants for the materials investigated in this thesis can be found in Tab. 2.1. For (In,Ga)N, the lattice constants can be approximated by a linear interpolation between those of the binary constituents according to Vegard's law.^[28]

WZ crystals can be grown either along the polar $\langle 0001 \rangle$ direction or along non-polar or semi-polar directions. Epitaxial layers are labeled according to the crystal plane which is parallel to the substrate, e.g. *C*-plane for polar growth and *M*- or *A*-plane for non-polar growth. Furthermore, for polar growth, the [0001] and [0001] directions are not equivalent [cf. Fig. 2.1(b)]. For GaN, structures grown along these directions are called Ga- and N-polar, respectively, according to the terminating layer at the surface. For the growth of WZ nanowires, the top surface is *C*-plane, while the side facets are non-polar planes. Nanowires with ZB crystal structure grow along the $\langle 111 \rangle$ direction.

2.2. Polarization fields in III-V semiconductors

Crystals belonging to a point group without an inversion center have one or more polar axes. As a consequence, strain can induce a deviation from the ideal tetrahedral coor-

	a (Å)	c (Å)	и
WZ GaAs ^[23]	3.989	6.564	0.373
ZB GaAs ^[29]	5.65325		
WZ GaN ^[22]	3.1884	5.1852	0.376
ZB GaN ^[30]	4.52		
WZ InN ^[22]	3.5377	5.7038	0.378
WZ AlN ^[22]	3.1113	4.9796	0.380

Table 2.1: Lattice constants *a* and *c* in units of Å and internal parameter *u* (ideal value 0.375) for the WZ and some of the ZB phases of GaAs and the group-III nitrides.

dination that leads to a piezoelectric polarization P_{pz} . If the point group has a singular polar axis (a single rotational axis with all mirror planes parallel to this axis) as it is the case for the WZ structure, a deviation from the ideal tetrahedral coordination in equilibrium is possible, which leads to a spontaneous polarization P_{sp} of the crystal lattice. The piezoelectric effect as a consequence of the former is well known for its "macroscopic" technological applications, but P_{pz} also plays a role in semiconductor heterostructures as the result of strain (deformation) induced by the lattice mismatch. For WZ crystals, the total polarization $P = P_{sp} + P_{pz}$, whereas $P = P_{pz}$ for ZB crystals.

In the classic picture, the displacement of cation and anion induces a microscopic dipole moment. In a crystal, all these microscopic dipole moments are aligned. For an infinite crystal, the succeeding dipoles in the polarized direction will cancel each other, but a discontinuity of the polarization at surfaces or at interfaces will lead to a charge density $\sigma = -\Delta P$ at the surface/interface. At surfaces, these charges are usually compensated by adsorbed charged particles.

This section discusses first the spontaneous polarization and then the piezoelectric polarization and its relation to strain. Finally, the technologically relevant manifestation of the polarization fields in semiconductor quantum wells through the quantum-confined Stark effect is introduced.

2.2.1. Spontaneous polarization

Already in 1971, Jerphagnon and Newkirk^[31] derived a point-charge model to describe the spontaneous polarization (see derivation in Appendix C):

$$P_{\rm sp} = \frac{-4Q}{a_h^2 \sqrt{3}} \left(u - 0.375 \right); \tag{2.1}$$

 a_h is the WZ lattice constant, while the charge Q of the cation is not so easily defined for a structure with partially ionic bonds. However, this simple model highlights that P_{sp} crucially depends both on the internal parameter u, which characterizes the deviation from the ideal tetrahedral coordination along the polar *c*-axis of a WZ crystal, and the ionicity of the crystal which is contained in Q. It can be directly seen from Eq. (2.1) and the values of u in Tab. 2.1 that P_{sp} in GaAs will have the opposite orientation from that of GaN (or the other group-III nitrides). As a consequence, the sign of P_{sp} has a similar dependence on u as the equilibrium crystal structure. A refined version of this pointcharge model that resolves the question of defining Q (see also Appendix C) actually leads to a quite fair agreement with values for P_{sp} calculated within the framework of density functional theory (DFT) across the range of III-V semiconductors.^[32]

Of course, though being very intuitive, this simple model falls short of the quantum mechanical picture. First, charge distributions need to be considered instead of point charges. Furthermore, the definition in the framework of the *modern theory of polarization* is based on an adiabatic flow of current through the crystal.^[33,34] As a major consequence of the latter approach, only polarization differences are well defined quantities.^[34] Therefore, $P_{\rm sp}$ is usually determined as the difference to a reference state. For WZ materials, the natural choice for such a reference used in computational studies of $P_{\rm sp}$ is the ZB phase.^[35–37] This choice is motivated by the close relation of the two structures and the higher symmetry of the ZB phase resulting in the absence of an equilibrium polarization.

Table 2.2: Piezoelectric constants in C/m^2 and selected elastic constants in GPa for the group-III nitrides and zincblende GaAs. For the WZ phase of GaAs, piezoelectric constants are not available. Recent DFT results for the spontaneous polarization in C/m^2 from Ref. 32 are added in the last column.

	e_{14}	e ₃₃	<i>e</i> ₃₁	<i>e</i> ₁₅	C_{13}	C ₃₃	$P_{\rm sp}$
WZ GaAs							0.002
ZB GaAs ^[29]	-0.16						
WZ GaN ^[39]		0.83	-0.45	-0.38	105	396	-0.018
ZB GaN ^[40]	0.4						
WZ InN ^[39]		0.95	-0.52	-0.44	98	245	-0.011
WZ AlN ^[39]		1.54	-0.45	-0.41	103	375	-0.040

2.2.2. Piezoelectric polarization

Any crystal with a polar axis can carry a piezoelectric polarization. During heteroepitaxy, i.e. the growth on a foreign substrate or the combination of different materials, the lattice mismatch usually induces strain in the epitaxial layer. This deformation of the crystal structure leads to an additional piezoelectric polarization along the polar directions. For ZB crystals, the contributions from the four polar axes cancel each other for growth in the [001] direction, but a crystal with [111] orientation may carry a piezoelectric polarization.

Strain and Stress

Strain describes deformations of a crystal lattice, while stress denotes the pressure applied to the crystal to achieve this deformation. Both can be described by tensors. Neglecting the anti-symmetric part which would describe rotations of the unit cell,^[38] the symmetric strain tensor encompasses the normal components ϵ_{xx} , ϵ_{yy} and ϵ_{zz} and the shear components ϵ_{xy} , ϵ_{yz} and ϵ_{xz} . Accordingly, the symmetric stress tensor is made up of σ_{xx} , σ_{yy} , σ_{zz} , σ_{xy} , σ_{yz} and σ_{xz} . In the Voigt scheme, these two tensors can be considered as (pseudo-)vectors with six elements which are then connected by a stiffness tensor C_{ij} of (pseudo-)second-rank in the context of the generalized version of Hooke's law.^[38] Note that these tensors are defined in a Cartesian coordinate system. Thus, for WZ crystals, the lattice vectors have to be converted accordingly.

In the case of a hexagonal crystal structure, the most basic example for strain is a thin epitaxial layer with the lattice constant a_l grown in the [0001] direction on a lattice mismatched substrate having the lattice constant a_s . Only the thin layer will be strained (pseudomorphic growth). Considering the case that this layer cannot relax, the in-plane strain is characterized by

$$\varepsilon_{xx} = \epsilon_{yy} = (a_s - a_l)/a_l. \tag{2.2}$$

For $a_l > a_s$, this results in a negative (compressive) in-plane strain. According to the Poisson effect, the out-of-plane strain ϵ_{zz} of the layer will then be positive (tensile), i.e. the layer is biaxially strained. For the given situation, the two strain components are related through the elastic constants C_{13} and C_{33} :

$$\epsilon_{zz} = -2\frac{C_{13}}{C_{33}}\epsilon_{xx}.$$
(2.3)

For layers grown along low-index directions, the shear components of the strain and stress tensors vanish. This reduction of the tensor is not necessarily the case for heterostructures embedded into nanostructures, where a more complex three-dimensional relaxation might occur.

For a more detailed discussion of strain and stress in the group-III nitrides, see e.g. Ref. 38.

The piezoelectric tensor

In the most general case, the piezoelectric polarization is a vector P_{pz} being related to the strain tensor ϵ_{ij} via the piezoelectric tensor e_{ij} . For a WZ crystal with the space group P6₃mc, this relation is:

$$\vec{P}_{pz} = \begin{pmatrix} 0 & 0 & 0 & e_{15} & 0\\ 0 & 0 & 0 & e_{15} & 0 & 0\\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon_{xx}\\ \epsilon_{yy}\\ \epsilon_{zz}\\ \epsilon_{yz}\\ \epsilon_{xz}\\ \epsilon_{xy} \end{pmatrix} = \begin{pmatrix} e_{15}\epsilon_{xz}\\ e_{15}\epsilon_{yz}\\ e_{31}(\epsilon_{xx} + \epsilon_{yy}) + e_{33}\epsilon_{zz} \end{pmatrix}.$$
 (2.4)

For the above example of a pseudomorphic epitaxial layer with vanishing shear components and in-plane isotropy of the strain, Eq. (2.4) reduces to

$$P_{\rm pz}^{[0001]} = 2e_{31}\epsilon_{xx} + e_{33}\epsilon_{zz}.$$
 (2.5)

A summary of the piezoelectric and selected elastic constants for the group-III nitrides and zincblende GaAs is given in Tab. 2.2. It is clear that, similar to P_{sp} , also P_{pz} will be opposite in direction and its magnitude lower for GaAs compared with GaN. P_{pz} is primarily of importance for heterostructures between different group-III nitrides or their ternary alloys. Taking Eqs. (2.2), (2.3) and (2.4) as well as the data from Tabs. 2.1 and 2.2, one obtains $P_{pz} = 0.177 \text{ C/m}^2$ for an InN layer on GaN and $P_{pz} = -0.043 \text{ C/m}^2$ for AlN on GaN. The former is much larger due to the higher lattice mismatch. A set of values for P_{sp} from recent DFT calculations is added to Tab. 2.2: Comparing the differences in P_{sp} with the values for P_{pz} , it is evident that the (In,Ga)N material system is dominated by P_{pz} , while for (Al,Ga)N both P_{pz} and P_{sp} have a comparable magnitude. Note that for the ternary group-III nitride alloys, a non-linearity of P_{pz} and P_{sp} was reported in the literature; thus, a simple linear interpolation of the polarization values is not accurate.^[41,42]

For heterostructures between the WZ and ZB phases of the same material, P_{pz} will usually be negligible compared to P_{sp} . For the specific cases of GaN and GaAs ZB/WZ heterostructures, the values from Tab. 2.1 together with Eq. (2.2) yield $\epsilon_{xx} < 2 \times 10^{-3}$. This value is an order of magnitude lower than for AlN/GaN and can be regarded as an upper limit due to the limited accuracy to which the lattice constants of the metastable zincblende GaN and wurtzite GaAs phases are known.

2.2.3. Quantum-confined Stark effect

The experimental manifestation of the polarization in semiconductor quantum wells is known as quantum-confined Stark effect (QCSE).^[43,44] As mentioned above, a discontinuity of *P* at the heterointerfaces will lead to a charge density σ in the plane of the inter-



Figure 2.3: Illustration of the QCSE by a comparison of Poisson-Schrödinger calculations of the band structure for 3 nm thick (In,Ga)N/GaN QWs with 20% In separated by 10 nm wide barriers grown on (a) the non-polar *M*-plane and (b) the polar *C*-plane. The conduction band (CB) and valence band (VB) profiles as well as first electron and hole states and their wavefunctions are displayed. The vertical arrows indicate the resulting transition energies. A typical background doping level of $N_d = 1 \times 10^{17}$ cm⁻³ was assumed for the calculations. In (b), the dotted lines show the band profiles for an increased doping level of $N_d = 1 \times 10^{19}$ cm⁻³.

face. The only exception is growth in a non-polar direction, where the polar axis would lie in this plane. For the case of an isolated quantum well (QW), a thin planar layer with lower band gap than the surrounding matrix) sandwiched by barriers of quasi-infinite extension, this QW can be pictured as a plate capacitor with two oppositely charged layers at the respective interfaces. Then the magnitude of the electric field \mathcal{E} that develops across the QW can be approximated as

$$\mathcal{E} = \sigma / (\epsilon \epsilon_0), \tag{2.6}$$

where ϵ denotes the dielectric constant of the QW material and ϵ_0 denotes the permittivity of free space.

The opposite extreme to the isolated QW is a quasi infinite superlattice of QWs and barriers.^[45] Then, the barriers between the QWs will experience a field of opposite sign, as from their perspective the signs of the sheet charge densities at the interface are reversed. For each layer *j*, Eq. (2.6) will hold with $\sigma = -\Delta P = P_b - P_j$; P_b being the polarization of the barrier material and P_j the polarization of the layer *j*. As a boundary condition, the drops in potential $\Delta V_n = \mathcal{E}_n d_n$ for all *n* layers need to cancel each other, i.e. $\sum_n \mathcal{E}_n d_n = 0$. These equations can be combined to calculate the electric field strength in an arbitrary stack of layers.^[45] This situation essentially equals that of plate capacitors connected in parallel. Limiting the superlattice to two types of layers, a barrier with polarization P_b and thickness d_b as well as a quantum well with P_w and d_w , the sum only runs over these two layers, and the electric fields can be calculated as

$$\mathcal{E}_{b} = \frac{\frac{d_{w}}{\epsilon_{0}}(P_{w} - P_{b})}{d_{b}\epsilon_{w} + d_{w}\epsilon_{b}}, \qquad \mathcal{E}_{w} = \frac{\frac{d_{b}}{\epsilon_{0}}(P_{b} - P_{w})}{d_{b}\epsilon_{w} + d_{w}\epsilon_{b}}.$$
(2.7)

For the group-III nitrides, the polarization fields in quantum wells can easily reach values on the order of MV/cm.^[46] For example, according to Eq. (2.6), an isolated

(In,Ga)N/GaN quantum well with 20% In experiences a field up to $\mathcal{E} \approx 3.56$ MV/cm (using a bowed polarization as specified in Appendix D). For low σ or high densities of free carriers (e.g. strong doping), the polarization charges may be partially compensated or screened. Also, for multiple QWs, the redistribution of fields between QWs and barriers according to Eq. (2.7) has to be taken into account. Therefore, it is more accurate to calculate \mathcal{E} in the framework of a self-consistent solution of the Poisson and Schrödinger equations. An example of such calculations that yield the band structure and the wavefunctions of the ground states is given in Fig. 2.3 for (In,Ga)N/GaN quantum wells of 3 nm thickness separated by 10 nm thick barriers grown both on the non-polar M-plane and the polar C-plane. The In content of the QWs is set to 20% and the background doping to a typical value of $N_d = 1 \times 10^{17}$ cm⁻³. To illustrate the effect of high doping densities, the dotted lines in Fig. 2.3(b) correspond to the band profile for a doping level increased by two orders of magnitude ($N_d = 1 \times 10^{19} \text{ cm}^{-3}$). A comparison of Figs. 2.3(a) and 2.3(b) visualizes the QCSE: For quantum wells affected by polarization fields, electrons and holes are confined at opposite ends of the QW, reducing the overlap of the wavefunctions and thus increasing the radiative lifetime. This effect increases the probability for non-radiative recombination and effectively reduces the luminous efficiency. At the same time, the polarization fields lead to a redshift (reduction) of the transition energy of the QW. The injection of high carrier densities for luminescence spectroscopy under strong excitation can partially screen the polarization charges and reduce the fields in a similar way as for high doping levels. This improves the wavefunction overlap and reduces the redshift, i.e. the emission is blueshifted compared to the unscreened case.^[47]

A comparison of the electric fields according to Eq. (2.7) to those from the Poisson-Schrödinger calculations in Fig. 2.3(b) gives $\mathcal{E}_w = 2.74$ MV/cm as well as $\mathcal{E}_b = -0.82$ MV/cm in the former case and $\mathcal{E}_w = 3.03$ MV/cm as well as $\mathcal{E}_b = -0.53$ MV/cm in the latter case.

Consequently, the QCSE is of technological relevance as it needs to be taken into account for the design of semiconductor devices, particularly when involving the group-III nitrides. For LEDs and laser diodes, this has sparked intense research into the possibilities for non-polar and semi-polar growth to avoid the polarization fields.^[7,48–50] On the other hand, the polarization fields are exploited for the design of (Al,Ga)N-based high electron mobility transistors.^[51]

2.3. Polytypism in III-V nanostructures

The existence of different crystal phases of the same material but with different stacking sequences of the constituent layers is known as polytypism. For the case of semiconductor nanostructures, the availability of free surfaces allows for the stabilization of different polytypes within a single structure such as a nanowire. A brief introduction to polytypism is given using the example of SiC, the material exhibiting the largest number of known polytypes. The main part of this section discusses the specific case of polytypic heterostructures between the ZB and WZ phases of III-V semiconductors with a focus on stacking faults in wurtzite crystals. Furthermore, it is shown how the spontaneous polarization of the WZ phase can be derived from the luminescence energies associated with stacking faults, an analysis that is carried out for GaN in Chapter 6. Finally, an introduction to the discussion concerning the band gap of the WZ polytype of GaAs is given, a question addressed in Chapter 5.

Table 2.3: The most common polytypes of close-packed crystals. The polytypes are indexed by the periodicity of the stacking and the crystal symmetry (C for cubic, H for hexagonal and R for rhombohedral). Furthermore, the stacking sequence, the space group, the number of atoms in the primitive cell and the hexagonality of the polytypes are given.^[52–54] The polytype with the largest documented periodicity is 393R.^[55]

Polytype	Stacking	Space group	Atoms	Hexagonality
3C	ABC	F43m	2	0%
2H	AB	P6 ₃ mc	4	100%
$4\mathrm{H}$	ABCB	P6 ₃ mc	8	50%
6H	ABCACB	P6 ₃ mc	12	33.3%
15R	ABCBACABACBCACB	R3m	15	40%
393R		R3m	786	

2.3.1. SiC: Prime example for polytypism

With the wurtzite and zincblende structures, the two most basic polytypes of closepacked crystals with a two-atom base have already been introduced. According to the periodicity of the structure and the crystal symmetry, the hexagonal WZ is referred to as 2H and the cubic ZB is referred to as 3C polytype (compare Fig. 2.1). Combinations of ZB and WZ stacking sequences lead to crystal structures with a larger periodicity. These structures exhibit either hexagonal or rhombohedral symmetry. Some examples of polytypes are given in Tab. 2.3. The ratio between the number of hexagonal layers and the total number of layers per period is called hexagonality, where a hexagonal layer is defined as having two neighboring layers of the same type.^[54] For SiC, the most common polytypes are 6H and 4H. However, more than 200 polytypes of SiC have been reported,^[53] with 393R-SiC having the largest documented periodicity resulting in a *c* lattice constant of 98.76 nm.^[55] The fact that so many different polytypes can be stabilized indicates that the differences in structural energy between the various polytypes is rather small. Still, the driving force for such a long-range ordering of the crystal structure is not really clear.^[54]

For non-polar growth of AlN on SiC, where the direction of stacking is perpendicular to the growth direction, it has been demonstrated that the crystal structure of the substrate can be reproduced and structures such as 6H-AlN may be obtained.^[56,57] For GaAs, InAs and InSb nanowires, the appearance of segments of the 4H^[58,59] and even the 6H^[60] polytypes has been reported.

Concerning the lattice constants of the polytypes, it has been shown experimentally for SiC, and more recently for InAs and InSb, that the *a* lattice constants show a linear decrease with increasing hexagonality, while the *c* lattice constants increase with hexagonality.^[54,59] Only for the group-III nitrides, the opposite trend is opposite. The change from 3C to 2H is on the order of -0.2% for *a* and 0.5% for *c*. As a consequence, also the internal parameter *u* and thus the spontaneous polarization show a linear dependence on hexagonality.^[32]

In a polytype, the specific stacking sequence is continuously repeated over at least several periods. Local changes in the stacking sequence induce planar, i.e. two-dimensional, structural defects in the basal plane. A twin defect is characterized by a reversal of the stacking sequence so that the crystals on both sides of the defect plane are of the same polytype, but mirror images of each other. For ZB crystals, twins correspond to a stack-



Figure 2.4: Stacking sequences for the intrinsic I_1 and I_2 as well as the extrinsic E stacking faults. The layers for which the ZB stacking sequence is upheld are highlighted in orange, while in the operator notation the breaches to the wurtzite stacking rule are highlighted. The coordinate system gives the crystal directions.

ing sequence ABCABCBACBA, while WZ crystals with their period of only two bilayers cannot exhibit twinning. When the stacking sequence is locally changed but returns to that of the initial polytype after a few bilayers, the defect is referred to as a stacking fault. Every polytype has its specific set of possible stacking faults. In the following, the different types of stacking faults for the WZ structure are introduced. When the stacking sequence of ZB in the WZ matrix is repeated at least twice, the structure will be referred to as a ZB segment.

2.3.2. Stacking faults in wurtzite crystals

In a wurtzite crystal, stacking faults in the basal plane can be regarded as the limiting case of very thin ZB segments in a WZ matrix. Three types of stacking faults (SFs) in WZ are distinguished in the literature, $^{[61-64]}$ where intrinsic SFs are formed by the change from one hexagonal-close-packed lattice to another one, i.e. from *AB* to *BC* or *AC* stacking, while extrinsic SFs are formed through the insertion of an extrinsic layer, i.e. a *C* layer in an *AB* sequence:

(a) intrinsic I_1 SFs involve one breach of the WZ stacking rule according to which the third-nearest neighbor should be the same. They exhibit a stacking sequence of ABABCBCBC.

(*b*) *intrinsic I*₂ *SFs* involve two breaches of the WZ stacking and have the stacking sequence *ABABCACAC*.

(c) *extrinsic E SFs* involve three breaches of the WZ stacking and have the stacking sequence *ABABCABAB*.

The stacking sequences related to these three types of SFs are illustrated in Fig. 2.4. Additionally to the in-plane positional labels, the operator notation^[61] is given: The successions $A \rightarrow B$, $B \rightarrow C$ or $C \rightarrow A$ are marked by \triangle , while their opposites are marked by ∇ . In this notation, the WZ stacking is an alternation $\triangle \nabla$, while the ZB stacking is represented by a sequence of the same operator. The stacking faults can then be characterized by the number of breaches of the WZ stacking rule as $(1\triangle)$, $(2\triangle)$ and $(3\triangle)$.^[61]

For GaN, calculations by Stampfl and Van de Walle^[65] confirm that the formation energy of the different SF types increases in the presented order, which was already inferred by Frank and Nicholas^[61] from the increasing number of breaches of the WZ stacking. In contrast to the other two types, I₂ SFs can be formed by a single slip in the basal plane^[61] and may therefore be introduced by post–growth deformation. When ending within a crystal, SFs must be terminated by dislocations. These are partial dislocations



Figure 2.5: Scheme of the band structures in (momentum) *k*-space close to the center of the Brillouin zone for zincblende and wurtzite, as well as calculated bands along two high symmetry lines in the Brillouin zone for the example of GaAs. The valence bands shown in (a) for ZB are the heavy hole (hh), light hole (lh) and split off (so) bands. For WZ (d), the common terminology for the valence bands is A, B and C. The calculations in (b) and (c) are aligned by their branch-point energy E_{BP} . The graphs are reproduced from Refs. 9 and 71.

with Burger's vector $\mathbf{b} = \frac{1}{6}[20\bar{2}3]$ in the case of I₁ SFs, Shockley-type partial dislocations with $\mathbf{b} = \frac{1}{3}[10\bar{1}0]$ in the case of I₂ SFs, and Frank-type partial dislocations with $\mathbf{b} = \frac{1}{2}[0001]$ in the case of E SFs.^[64,66] Otherwise, SFs can be terminated by free surfaces or heteroepitaxial interfaces (in the case of non-polar or semi-polar growth). Having the lowest formation energy, I₁ SFs are the most common type observed. Recently, it has been shown for non-polar growth directions that the formation of I₁ SFs is related to the coalescence of three-dimensional islands in the Volmer Weber growth mode.^[67] However, also I₂ SFs are commonly observed in non-polar samples.^[68,69] Their nucleation might for example become favorable at atomic steps at the substrate interface. The probability of E SFs or thicker ZB segments being formed increases when free surfaces are available, such as for the growth of nanowires.

Besides on (0001) basal planes, stacking faults can occur on prismatic (11 $\overline{2}0$)-planes (*A*-planes) of WZ crystals.^[63,66] These prismatic stacking faults (PSFs) exhibit a displacement vector of $\mathbf{b} = \frac{1}{2}[10\overline{1}1]$ and always connect two I₁ SFs with stair-rod dislocations forming at the intersection.^[66] This folding of stacking faults can lead to step-like arrangements and even loops.^[63] Only the tetrahedral bond angles in the prismatic plane are changed in the creation of PSFs so that again no dangling bonds are formed.^[66] Their atomic configuration can be seen in high-resolution transmission electron micrographs of (0001) cross sections, e.g. in Ref. 70.

2.3.3. Stacking faults as quantum wells

Similar to the lattice constant mentioned above, the band gap of SiC also shows a linear dependence on the hexagonality, being highest for 2H-SiC and lowest for 3C-SiC with $E_g^{WZ} - E_g^{ZB} = 0.9 \text{ eV}.^{[54,72]}$

[°]Figure[°] 2.5 compares the band structures of zincblende and wurtzite GaAs in a schematic representation as well as based on DFT calculations.^[71] Actually, the band structures of the ZB and WZ polytypes of a material are closely related through zone folding relationships.^[15,73] This is a direct consequence of the structural similarity be-



Figure 2.6: (a) Schematic comparison of QWs with a type-I and type-II band alignment for flat-band conditions. (b) Sketched band diagram of a stacking fault in GaN for a type-I band alignment. The polarization induced sheet charges leading to the QCSE and the resulting change in the transition energy E_{ex} by ΔE are indicated.

tween these structures. While WZ has four atoms in the unit cell, there are two atoms in the ZB unit cell (cf. Tab. 2.3). The mapping of the first ZB Brillouin zone onto that of WZ yields twice as many bands per *k* point in momentum space. This mapping can be seen in Fig. 2.5(b) and (c), where the L point of ZB is folded onto the Γ point in WZ. A repulsive interaction of the folded states with similar symmetry leads to the prediction that for all WZ semiconductors the fundamental gap at the Γ point is slightly larger than for the ZB equivalent.^[15] For the group-IV compound SiC with an indirect gap (not at the Γ point), the difference $E_g^{WZ} - E_g^{ZB}$ should be significantly larger than for III-V or II-VI compounds with (largely) direct band gaps. For GaN $E_g^{WZ} - E_g^{ZB} \approx 0.2$ eV, while for GaAs the sign and actual magnitude of this difference is still under dispute as detailed in Section 2.3.5.

For heterostructures of different polytypes, the alignment of the conduction and valence bands at the interface is of importance. In the case of a type-I band alignment, the conduction and valence band offsets have opposite signs ($\Delta E_C \Delta E_V < 0$), while staggered band offsets ($\Delta E_C \Delta E_V > 0$) give a type-II alignment. The two situations are sketched in Fig. 2.6(a). From DFT calculations, the band offsets can be determined by aligning the branch-point energies [cf. Fig. 2.5(b) and (c)].^[71]

As a consequence of the difference in band gaps of the polytypes, SFs or thin ZB segments in a WZ crystal constitute a quantum well. For a type-I band offset, both electrons and holes are confined in the QW, whereas for a type-II offset, the holes reside outside the QW as indicated in Fig. 2.6(a). In a way, SFs can be considered as *ideal* QWs with atomically flat interfaces, negligible lattice mismatch and without alloy fluctuations.

The specific case of GaN

In the case of GaN, the emission of free excitons is found at 3.478 eV for the WZ phase^[74] and at 3.276 eV for ZB.^[27,75] The difference in band gap between these two polytypes of GaN amounts to 202 meV. Rebane et al.^[76] were the first to introduce the notion of stacking faults in GaN acting as quantum wells. At low temperatures, the carriers will form excitons bound to these structural defects. In contrast to the ZB polytype, the WZ phase of GaN exhibits a significant spontaneous polarization that leads to electric fields across the SF quantum wells. The necessity to take polarization fields into account was first pointed out by Sun et al.^[68] in their observation of I₂ SFs. Such a quantum well structure is sketched in Fig. 2.6(b).

At this point, the question arises, whether the band alignment for WZ/ZB heterostruc-

tures in GaN is of type-I or type-II. Calculations by DFT disagree on this point with some studies giving a type-II^[65,77] and others a type-I^[78,79] band alignment. In experimental studies, a dependence of the QW emission energy on the excitation intensity is sometimes seen as evidence for a type-II band alignment.^[80,81] However, due to the strong spontaneous polarization of wurtzite GaN, electron and hole are spatially separated at SFs independent of the actual band alignment [cf. Fig. 2.6(b)].^[79] In fact, the DFT calculations in Ref. 79 give a type-I band alignment, but when calculating the wavefunctions of electrons and holes for a WZ/ZB heterostructure, the holes are mostly confined in the WZ region as for a type-II offset. This issue is so far unresolved.

Another critical point is to define the thickness of stacking faults (cf. Fig. 2.4). This question is crucial for band structure calculations of stacking fault heterostructures. A first possibility is to take the number of breaches of the hexagonal stacking rule, i.e. layers for which the third-nearest neighbor is not the same. According to this definition, the thickness of the I₁, I₂ and E SF would be 1, 2 and 3 bilayers (or 0.5*c*, *c* and 1.5*c*; where *c* is the c-lattice constant), respectively. A second definition uses the number of bilayers for which the cubic *ABC* stacking sequence is upheld.^[76] This definition gives 3, 4 and 5 bilayers (or 1.5*c*, 2*c* and 2.5*c*) for the three types of SFs and would be intuitive from the structure of the stacking faults seen in Fig. 2.4. This issue is resolved in Chapter 6 by defining an *effective electronic thickness* for the purpose of band structure calculations.

Such *ideal* quantum wells should result in a narrow linewidth of the associated luminescence spectra (cf. Fig. 6.3). However, several factors can lead to a shift in emission energy for excitons bound to SFs. In result, the observed peaks are broadened as soon as several SFs are probed, as usually the case even in μ PL measurements, while in CL spectroscopy already the higher excitation density leads to broader peaks. Also, shifts in emission energy are probably the reason why different reports in literature exhibit a certain range for a specific type of stacking fault (e.g. 3.40–3.42 eV for the I₁ SFs).

On the one hand, stacking faults often occur in closely spaced bundles. For distances of only a few atomic layers, this bundling leads to a coupling of the electronic states in neighboring SFs and thus to a redshift of the emission energy, as first suggested by Paskov et al.^[82,83] In turn, a redistribution of the electric fields for SF bundles with a slightly larger separation could lead to a blueshift of the emission as discussed in Section 2.2.3. Recent calculations show that the coupling plays a role for inter-SF distances of less than 5 nm and can shift the emission energy by 30–40 meV (2 or 3 SFs) for the limiting case of only one layer distance^[84]—taking into account the spontaneous polarization could, however, alter these results.

On the other hand, Corfdir et al.^[85–87] proposed a coupling between a SF and donor atoms residing in the vicinity of this SF. Such a coupling would influence the emission energy and lead to a localization within the plane of the SF. Their calculations for I₁ SFs suggest that donors with a distance of up to about 10 nm have an influence on the emission energy associated with the SFs: The energy difference with respect to a bare SF ranges between 10 meV at 10 nm distance to 53 meV when the donor resides exactly on the SF.^[87] For a typical background doping level of $N_d = 1 \times 10^{17}$ cm⁻³, the lateral distance of donors coupling to a SF should be 20 nm on average. Thus, the statistical distribution of donor-SF distances (assuming that the presence of SFs does not influence donor incorporation) essentially leads to a broadening of the peaks associated with individual SFs. In fact, this mechanism should lead to a full width at half maximum (FWHM) of about 26 meV for SF-related emission lines according to Ref. 87.

Another factor able to shift the emission energies related to SFs is strain.^[88] The band



Figure 2.7: Sketch of the band profiles of the I₁, I₂ and E SFs, where the dominant role of the spontaneous polarization fields leads to a change $\Delta E = \Delta V$ of the associated transition energy when the thickness of the QW is changed by Δd (one bilayer) in going from one type of SF to the next.

gap and thus the excitonic transition energies in bulk GaN are affected by strain, with a compressive strain leading to a blueshift and a tensile strain to a redshift of the emission energy.^[89,90] Following the quantum well model of SFs, the emission energy of excitons bound to these should be shifted accordingly when the band gap of the matrix is changed. Note again, that only a change in the strain state at an interface induces a change in P_{pz} which then has to be considered as well.

For (Al,Ga)N and (In,Ga)N quantum well structures grown in non-polar directions, it has been reported that the intersection of SFs with the QWs leads to the formation of onedimensional quantum wires.^[91–94] In these, the confinement of the QW and the SF add up at the intersection resulting in an additional peak redshifted with respect to the QW emission. The one-dimensional character of the emission is evidenced by polarization-dependent PL measurements.^[93]

2.3.4. A model system to determine the spontaneous polarization

As the transition energy of excitons at SFs should be influenced by the spontaneous polarization, SFs might actually serve as a test bed to experimentally determine P_{sp} .

Usually, band structure calculations in the framework of the effective mass theory are employed to predict emission energies of quantum wells. When this energy is known from luminescence spectroscopy, P_{sp} can be taken as a free parameter and adjusted to reproduce the experimentally observed energies. However, the calculations also show a significant dependence on the effective masses and other parameters. For a series of QWs with different thicknesses, e.g. different types of SFs, it is possible to consider the difference in emission energies ΔE instead of the absolute energy. In this case, the uncertainties will cancel to some extent, and the reliability is improved. Soon after the spontaneous polarization of the group-III nitrides was predicted in the late 1990s, ^[36] several experimental studies used a similar approach to determine the total polarization for wurtzite (Al,Ga)N heterostructures.^[95–98] For the ternary system, disentangling the contributions from P_{sp} and P_{pz} is a challenge, and the reports were only able to conclude an overestimation of P_{sp} in the calculations by Bernardini et al.^[36] Only for SiC, such an approach has been applied to heterostructures of different polytypes of a binary semiconductor.^[99]

Considering the relatively strong spontaneous polarization of GaN, it makes sense to assume that the difference in emission energy between ZB quantum wells of varying thickness is in fact dominated by P_{sp} . Figure 2.7 sketches this situation: Due to the trian-

gular profile of the QWs, it may be assumed that the change in confinement of electrons and holes is negligible when going from one type of SF to the next. Then, ΔE is equal to the difference in the potential ΔV associated with a change in QW width by Δd . With $\Delta V = \mathcal{E}\Delta d$, Eq. (2.6) can be rewritten as

$$|P_{\rm sp}| = \sigma = \frac{\Delta V \epsilon \epsilon_0}{\Delta d}.$$
(2.8)

This plate capacitor model applies to isolated SFs, where the emission is not shifted by any external factors. Following this approach, P_{sp} can be determined in an essentially parameter-free way. Only the dielectric constant ϵ and the vacuum permittivity ϵ_0 enter the calculation.

In Chapter 6, both approaches, based on self-consistent band structure calculations and the plate capacitor model, are employed to derive an experimental value for P_{sp} of GaN.

2.3.5. The controversy concerning the band gap of wurtzite GaAs

The wurtzite polytype of GaAs was of little interest until the advent of nanowires, ^[100,101] which has also sparked an interest in the structural and electronic properties of this polytype, notably the optical band gap E_g^{WZ} . Only in recent years, a few groups have reported the growth of bulk GaAs with WZ structure. McMahon and Nelmes^[23] analyzed the structural parameters of wurtzite GaAs that formed after a high pressure growth procedure, while recently Gurwitz et al.^[102] reported on a 100 nm thick wurtzite GaAs (0001) layer on a zincblende GaAs (001) template. Due to the lack of bulk WZ samples, the standard route to determine the band gap via transmittance or reflectance measurements is not accessible. Instead, PL spectroscopy^[103–107] or Raman scattering^[108–110] have been employed to this end.

In most theoretical studies, a WZ band gap energy slightly larger than that of the ZB polytype and a type-II band alignment between the two polytypes are predicted. ^[15,71,77,111–113] In fact, Yeh et al. ^[15] arrive at this conclusion not only by DFT calculations, but also by considering the zone folding relationships between the ZB and WZ Brillouin zones as well as the interaction of the resulting states at the Γ point. It should be added that a few recent DFT calculations arrived at $E_g^{WZ} < E_g^{ZB}$. ^[107,114] However, their approaches have already been contested. ^[71,113]

Experimentally, the picture is comparably diverse. Using resonant Raman scattering at low temperatures, Ketterer et al.^[109] placed the band gaps of both polytypes at the same energy. In the meantime, their conclusion has been challenged through measurements at 300 K by Peng et al.^[115] as well as Kusch et al.^[110] These groups take into account not only the polarization of the incoming light, but also that of the outgoing light. Kusch et al.^[110] arrive at a band gap difference of $E_g^{WZ} - E_g^{ZB} = 35$ meV. In photoluminescence studies on GaAs nanowires containing both polytypes, the failure to observe any emission above E_g^{ZB} has led some groups to report values for E_g^{WZ} up to 41 meV lower than E_g^{ZB} .^[103,107,116] In contrast to this, other groups have reported low-temperature PL peaks at up to 30 meV above E_g^{ZB} .^[104–106] Since the carrier diffusion length in GaAs is usually large (on the order of 1 µm), electrons are very efficiently captured within ZB segments. This results in a large probability to predominantly observe luminescence at energies lower than the band gap energies of either polytype, even if only a small number of ZB segments exists within the structure, and therefore could account for the aforementioned discrepancy. Moreover, the presence of defect levels often favors the observation of luminescence at energies

below that of the band gap, particularly, for measurements at low temperatures.

This tendency of luminescence measurements to probe the lowest available states highlights that a clear interpretation of luminescence spectra of GaAs nanowires requires very detailed investigations. Furthermore, measurements at room temperature should result in a better representation of the band gap energies since shallow defects are ionized with increasing thermal energy. Such a careful spectroscopic study is presented in Chapter 5.

2.4. Carrier localization in (In,Ga)N heterostructures

Despite the polarization fields in quantum well structures grown in the polar direction and dislocation densities several orders of magnitude in excess of those known for classic III-V semiconductors, quantum wells based on (In,Ga)N/GaN exhibit remarkably high luminous efficiencies enabling their application in LEDs and laser diodes.^[117,118] This is attributed to carrier localization at microscopic potential fluctuations in the ternary alloy (In,Ga)N, which effectively reduces the diffusion length and prevents carriers from reaching non-radiative recombination centers. A fraction of the excitons might even be localized sufficiently to render them insensitive to the polarization fields. Several mechanisms that contribute to such a carrier localization are discussed in the literature:^[119]

(i) Atomic ordering in the cation sub-lattice, e.g. the formation of In–N–In chains, has been proposed theoretically^[120] and some experimental evidence for such a mechanism leading to localization in the sub-nm range has been presented.^[118,121]

(ii) The possibility of phase separation in the ternary alloy leading to nm-sized clusters with higher In content is discussed rather controversially. Early reports of a significant clustering were later attributed to artifacts introduced during the investigation by TEM.^[122] Nevertheless, evidence for both an essentially random alloy^[123] as well as for subtle fluctuations of the In content^[124] are given in the more recent literature. It is reasonable to assume that different growth methods and conditions can lead to more or less homogeneous (In,Ga)N layers.

(iii) Interface roughness of QW structures has been observed experimentally.^[123,125] This roughness results in a varying QW thickness that induces microscopic fluctuations of the band structure on a nm-scale.

The first two factors are linked to the strong ionicity combined with the large difference in size of the Ga and In atoms and are less pronounced for (Al,Ga)N alloys. Experimentally, both the localization of excitons in individual localization centers and the separate localization of electrons and holes have been observed by continuous-wave and timeresolved micro-photoluminescence:

(i) Localized excitons lead to sharp emission peaks in low excitation μ PL spectra: Using nano-apertures, Schömig et al.^[126] measured peaks with a linewidth down to 0.8 meV which do not shift with increasing excitation density.^[126] In time-resolved measurements, higher excitation densities are usually necessary, and it is not possible to measure such individual peaks.

(ii) When electrons and holes are localized at an essentially random distance to each other, the resulting luminescence band will be broader. Some reports of (In,Ga)N/GaN QW emission have found features more consistent with such a model than with localized excitons.^[127–129] Notably, the decay dynamics often follow a power law resembling the case of a disordered system such as for the donor-acceptor pair luminescence.^[128,129]

In Chapter 7, carrier localization is discussed in the context of (In,Ga)N insertions in GaN nanowires.

3. Luminescence spectroscopy

The presence of a finite band gap of energy E_g is the central characteristic of a semiconductor. It corresponds to the energy width of the forbidden band separating the highest (fully) occupied band (valence band) from the lowest unoccupied band (conduction band). The excitation of an electron from the valence into the conduction band leaves behind an unoccupied state in the valence band which is referred to as a *hole* and can be pictured as the quasi-antiparticle of the electron. The energy released during the recombination of an electron and a hole can be transmitted to phonons^a in a non-radiative or to photons in a radiative process. The latter process is the foundation of luminescence spectroscopy. The observable transition energies are influenced by defects or impurities acting as radiative or non-radiative recombination centers. Quantum well structures of different semiconductors or polytypes also shift the emission energy as discussed in the previous chapter for the case of stacking faults. As luminescence spectroscopy tends to probe the lowest available states, it is a sensitive tool to elucidate the nature of heterostructures, crystal defects and incorporated impurities.

This chapter gives a brief review of the recombination mechanisms at the foundation of luminescence spectroscopy. Then, the setups used for continuous wave and timeresolved photoluminescence measurements are introduced where a laser beam is used as excitation source. The major part of the experimental work in this thesis is based on cathodoluminescence in a scanning electron microscope where the electron beam provides the excitation. Therefore, not only the experimental setup, but also characteristic aspects pertaining to cathodoluminescence spectroscopy such as the spatial resolution are discussed. In this context, an observed reduction of the cathodoluminescence intensity from GaN nanowires under the electron irradiation is discussed.

3.1. Recombination mechanisms in semiconductors

Prior to discussing different recombination mechanisms, the excitation process is introduced. Especially at low temperatures, exciton states, which can further interact with impurities acting as donors or acceptors in the crystal, dominate radiative recombination processes. All these processes affect the recombination probability and the associated emission energy. For details on recombination mechanisms in semiconductors going beyond the discussion in this section, the reader is referred to Refs. 9 and 130.

Excitation and relaxation to the band edge

For the excitation of an electron-hole pair, the supplied energy must exceed the band gap energy E_g of the semiconductor. In the case of photoluminescence (PL), this condition is met for light with the photon energy $\hbar \omega = hc_0/\lambda \ge E_g$, where λ and ω are the wavelength and angular frequency of the light, *h* is Planck's constant, $\hbar = h/(2\pi)$, and c_0 is the vacuum speed of light. As a consequence, the semiconductor is transparent for light with

^aPhonons are the quantum mechanical quasiparticles associated with crystal vibrations.

3. Luminescence spectroscopy



Figure 3.1: In a semiconductor, an excitation with an energy larger than the band gap, e.g. by photons with $\hbar \omega_{\text{exc}} \geq E_g$, lifts an electron from the valence into the conduction band. This process leaves behind a hole in the valence band. Through the emission of longitudinal optical (LO) phonons, the electron and hole will thermalize (relax) to the conduction and valence band edges, respectively. Sketch reproduced from Ref. 9.

 $\hbar\omega < E_g$. Usually, the excitation energy E_{exc} will exceed E_g and the excess energy will be emitted in the form of (longitudinal optical) phonons, whereby the electron and hole thermally relax (thermalize) to the conduction and valence band edges as sketched in Fig. 3.1. This thermalization or "cooling" of the carriers takes place on a sub-picosecond timescale and does not normally influence the subsequent recombination of the carriers.

Emission from excitons

A quasiparticle (bound state) formed by an electron–hole pair in a semiconductor as a result of the Coulomb attraction of these charged particles is called an exciton. Excitons are stable, i.e. the dissociation probability is low, when their kinetic energy ($E_{kin} = 3k_BT/2$, where k_B is the Boltzmann constant and *T* the temperature) does not exceed the exciton binding energy E_{FX} . With increasing thermal energy, excitons dissociate. Therefore, luminescence at low temperatures is always dominated by excitonic emission. However, for GaN, excitonic emission plays a role even up to room temperature; Tab. 3.1 shows that the binding energy of free excitons in GaN is close to $k_BT = 25.8$ meV at T = 300 K.

An exciton can be formally described as a hydrogen atom, only that the effective electron and hole masses m_e^* and m_h^* are roughly of the same order of magnitude, and the dielectric constant ϵ of the material screens the Coulomb interaction. The Schrödinger

Table 3.1: Characteristics of excitons in GaN and GaAs. Only the values for the A excitons
(involving the highest valence band) in WZ GaN are given, the emission energy is
a little higher and the binding energy varies slightly for the excitons involving the
B and C valence bands. ^[9]

	WZ GaN	ZB GaN	ZB GaAs
Exciton binding energy E_{FX} (meV) Exciton emission energy $\hbar\omega$ (eV) Exciton Bohr radius a_B^* (nm)	24.8–26.7 ^[131,132] 3.478 ^[74] 3 ^[135]	≈25 ^[27] 3.276 eV ^[27,75]	4.2 ^[133] 1.5153 ^[134] 11 ^[136]


Figure 3.2: Schematic representation of the energy levels for excitons. Their generation (blue), dissociation (red) and recombination (green) are indicated by arrows. $|0\rangle$ is the crystal ground state, $|C\rangle$ the crystal continuum state, $|FX\rangle$ the free exciton ground state and $|DX\rangle$ the donor-bound exciton ground state.

equation of this system can be solved in analogy to the hydrogen atom, and the following relations are obtained for the binding energy E_{FX} as well as the Bohr radius a_B^* of a free exciton, where a_B^* characterizes the spatial extent of the exciton (for the derivation see Ref. 137):

$$E_{\rm FX} = \frac{m_r^* e^4}{2(4\pi\hbar\epsilon_0 \epsilon)^2 n^2} = \frac{m_r^*}{m_0} \frac{1}{\epsilon^2 n^2} R_y, \tag{3.1}$$

$$a_B^* = \frac{4\pi\hbar^2 \epsilon_0 \epsilon}{m_r^* e^2} n^2 = \frac{\epsilon n^2}{m_r^* / m_0} a_0, \tag{3.2}$$

where n = 1 denotes the ground state of the exciton. The Bohr radius and the Rydberg constant of the hydrogen atom are $a_0 = 0.529$ Å and $R_y = 13.6$ eV, respectively, while m_0 and e are the mass and the elementary charge of the electron. The reduced effective mass m_r^* is defined by $1/m_r^* = 1/m_e^* + 1/m_h^*$.

For GaN with $m_e^* = 0.2m_0$, $m_h^* = 0.8m_0$ and $\epsilon = 9.5$,^[138] these equations yield $E_{FX} = 24 \text{ meV}$ and $a_B^* = 3.1 \text{ nm}$ in good agreement with the experimental values listed in Tab. 3.1. For compound semiconductors in general, a trend of increasing effective mass with increasing band gap can be seen, which manifests itself in an increase of E_{FX} and a reduction of a_B^* .^[137]

Note that instead of directly emitting light, free excitons form a coherent state with photons described by a quasiparticle named exciton-polariton. In a very simplified way, this can be imagined as the consecutive emission and resonant reabsorption of excitons and virtual photons in the crystal. The exciton-polariton is annihilated when a photon is emitted at the surface of the crystal or due to interaction with phonons.

So far, free excitons were considered. Impurities from either intentional or residual doping act as efficient traps for excitons and lead to the formation of bound exciton complexes, with the binding energy E_{DX} (E_{AX}) to the donor (acceptor). The bound excitons are localized and do not have any kinetic energy. At low temperatures and excitation densities, bound exciton recombination will dominate the emission spectra even for low (residual) doping densities making luminescence spectroscopy the most sensitive tool to probe certain impurities. With increasing temperature, bound exciton complexes will dissociate ($k_BT \gtrsim E_{\text{DX}}$), while for high excitation densities, the bound exciton emission will saturate when all available impurity sites are occupied and emission from free excitons sets in.



Figure 3.3: Scheme of carrier generation and different radiative and non-radiative recombination paths in semiconductors. *Blue:* carrier generation and relaxation to the band edge. *Green (from left to right):* band-to-band recombination, free-to-bound (conduction band acceptor and donor valence band) recombination, as well as donor-acceptor pair recombination. *Red:* non-radiative recombination via a deep (mid-gap) energy level as well as through an Auger assisted process.

Excitons can not be described in the single particle representation of the band structure in semiconductors. The energy levels of these two particle states are related to the crystal continuum state $|C\rangle$. This situation is sketched in Fig. 3.2 for the ground states of bound and free excitons, where the crystal ground state is denoted as $|0\rangle$. The picture illustrates that the emission energy of free excitons is $\hbar\omega_{FX} = E_g - E_{FX}$ and that of donor bound excitons is $\hbar\omega_{DX} = E_g - E_{FX} - E_{DX}$. When the associated energies are known, specific impurities can be identified by the associated emission energy. Additional emission lines at slightly higher energies will arise for free excitons involving the B and C valence bands in wurtzite crystals [cf. 2.5(d)] or higher excited states of the exciton such as n = 2 [cf. Eq. (3.1)]. In the context of this thesis, the excitonic luminescence is subsumed as nearband edge (NBE) emission, because the spectral resolution of the measurements usually is insufficient to distinguish the different excitonic emission lines.

A more significant shift of the emission energy results from the simultaneous emission of a phonon, usually a longitudinal optical (LO) phonon. Thereby, the luminescence energy is reduced and *phonon replicas* of the zero-phonon line appear in the spectrum with a spacing characteristic for the LO phonon energy of the investigated material.

Emission from free carriers

Especially at elevated temperatures and for semiconductors with a relatively small exciton binding energy such as GaAs, emission from the recombination of electrons and holes not forming excitons needs to be considered. Again, impurities will play a role. Figure 3.3 sketches different recombination paths of this type, notably band-to-band, free-to-bound and donor-acceptor pair (DAP) recombination. For GaN, the latter one plays a role as soon as acceptors are present. This process can be described as recombination between the electron at a neutralized donor and the hole at a neutralized acceptor. Therefore, it is necessarily a spatially indirect transition and the random distance between donors and acceptors in the lattice leads to slightly varying emission energies. When these different energies are not resolved, the emission band is broadened. Due to the tendency of carriers to occupy the lowest available states, band-to-band recombination plays a role only for temperatures at which the carriers can escape from bound states, whereas DAP recombination plays a significant role at low temperatures.

Non-radiative recombination

The release of energy during the recombination of electron hole pairs does not necessarily lead to the emission of photons. Non-radiative recombination denotes such processes where the energy is dissipated through a different path. The most relevant path of this type is the emission of phonons, i.e. a heating of the crystal. Especially for wide gap semiconductors, the emission of *n* phonons to bridge the band gap is highly unlikely. However, deep energy levels positioned close to the middle of the gap as sketched in Fig. 3.3 can significantly increase the probability for non-radiative recombination to take place. This process is known as Shockley-Read-Hall recombination.^[139,140]

Another recombination process involving phonons is similar to the *Auger* process involving deep atomic levels where an electron is emitted during the relaxation of an excited state. In the band model of a semiconductor, a third quasiparticle is involved and the released energy will catapult this electron (hole) higher (deeper) into the conduction (valence) band (see Fig. 3.3). Subsequently, the excited carrier will thermalize back to the band edge through the emission of phonons. Again, Auger recombination depends on the presence of mid-gap states.

The nature of mid-gap states mediating non-radiative recombination is often unclear. Their origin can include vacancies, dislocations or impurities. A specific case is *surface recombination* where dangling bonds can induce mid-gap levels. This effect can lead to a strongly reduced luminescence towards the surface. In the case of nanowires, surface recombination can become significant as this thin "dead layer" may actually comprise a large portion of the nanowire volume.

Luminescence decay

The decay dynamics of the luminescence, i.e. its evolution over time after the excitation process is stopped, carries complementary information on the recombination processes. In general, an effective lifetime τ_{eff} is probed, which relates to the radiative and non-radiative lifetimes τ_{r} and τ_{nr} through

$$\tau_{\rm eff}^{-1} = \tau_{\rm r}^{-1} + \tau_{\rm nr}^{-1}.$$
(3.3)

The relation between different contributions can be modeled by rate equation systems taking into account the different available recombination channels and possible interactions between available states (in case of steady-state conditions also the generation).

In the simplest situation, the decay I(t) of the initial intensity I(t=0) obeys a single exponential behavior

$$I(t) = I(t=0) \exp^{-t/\tau_{\text{eff}}}$$
 (3.4)

Often, the combination of different recombination channels will lead to biexponential or even more complex non-exponential dynamics.



Figure 3.4: Sketch of the confocal µPL setup. Reproduced from Ref. 9.

3.2. Micro-photoluminescence

The most common way to excite luminescence for a spectroscopic analysis is by optical means. Generally, a laser beam is used for the excitation, but also a white light source or a combination of the latter with a monochromator may be employed. In microphotoluminescence (μ PL), the light is focused to a spot on the sample by a microscope objective, and spot diameters of 1 μ m and below are achieved. By optical filters, the excitation density can be varied over several orders of magnitude.

When performing PL measurements on a nanowire ensemble illuminated from the top, the sub-wavelength diameter of these nanostructures comes into play, and the basic principles of geometric optics employed for layers fail. Light will not be able to couple in and out of the top facets of the wires. The nanowire tips will diffract the incoming light wave, and the light is then coupled into the nanowires through the sidewalls.^[9]

As a consequence, also the excitation depth will be different from layers, where the penetration of light is described by the absorption coefficient α and the exponential Lambert-Beer law relating the intensity I(z) at a distance z from the surface to the initial intensity I(z=0) through

$$I(z) = I(z=0) \exp^{-\alpha z}$$
. (3.5)

Instead, essentially the whole nanowire will be excited through the sidewalls. Similar considerations hold for the emission of light. Note that for such processes the nanowire diameter and spacing play a significant role, and photonic crystal effects may come into play.

Micro-photoluminescence setup

The continuous-wave (cw) PL data presented in this thesis was recorded with a Jobin-Yvon μ PL setup. A sketch of this experimental setup is shown in Fig. 3.4. As the excitation source for GaN with its rather large band gap, the 325 nm line of a Kimmon He–Cd laser with a maximum power of 30 mW was used. For GaAs, the 633 nm line of a Melles-Griot He–Ne laser was used. To attenuate the excitation power for low-excitation or excitation dependent measurements, both a filter wheel housing different neutral density filters and a filter wheel with a gradual change in optical density were used. In the ultraviolet range (He–Cd laser), the beam was focused by a $15 \times$ microscope objective to a spot diameter of about 3 µm, whereas for the He–Ne laser a spot diameter of about 1 µm was achieved by a $50 \times$ objective. The PL signal was collected by the same objective (confocal arrangement), dispersed spectrally in a single spectrograph (600 mm⁻¹ grating, 800 mm focal length), and detected by a liquid-nitrogen-cooled charge-coupled device (CCD) detector. The spectral resolution chosen for most of the measurements is 1 meV. For measurements at low temperatures, the samples can be placed in a cryostat and cooled by liquid He to a temperature of 10 K.

Further details on this μ PL setup can be found in the Ph. D. thesis of Carsten Pfüller,^[9] who also collected some of the presented μ PL data (for Chapters 5 and 7).

Time-resolved photoluminescence setup

For sample *A* in Chapter 7, time-resolved PL measurements were carried out on the nanowire ensemble at 20 K using a spectrometer with 5 meV spectral resolution together with a Hamamatsu streak camera for detection. This sample was excited by laser pulses with a wavelength of 325 nm and a duration of 200 fs using the second harmonic obtained from an optical parametric oscillator (APE OPOPPAutomatic) synchronously pumped by a femtosecond Ti:sapphire laser (Coherent Mira 900). The latter is pumped by a frequency-doubled Nd:vanadate continuous-wave laser (Coherent Verdi V 10). The repetition rate of the laser system is 76 MHz. Again, a microscope objective was used to focus the laser beam to a spot size of about $3 \times 11 \ \mu m^2$ on the sample surface, and the light was collected in a confocal arrangement.

For sample *B* in the same chapter, measurements were performed both at 20 and at 300 K. In this case, the sample was excited by laser pulses with a wavelength of 389 nm. To obtain this wavelength, the second harmonic of the Mira 900 is used directly without the additional optical parametric oscillator. The repetition rate was reduced to 603 kHz using a pulse picker to address the longer decay times. The excitation intensity can be varied using optical density filters.

The TRPL data presented in Chapters 6 and 7 were collected by Timur Flissikowski.

3.3. Cathodoluminescence

For the investigation of nanostructures having sub-wavelength dimensions, cathodoluminescence (CL) spectroscopy can provide the necessary spatial resolution. Such a setup is usually attached to a scanning electron microscope (SEM), where the electron beam provides the localized excitation. As an example, the luminescence along the axis of a nanowire can be resolved, where μ PL can only provide integral spectra of the nanowire. This section introduces scanning electron microscopy as the basis of cathodoluminescence spectroscopy, followed by a description of the CL system and a summary of the specific characteristics of cathodoluminescence. In this context, the limit of the spatial resolution is discussed. A dose-dependent quenching of the cathodoluminescence of GaN nanowires under the electron beam irradiation in the SEM is observed, the origin of which is investigated in Section 3.3.4.



Figure 3.5: (a) Sketch of a scanning electron microscope. (b) Sketch of the interaction volume of the electron beam with the sample marking the origin of the different signals. The best imaging resolution is obtained using secondary electrons, which can only leave the sample when created close to the surface. Most analytical methods (CL, EDX) rely on signals from a much larger region. For samples incorporating a junction of p- and n-doped layers, an electron beam-induced current (EBIC) signal can be measured between the respective sides of the sample.

3.3.1. Scanning electron microscopy

De Broglie's hypothesis of wave-particle duality and the resulting association of a wavelength $\lambda = h/p$ to any particle, where p is the particle's relativistic momentum, opened the possibility of imaging beyond the diffraction limit of optical microscopy using the much shorter wavelengths of electron beams.

Secondary electrons emitted by the sample following the excitation from the incident beam and to a certain extent also backscattered electrons form the base of scanning electron microscopy. Here, the beam is focused to a nm-sized spot by electromagnetic condenser lenses and scanned across the surface of the specimen by use of deflection coils, as sketched in Fig. 3.5(a). A wide range of magnifications (roughly from $100 \times$ to $100000 \times$) can be accessed simply by changing the dimensions of the scanned area. The resolution is limited by the chromatic aberration of the electromagnetic lenses and the interaction volume of the electron beam with the sample. Field emission SEMs reach spot sizes around 1 nm. The interaction volume and the regions from which different signals originate are sketched in Fig. 3.5(b). Because low energy (< 50 eV) secondary electrons easily loose their energy in further scattering processes, only those secondary electrons created within a small volume close to the surface can overcome the work function of the material and leave the sample. The emitted secondary electrons are deflected towards a detector with a grid biased at a low voltage (around +400 V). In the detector, a scintillator is set at a much higher potential to sufficiently accelerate the electrons for them to cause cathodoluminescence in the scintillator, which in turn is detected in a photomultiplier. The secondary electron yield from the specimen depends on the topography through the angle between the incident beam and the surface, whereby detection of the electron signal for each point of the raster gives a surface image which in modern systems

3.3. Cathodoluminescence



Figure 3.6: Picture of the Zeiss Ultra 55 SEM used for CL and other analytical measurements. The different components attached to the SEM are labeled. The CL system is mounted on the right side of the specimen chamber.

is directly recorded in a computer system. However, the signal also contains components from other contrast mechanisms.

The size of the volume into which electrons are scattered depends on the acceleration voltage V_{acc} of the electron beam^b (compare Fig. 3.8). A variety of signals are created during the elastic and inelastic scattering of the electron beam as summarized in Fig. 3.5(b). Some of the incident electrons are scattered back out of the sample. The backscattering of electrons is stronger for heavier elements (larger scattering cross section) so that images based on these electrons have a significant material contrast with heavier elements appearing brighter. An increase in the number of backscattered electrons will also increase the creation of secondary electrons close to the surface by further scattering processes. Therefore, a material contrast is also contained in the signal from secondary electrons. Furthermore, several processes lead to the emission of X-rays. In energy-dispersive X-ray spectrometry, characteristic X-rays are used to identify constituent elements in the sample as described in Section 4.3. The emission of cathodoluminescence is discussed in the next section.

The scanning electron microscope used in the course of this work is a Zeiss Ultra 55 with a field-emission gun. The latter provides a high electron current beneficial to analytical applications and facilitates small spot sizes. A picture of the instrument is shown in Fig. 3.6 with labels for the attached analytical instruments, notably the CL system on the right and the Helium cooling stage in the front.

3.3.2. Setup and conditions for cathodoluminescence measurements

The setup used for the cathodoluminescence measurements presented in this work is a Gatan MonoCL 3 system attached to the Zeiss Ultra 55 field-emission SEM depicted in Fig. 3.6. A schematic diagram of the CL setup is shown in Fig. 3.7. The sample can be

^bThe beam (kinetic) energy in units of eV is equal to the accelerating potential V_{acc} in units of V as $E_{kin} = e \cdot U$ for electrons accelerated in an electrostatic field (*e* is the elementary charge).



Figure 3.7: Sketch of the CL system used in this work: The electron beam passes through a small aperture in the parabolic mirror which collects the light and reflects it into the spectrometer. A charge-coupled device (CCD) or photomultiplier (PMT) can be used for parallel or monochromatic detection, respectively. An EBIC signal may be recorded simultaneously.

placed on a Helium cooling stage for measurements at temperatures down to about 5–10 K. The cathodoluminescence is collected and directed towards the spectrometer by a parabolic mirror placed above the sample. The specimen surface has to be positioned to lie in the focal point of the mirror. The electron beam is passed through a small aperture in the mirror which is aligned with the focal point. This system ensures an efficient collection of the emitted cathodoluminescence, but it limits the minimum magnification for which the CL signal across the image is fairly homogeneous to about $2000\times$. Also, the working distance^c of the SEM is fixed to around 6.5 mm with the mirror in place. The parallel light beam from the mirror is passed to a 300 mm Czerny-Turner grating spectrometer which is directly mounted on one of the ports of the vacuum chamber of the SEM. A retractable mirror is used to choose between two detection systems:

(i) Either, the light is directed through the exit slit of the spectrometer and the light from the selected bandwidth is focused onto the active area of a photomultiplier. This serial detection scheme allows for the simultaneous collection of secondary electron and monochromatic CL images at the imaging speed of the SEM. For the acquisition of spectra, the spectrometer has to step through the wavelength range of interest. The transmitted bandwith is determined by the chosen grating and the width of the entrance and exit slits.

(ii) Or, the diffracted light can be reflected onto a liquid nitrogen cooled charge-coupled device array, whereby the spectrum is directly imaged on the pixels of the detector. In this parallel acquisition mode, a spectrum can be recorded with exposure times typically between 0.5 and 10 s. The choice of the diffraction grating determines the spectral range projected onto the detector, while the width of the entrance slit can be used to adjust the

^cThe working distance in an SEM is defined as the distance between the end of the objective lens and the sample surface which is in focus. To achieve the maximum resolution in SEM images, a small working distance of a few mm is necessary.

spectral resolution. For overview spectra, the beam is scanned over the sample at a fast rate. With the electron beam in spot mode, spectral images, i.e. line scans or maps, can be recorded. Here, a whole spectrum is acquired at every measured point. For extended exposure times or a larger number of acquisition spots, the Gatan software corrects the spatial drift of the sample based on a cross-correlation analysis of SEM images.

The acceleration voltage $V_{\rm acc}$ and the aperture of the SEM as well as the slit width and grating of the spectrometer and the exposure times of the detectors were varied to suit the respective experiments. A summary of the experimental parameters for each figure in this thesis that includes CL data is given in Appendix F. As detailed in the next section, the acceleration voltage controls the spatial resolution and probing depth of CL measurements, but the increase in the deposited energy with larger $V_{\rm acc}$ also influences the CL intensity. To achieve a high spatial resolution, an acceleration of 2–3 kV was chosen. Otherwise 5 kV or, for a larger penetration depth, 8 kV were applied. The beam current is controlled by different apertures, e.g. with diameters of 30, 60 or 120 µm. Additionally, the Ultra 55 SEM has a high current (HC) mode, where a change in the beam path changes the angle at which the beam is passed through the aperture. This mode enhances the beam current roughly by a factor of two. The actual current depends on the age of the cathode filament and the apertures and will decrease over time through a degradation of the filament and the deposition of residual carbon onto the aperture. As an example, the measurements in Chapter 6 were performed after installing a new filament and new apertures, and a beam current of 1.8 nA was determined for $V_{\rm acc} = 3 \, \rm kV$ using an aperture of 60 µm (HC mode). For lower excitation densities, a lower beam current may be chosen, but this will also reduce the CL yield and require longer exposure times on the detection side.

Concerning the spectrometer, either a grating with 1200 l/mm or one with 300 l/mm, both blazed for optimal reflection at a wavelength of 500 nm, was used. The latter was necessary to record the rather broad luminescence band of (In,Ga)N heterostructures investigated in Chapter 7, whereas the former offers a higher spectral resolution. For the two gratings, the dispersion (bandwidth per slit width) is 2.7 nm/mm and 10.8 nm/mm, respectively. Around the band gap energy of GaN, these dispersions correspond to spectral resolutions for the two gratings of 1.3 and 5 meV (0.5 and 2.1 meV) for 0.5 mm (0.2 mm) slits.

3.3.3. Characteristics of cathodoluminescence spectroscopy

The most obvious advantage of cathodoluminescence spectroscopy in a scanning electron microscope is the direct correlation with an image of the sample surface. Thereby, it is possible to pinpoint the spatial origin of spectral features. Especially for nanostructures not resolvable in an optical microscope, this feature is of importance. However, also the absence of luminescence associated with non-radiative recombination is reflected in the contrast of CL images, e.g. dislocations can be identified.^[141] Even though the spectral resolution and fine control over the excitation density attained in PL spectroscopy are typically not matched, CL offers a wealth of complementary information.

For CL, the excitation process is quite different from PL where the energy of the incident photons only slightly exceeds the band gap energy of the semiconductor. The electron beam in an SEM is accelerated to several keV. These primary electrons carry far too much energy to directly excite electrons from the valence to the conduction band. Instead, secondary electrons, Auger electrons and X-rays are emitted when the incident



Figure 3.8: Illustration of the excitation volume of the electron beam obtained from Monte-Carlo simulations^[144] for different acceleration voltages. Plotted are both the path of the scattered and backscattered electrons (for 200 incident electrons) as well as contours (calculated for a larger number of electrons) marking which portion of the energy is deposited within the respective regions for the example of GaN.

beam is inelastically scattered [cf. Fig. 3.5(b)]. Monte Carlo simulations of the scattering path for different acceleration voltages are presented in Fig. 3.8. Each primary electron is scattered several times before it has lost its kinetic energy or is scattered back out of the crystal. The X-rays and Auger electrons still carry a comparably large energy, but their reabsorption prior to leaving the sample can contribute to the population of secondary electrons. This cascade process produces on the order of 10^3 secondary electrons per incident electron.^[142] These are electrons which were only weakly bound and carry a kinetic energy E_{kin} in the range of 2–50 eV. Thus, they may indeed excite electrons from the valence to the conduction band, a process for which, on average, an energy of $E_{kin} \approx 3E_g$ is used up.^[143] The excess energy in this relation goes to the lattice, i.e. the emission of phonons.

A variety of consequences arise from this cascade excitation process. First, any wide gap semiconductor may be excited, in contrast to PL which is limited at short wavelengths by the availability of appropriate lasers. Only the use of refractive optics may restrict the accessible spectral range in CL. In turn, there is no control of the excitation energy, whereas in PL the resonant excitation of e.g. only the quantum wells in a sample is possible. Furthermore, the comparatively high excitation densities may saturate lowenergy states or defect levels and can lead to a screening of internal electric fields in a sample. These effects can alter the observed emission energy and need to be considered in the interpretation of results from CL.

Spatial resolution of cathodoluminescence measurements

Of course, the achievable spatial resolution is of particular interest. The spatial resolution of CL measurements is governed by three factors:^[146,147] (i) The beam diameter, which is usually negligible for field-emission SEMs, (ii) the scattering volume of the electron beam, and (iii) the diffusion of carriers prior to recombination.

The most important of these three factors is the scattering of incident electrons. It is also the only adjustable parameter concerning the spatial resolution. For the example of GaN, Fig. 3.8 illustrates the scattering volume of the electron beam for different acceleration



Figure 3.9: Diameter (purple) and depth (red) of the scattering volume into which 75% (solid lines) and 95% (dashed lines) of the energy are deposited. The values are obtained from Monte-Carlo simulations for GaN and are plotted for acceleration voltages between 1 and 10 kV. For comparison, the penetration depth according to the empirical equation of Everhart and Hoff^[145] is given. The inset zooms into the range of 1 to 4 kV.

voltages with the help of Monte-Carlo simulations using Casino V2.42.^[144] Exemplary scattering paths for 200 primary electrons are given and superimposed by isoenergy contours marking the percentage of the total energy deposited within the respective regions. The lateral diameter as well as the depth into which 75% (95%) of the energy is deposited are plotted in Fig. 3.9 as solid (dashed) lines for acceleration voltages from 1 to 10 kV. Note that at low acceleration voltages, the 75% isoenergy curves exhibit a significantly larger depth than diameter, while for 95% of the energy the volume gets almost spherical with the diameter slightly in excess of the depth. An empirical expression for the penetration depth R_G was given by Everhart and Hoff^[145]

$$R_G = \frac{39.8}{\rho} (V_{\rm acc})^{1.75}.$$
(3.6)

Here, R_G is given in units of nm for V_{acc} in units of kV. The density ρ of the material is 6.15 g/cm³ for GaN.^[40] This model has been found to give a reliable estimate for the interpretation of CL and EBIC measurements.^[146] In Fig. 3.9, the values from Eq. (3.6) roughly correspond to the scattering depth for 95% of the energy.

As the volume for the additional 20% is a multiple of that into which 75% of the energy are deposited, the latter (i.e. the solid lines in Fig. 3.9) will essentially govern the contribution of the scattering volume to the spatial and depth resolution of CL measurements. Summarizing, the acceleration voltage has a significant impact on the spatial resolution of CL measurements. To achieve a high spatial resolution, the acceleration voltage has to be reduced below 5 kV, preferably in the range of 2–3 kV. However, this comes at the cost of CL intensity, especially as the sensitivity to surface effects, e.g. non-radiative recombination, increases. At the same time, the variation of the penetration depth with acceleration voltage allows for a depth profiling of the luminescence.^[148]

Finally, the diffusion of carriers can reduce the spatial resolution of CL measurements. While the excitation is very *localized*, the detection in most CL systems, e.g. by parabolic mirrors, is fairly *global*. In other words, no matter where the carriers recombine, the signal is attributed to the current position of the exciting electron beam. The diffusion of carriers



Figure 3.10: (a) Line profiles of the CL intensity obtained from the areas marked in the CL spectral image (linear heat map color scale) depicted in (b). The spectral line scan was recorded along the arrow marked on the cross section of the GaN microcrystal shown by the SEM image in (c). The stacking fault acts as a sink for diffusing excitons generated in the bulk of the microcrystal. This measurement highlights the competition between recombination processes at different positions of the sample. The blue line in (a) is a fit to Eq. (3.7) used to derive the exciton diffusion length.

to radiative or non-radiative recombination centers within the range of the carrier diffusion length will therefore decrease the spatial resolution. Contrast features of radiative or non-radiative nature will have an enlarged footprint in CL images. At low temperatures, mainly the diffusion of free excitons and their binding to donors or acceptors plays a role. The latter process indicates that the states probed by luminescence spectroscopy have a direct influence on how the diffusion length is reflected in the measurements.

An illustration of carrier diffusion is given in Fig. 3.10. The sample discussed in more detail in Chapter 6 is used. A GaN microcrystal with emission from a stacking fault at the base, but high-quality GaN free of extended defects in the upper part^[149] is investigated to this end. Intensity line profiles of the GaN near-band edge as well as the stacking fault emission along the cross section of this microcrystal are given in Fig. 3.10(a). These profiles are extracted from the spectral line scan depicted in Fig. 3.10(b) and recorded along the arrow on the SEM image of the microcrystal shown Fig. 3.10(c). The observed slopes are clearly not a result of the beam profile, because at an acceleration voltage of 3 kV the isoenergy curve for the deposition of 75% of the energy has a diameter of 16 nm according to the data plotted in Fig. 3.9.

The stacking fault at the base of the crystal acts as a sink for diffusing free excitons excited in the *bulk* of the crystal. At low temperatures, the probed near-band edge emission is dominated by the recombination of donor-bound excitons. Therefore, the donors in GaN and the stacking fault compete for the excitons. The diffusion process is reflected in the shape of the luminescence intensity profiles in Fig. 3.10(a). Despite of the broadening by diffusion, the spatial peak position of the stacking fault emission in the profile is well defined. The step size in the line scan was 12 nm, and the error in determining the peak position is of the same order. Also, the spectral resolution improves the spatial resolution, because as long as two features do not emit at roughly the same emission energy, their position can be determined independently.

3.3. Cathodoluminescence



Figure 3.11: Superposition of a monochromatic CL image acquired at 10 K of the NBE emission (3.47 eV) of GaN nanowires onto the corresponding SEM image of the nanowires. The left part of the image has been exposed to the electron beam for a few ten seconds to illustrate the quenching of the GaN emission, while the right part was freshly exposed prior to taking the images.

Diffusion length of excitons in GaN

In fact, CL measurements have repeatedly been used to derive a carrier diffusion length L in semiconductors.^[150–154] This can be achieved by monitoring either the exponential decay of the emission intensity with increasing distance of the beam from the radiative emission center or the rise in emission intensity I in the bulk of a sample with increasing distance r from a (radiative or non-radiative) carrier sink. The latter process can be approximated by^[154]

$$I(r) = I_0 \left[1 - \exp\left(-\frac{r}{L}\right) \right].$$
(3.7)

Here, I_0 is the maximum emission intensity in the bulk of the sample. For the interpretation of *L*, it has to be clarified what is being measured. Taking the example of Fig. 3.10, the emission from donor bound excitons is being monitored at low temperatures. The diffusion length can be expressed as $L = \sqrt{D\tau}$ in terms of the diffusion coefficient *D* and a lifetime τ . Note that in this specific case, τ does not represent the radiative recombination time of the free excitons, but rather the capture time by donors leading to the formation of donor-bound exciton complexes. Therefore, the exciton diffusion length at low temperatures explicitly depends on the donor concentration.

Alternatively, the emission intensity associated with the stacking fault might be used as a probe for the diffusion length, but it is also affected by changes of the polarization fields under the increasing excitation density, when the electron beam approaches the stacking fault (see Chapter 6). Instead, Eq. (3.7) is fitted to the slope of the emission at 3.47 eV in the profile of Fig. 3.10(a) giving L = 239 nm. From measurements on several such microcrystals, an exciton diffusion length of $L = (200 \pm 50)$ nm is obtained. Incidentally, this value compares well with a value of 190 nm obtained by Ino and Yamamoto^[155] at 20 K using threading dislocations as a non-radiative carrier sink. Note again that such a diffusion length is specific for each sample and furthermore may be affected by surface recombination because most carriers were excited up to a depth of only about 30 nm ($V_{acc} = 3$ kV).

3.3.4. Cathodoluminescence quenching in GaN nanowires

When GaN nanowires are investigated by cathodoluminescence, a strong decrease of the near-band edge emission resulting from the exposure to the electron beam can be observed. This quenching has been mentioned in the literature,^[156,157] but is to date not



Figure 3.12: Temporal evolution of the CL intensity under electron beam irradiation for a GaN nanowire (NW) ensemble continuously scanned in top-view geometry plotted on a logarithmic scale. The intensity decreases by almost two orders of magnitude for the presented ensemble with a steep decline during the first 2–3 min, which then slows down, but does not saturate completely even after 40 min. Treatment of the sample in a plasma cleaner for 5 min prior to the placement in the SEM improves the final intensity by a factor of two. The inset shows the CL evolution for another nanowire ensemble with embedded (In,Ga)N insertions (QW). Both the GaN (solid) and (In,Ga)N (dashed) emission are measured at low $(2 000 \times)$ as well as high $(10 000 \times)$ magnification. The latter corresponds to the magnification used in the main figure. Clearly, the (In,Ga)N is only weakly affected by the quenching. The increased dosage per area at a higher magnification significantly speeds up the quenching process.

fully understood. Robins et al.^[156] argue that neither carbon contamination^d nor the formation of point defects are likely origins of the quenching and instead attribute it to charging effects which increase the non-radiative recombination.

In our laboratory, this quenching process has been generally observed on a variety of nanowire samples grown in different MBE systems both in house and by collaborators. The quenching can be observed both at room temperature and at cryogenic sample temperatures and, though its magnitude varies from sample to sample, can amount to a reduction in emission intensity by one to two orders of magnitude. An illustrative view is given in Fig. 3.11, where a CL image was recorded directly after shifting the field of view so that half of the image is freshly exposed to the electron beam and shows a strong NBE emission, while the other half was pre–exposed to the electron beam and basically appears dark.

A more detailed idea about this quenching can be obtained by recording the CL intensity over time. Figure 3.12 shows several such measurements for both a simple GaN nanowire array and for nanowires containing embedded (In,Ga)N insertions (sample *B* in Chapter 7). The latter was measured at different magnifications, while for the former the effect of a plasma-cleaning step is investigated. Several conclusions on the quenching

^dContamination of the sample surfaces by carbon deposited in an SEM is a well known problem.^[158] Modern instruments employ oil-free vacuum pumps to avoid this effect. Nevertheless, the electron beam can crack hydrocarbon molecules adsorbed to the specimen prior to insertion into the vacuum leading to the deposition of a thin carbon film. Polar molecules may be attracted to the exposed area due to electric fields induced by the electron irradiation and enhance this effect.^[159]



Figure 3.13: Recovery of quenched CL intensity over time during beam blanking: After an initial exposure time of 3 min (shaded yellow), the beam was blanked for 45 s to 24 min. The evolution of the signal upon re-exposure is plotted in different colors. In the inset, the relative change in CL intensity between start and end of the blanking period normalized to the initial intensity $\Delta I_{\rm CL}/I_0$ is shown for three series of measurements with different initial exposure times. After about 10 min, the recovery saturates.

process can be drawn from these measurements. Note, at this point, that no shift of the emission energy is observed over time. First, the quenching is a dose dependent process: Both an increased magnification, which effectively increases the electron dose per area, and an increased beam current (not shown) lead to a faster quenching. Second, it is a surface-related process, which is already inferred by the fact that such a significant quenching has not been reported for layers. The luminescence from heterostructures such as embedded (In,Ga)N insertions as well as from stacking faults (not shown) suffers only a minor quenching. The same holds true for GaN nanowires covered with an (Al,Ga)N shell. Also luminescence from strongly localized states, e.g. the donor-acceptor pair transition, are less affected by the quenching. Third, carbon contamination clearly plays a role in this quenching process, but is not the sole cause. A pre–treatment of samples in a combined oxygen and hydrogen plasma for a few minutes is known to reduce the adsorbed hydrocarbon molecules and thereby mitigate the carbon contamination during electron beam exposure. This cleaning improves the quenched CL intensity by a factor of two and slows down the initial steep decline in intensity.

The question arises, whether the quenching process is reversible. To this end, the CL intensity was recorded over time, and the beam was "blanked" (deflected from its usual path in the electron column) for intermittent periods. An example of such measurements is given in Fig. 3.13 for which the initial exposure time was 3 min and the time allowed for the signal to recover before continuing the measurements was varied. In the inset of Fig. 3.13, the relative change in CL intensity during the beam blanking period is summarized for several series of such measurements using different initial exposure times. Independent of the degree of initial quenching, the intensity reached during the recovery saturates after about 10–20 min without irradiation. Even after an initial exposure of only 10 s or after extended times for the recovery (over night, not shown), the intensity was not restored to its original value. In fact, the maximum recovery observed amounts to only about 10% of the initial signal intensity I_0 , i.e. only a fraction of the quenched intensity

is recovered. The partial reversibility of the quenching process is a clear indication that besides carbon contamination also charge trapping contributes to the CL quenching. For sufficiently long initial exposures, the recovery process seems to be independent of this initial quenching time. For a very short initial exposure (e.g. 10 s), where the quenching is not yet as significant, only a smaller portion of the luminescence can be restored. Therefore, charge trapping seems to occur within the first minute or so, where the intensity exhibits a steep decline. In contrast, carbon adsorption continues for a longer time.

For GaN, the Fermi level is pinned at about 0.6 eV below the conduction band edge.^[19,160] Therefore, at typical background doping levels, the resulting surface depletion layer will span the entire nanowire cross-section up to diameters of about 100 nm (compare Fig. 7.4).^[19] The resulting lateral electric field reduces the radiative recombination efficiency of the excitons. Pfüller et al.^[161] reported an unpinning of the Fermi level due to oxygen desorption from the surface under irradiation by an ultraviolet laser. Thereby, the lateral electric field is reduced, and the PL intensity is enhanced. In our case, the Fermi level is already pinned, but the trapping of additional negative charges at surface states may increase the lateral electric fields, thus inhibiting the radiative recombination of excitons.

The deposited carbon layer may reduce the emission intensity by absorption of emitted photons, but the thickness of the carbon layer would need to be tens of nanometers for a significant absorption (cf. Ref. 162 for the absorption coefficient of amorphous carbon). A more likely explanation is an increase of the surface recombination velocity, when carbon is adsorbed at the surface. Time-resolved PL measurements on areas of a nanowire sample exposed to the electron beam for different times show a faster decay of the NBE luminescence with longer exposition. This effect does not immediately set in for exposure times of only a few seconds. The faster decay suggests that indeed the surface recombination velocity increases as a result of carbon adsorption. Note that for GaN nanowires a comparatively low surface recombination velocity of $S = 9 \times 10^3$ cm/s has been reported.^[163] In contrast, GaAs has a high surface recombination velocity of $S = 3 \times 10^7$ cm/s.^[164] Consequently, GaAs nanowires can hardly be investigated by luminescence spectroscopy without a passivating (Al,Ga)As shell.^[165]

In summary, the observation of a luminescence quenching under electron beam exposure was related to the interplay of charge trapping and carbon adsorption at the surface. For GaN layers, the surface clearly plays a less significant role. Nevertheless, at low acceleration voltages and thus penetration depths, a slight quenching could be observed also for the GaN near-band edge luminescence in layers, which previously has been reported also in Ref. 166.

As a consequence, the quenching effect has to be accounted for in the investigation of nanowires using cathodoluminescence spectroscopy. The relative height of different spectral contributions can be significantly altered. However, also for time-resolved PL measurements, the transients might be affected by a prior investigation in an SEM. In the context of this thesis, the focus lies on quantum well structures in nanowires. Therefore, the quenching has to be kept in mind for the interpretation of peak intensities in overall spectra, but does not significantly affect the luminescence of the investigated heterostructures.

4. Samples and experimental background

This chapter briefly reviews the growth of the different types of nanowire samples investigated in this thesis, the preparation of samples prior to luminescence measurements, as well as experimental methods that provided complementary data for the analysis and interpretation of the emission properties of the nanowire-based heterostructures. Further details can be found in the cited references.

4.1. Nanowire growth and overgrowth

Semiconductor nanostructures can be achieved by direct epitaxial growth (bottomup)^[167] or by post–growth etching procedures (top-down). A variety of methods for the epitaxial growth have been demonstrated.^[167,168] Among the best growth control is achieved using molecular beam epitaxy (MBE). All the samples investigated in this thesis by luminescence spectroscopy were grown by MBE at the Paul-Drude-Institut. This growth method is briefly introduced, followed by details for the different types of samples.

Molecular beam epitaxy (MBE)

Molecular beam epitaxy is a physical vapor deposition technique for crystal growth. In an ultra high vacuum chamber, source elements of very high purity are evaporated from effusion cells and then redeposited onto the chosen substrate. The mean free path of the evaporated atoms in the vacuum is larger than the chamber diameter so that the molecular beam reaches the substrate without interaction among the atoms or with other particles. For the growth of semiconductors, the substrate will usually be a wafer of the same (homoepitaxy) or a different material (heteroepitaxy). Advantages of MBE include a high crystal purity and a high degree of growth control (e.g. layer thickness). Furthermore, the growth can be monitored and controlled in-situ by methods such as reflection high-energy electron diffraction (RHEED).^[169]

Essential parameters governing the crystal growth are the substrate temperature and the ratio of the atomic fluxes of the deposited elements. Depending on the growth conditions, different growth modes such as layer-by-layer (Frank–van der Merwe) growth or island (Volmer–Weber) growth can be achieved.^[170] In the extreme case, when the islands do not coalesce, the growth of nanowires is obtained. An alternative mode to grow nanowires is the collector-assisted vapor-liquid-solid growth.^[171] Liquid droplets of a metal collect the growth species with supersaturation leading to a precipitation of the material below this droplet. The droplet thus moves upwards on the growing nanowire.

4.1.1. Ga-assisted GaAs nanowire growth

The growth of GaAs nanowires by MBE is achieved using the vapor-liquid-solid mechanism. The most commonly employed collector is Au.^[167] However, also Ga droplets can



Figure 4.1: Side-view SEM image of a GaAs nanowire ensemble grown in the Ga-assisted growth mode (sample #1). The Ga droplets are visible at the top of the nanowires.

be used (Ga-assisted) with the advantage of no extra element being involved.^[172] The latter approach was reported to lead to superior optical properties.^[165] The growth of nanowires offers a route to grow the metastable wurtzite polytype of GaAs.^[24] In particular, GaAs nanowires often exhibit a mixed crystal structure with zincblende and wurtzite segments alternating along the nanowire axis.^[18,101,173] This mixture of polytypes has been attributed to the interplay of the formation energies which favor the nucleation of zincblende layers and of the surface energies that favor the nucleation of wurtzite segments. The preference of either polytype has then been linked to the degree of supersaturation of precursors in the metal droplet,^[174] but the exact relation to specific conditions during the nucleation and growth is still under discussion.^[173,175,176]

An example for a GaAs nanowire ensemble grown in the Ga-assisted mode is depicted in Fig. 4.1. This growth mode usually is accompanied by a parasitic GaAs layer that develops between the nanowires. Vapor-liquid-solid grown nanowire arrays usually have a rather low density on the order of 10^8 – 10^9 cm⁻².

The samples investigated in Chapter 5 were grown by the Ga-assisted vapor-liquidsolid mechanism on phosphorus-doped Si(111) substrates at a temperature of 580 °C. A constant As₄ beam equivalent pressure of 1.2×10^{-5} mbar was set, and GaAs nanowire growth started upon opening of the Ga shutter. For sample #1, the Ga supply was set to match a planar growth rate of 820 nm/h, which led to a V/III ratio of the atomic fluxes equal to one. In contrast, sample #2 was grown using half the Ga flux (V/III ratio of two) under otherwise identical growth conditions. For both samples, the growth of an (Al,Ga)As shell with a nominal Al content of 10% was initiated after 30 min by opening the Al shutter. A coverage of the GaAs nanowires with an (Al,Ga)As shell was necessary to reduce surface recombination and thus enhance the luminescence efficiency enabling optical investigations at moderate and low excitation densities.^[165] The total growth time was 1 hour.

As a reference sample (#Ref), bare GaAs nanowires were deposited on Si(111) by Auinduced vapor-liquid-solid growth. These are known to crystallize predominantly in the wurtzite structure and grow in the [0001] direction.^[177] Au droplets were prepared on the oxide-free substrate by deposition of a 0.6 Å thin Au layer and subsequent heating. The Ga and As fluxes were then set alike to sample #2, and nanowires were grown for 30 min at 500 °C. Further details on the growth of GaAs nanowires can be found in the Ph. D. thesis of Steffen Breuer,^[20] who provided the investigated samples.

4.1.2. Growth and overgrowth of GaN nanowires

The growth of GaN nanowires by MBE does not necessitate the use of a collector particle.^[178] Instead, the growth parameters have to be chosen in such a way that the vertical growth rate is enhanced and simultaneously suppressing lateral growth. This is achieved for a V/III ratio larger than one, i.e. N-rich growth conditions,^[10] and is often termed self-induced growth mode as these nanowires form spontaneously. Another important growth parameter is the substrate temperature, which governs both the diffusion and the desorption of Ga atoms impinging on the substrate. For nanowire growth, the temperature has to be sufficiently high so that the adsorbed atoms can diffuse to the nanowire



Figure 4.2: (a) Side-view and (b) top-view SEM images of the overgrown GaN nanowire ensemble investigated in Chapter 6. The resulting layer contains microcrystals in a matrix of smaller grains. (c) A detached microcrystal lying upside-down on the layer. The inset in (a) visualizes an uncoalesced nanowire template at the same scale.

4. Samples and experimental background

nuclei, but sufficiently low to limit the desorption of atoms. As a result, increased growth temperatures lead to a reduced nanowire density. GaN nanowire growth is possible in the temperature range from 750 °C to 825 °C.^[179] The self-induced nucleation and growth process is more complex and thus not as well understood as the vapor-liquid-solid mechanism. Initial nanowire nuclei on silicon substrates or AlN buffer layers have a spherical cap-shape and undergo one or several shape transitions prior to growing in the vertical direction along the *c*-axis.^[180,181] Then, the growth continues with the Ga atoms diffusing to and being incorporated at the top facet, i.e. the incorporation is higher on the *C*-plane than on the *M*-plane sidewalls. Due to the N-rich conditions, the amount of Ga reaching the top facet determines the growth rate.^[182] Self-induced GaN nanowires grown by MBE have a N-polar crystal orientation.^[183–185] The resulting nanowire ensemble will exhibit a distribution of nanowire diameters and also of nanowire lengths as a result of the statistical nature of the nucleation process.^[186]

An approach to obtain a GaN layer with possibly reduced dislocation densities on highly mismatched but technologically interesting Si substrates is the pendeoepitaxial overgrowth of nanowire arrays.^[149] To achieve such overgrowth, the growth parameters have to be changed to Ga-rich conditions (V/III ratio smaller than one). This promotes lateral growth and eventually leads to the formation of a coalesced GaN layer. To this end, both the Ga flux is increased and the substrate temperature lowered.

For the sample investigated in Chapter 6, a nanowire array was grown on a Si(111) substrate at 800 °C for 1 hour with a V/III ratio of 3. The resulting nanowires have a length up to 500 nm and an average diameter of 30 nm. Subsequently, the nanowires were overgrown for 2 hours at 740 °C with the Ga flux increased by a factor of four. SEM images of the resulting coalesced layer are shown in Fig. 4.2. The layer consists of microcrystals with a diameter of 1–3 μ m embedded in a matrix of smaller grains. The cross-sectional image in Fig. 4.2(a) shows that every microcrystal originates from the overgrowth of a single nanowire. The inset in Fig. 4.2(a) shows a nanowire template grown under the given conditions and reveals an inhomogeneous length distribution. Thus, the longest nanowires probably lead to the formation of the microcrystals with the developing crystal shadowing the surrounding nanowires from the incoming fluxes. The top-view SEM image in Fig. 4.2(b) as well as the detached and flipped microcrystal in Fig. 4.2(c) visualize the perfect hexagonal shape of the crystals reflecting the crystal structure of wurtzite GaN. Probably, the shape transitions during the lateral expansion of the crystal evidenced in Fig. 4.2(c) are related to the formation of the basal plane stacking faults and zincblende segments that are the focus of Chapter 6.

More details on the GaN microcrystals grown by Pinar Dogan can be found in Refs. 149 and 187.

4.1.3. Growth of (In,Ga)N insertions in GaN nanowires

Aiming at LED applications, a first step is the integration of quantum well structures into the nanowires. Quantum wells offer a way to enhance the radiative recombination rate at the desired emission energy.^[188] While early work on heterostructures in group-III nitride nanowires concerned the combination of GaN and (Al,Ga)N,^[189] the combination of GaN and (In,Ga)N is relevant for optoelectronic applications as it offers the possibility to cover the visible spectral range. On the one hand, axial heterostructures in nanowires should suffer less from the large lattice mismatch between GaN and InN (cf. Tab. 2.1) than their planar counterpart. The possibility for strain relaxation at the side-facets of



Figure 4.3: (a) Sketch of an (In,Ga)N insertion embedded along the axis of a nanowire. (b) Birds-eye view SEM image of an ensemble of GaN nanowires with (In,Ga)N insertions grown by the self-induced growth mode. (Sample *B*, SEM image recorded by Anne-Kathrin Bluhm)

the nanowires could enable the incorporation of higher In fractions prior to the onset of plastic relaxation through the formation of dislocations at the interface to GaN.^[6] On the other hand, the integration of In into GaN nanowires is challenging. At typical substrate temperatures used for the growth of GaN nanowires, (In,Ga)N would decompose, and also the impinging In would desorb completely. Thus, the substrate temperature has to be lowered to incorporate In.^[190] Further obstacles for the growth of (In,Ga)N are known from planar epitaxy, including compositional fluctuations in the ternary alloy^[118] and In segregation on the growth front leading to thicker layers than intended.^[191] An aspect specific to the nanowire geometry and to the self-induced growth process is that from the distribution of diameters (cf. Fig. 4.3) one can expect a variation in the dimensions and possibly even in the In content of (In,Ga)N insertions in nanowires.

As it is not straightforward to conclude that the (In,Ga)N structures in nanowires behave similar to planar quantum wells, the term (*In*,*Ga*)*N* insertions is used throughout this thesis. Again, self-induced GaN nanowire arrays on Si(111) serve as a base for the growth of the samples. The nanowires have an average diameter of around 80 nm. Prior to the opening of the In shutter, the growth process is interrupted, and the substrate temperature is reduced to about 600 °C. Then, alternating (In,Ga)N insertions and GaN barriers are grown. Care has to be taken for the N-rich conditions at the growth front to be maintained even for the lower desorption rate of Ga at the reduced temperature. Finally, the structure is capped with a GaN segment of about 30 nm without raising the temperature.

The luminescence properties of two samples are investigated in Chapter 7: Sample *A* contains six (In,Ga)N insertions of about 3 nm thickness separated by 7 nm wide barriers, while sample *B* contains only two thicker insertions (\approx 11 nm) separated by a thin barrier (2–3 nm). A birds-eye view SEM image of sample *B* is displayed in Fig. 4.3.

The growth of (In,Ga)N insertions in GaN nanowires is discussed in great detail in the Ph. D. thesis of Martin Wölz,^[192] who grew sample *A*. Sample *B* was grown by Matthias Knelangen.^[193]

4.2. Sample preparation

This section gives a description of the preparation of sample cross sections and different methods applied for the isolation of single nanowires for spectroscopic measurements.

Preparation of cross-sectional samples

For CL measurements on nanowires or microcrystals, it is often desirable to look at a cross section of the sample to resolve features at various depths. The simplest way to produce such a cross section is by cleaving the sample along preferential directions of the substrate. For nanowire samples, care has to be taken that the nanowires directly at the cleavage edge are not shaved off in the process.

For layers or microcrystals, this may not always result in smooth surfaces over a larger area. An alternative approach is the preparation of cross sections by ion-milling. Some of the CL measurements on GaN microcrystals in Chapter 6 were performed on cross sections prepared either (i) through a conventional process for TEM samples where a mechanical grinding step is followed by Ar^+ milling, or (ii) using a dedicated Gatan Ilion⁺ system that employs two focused beams of Ar^+ and hardened blades as mask for selective milling. The ion milling might induce surface damage that leads to a reduced CL signal. Reduced sputtering rates and sample cooling can help to minimize such damage.

Dispersion of nanowires for single nanowire spectroscopy

To look at the detailed emission properties of nanowires, it is essential to investigate individual nanowires. Otherwise, already minor differences in the spectra will lead to a strong peak broadening.^[9] There are two approaches: Either the investigation of sparse enough nanowire arrays so that individual nanowires can be addressed, or the dispersion of nanowires on a foreign substrate. The first approach allows the in- and outcoupling of light from the top in μ PL investigations, which is the geometry envisaged for many nanowire device applications. However, potential parasitic growth between the nanowires will also contribute to the signal. The dispersion of nanowires is especially suited for CL measurements on the cross section of nanowires, but the emission energy might be slightly affected by strain induced through the interaction of the nanowire with the substrate it is deposed on. This is a drawback when a sub-meV resolution is necessary to look at the detailed characteristics of the near-band edge excitons,^[9] but not crucial for the measurements performed in this thesis.

The dispersion of nanowires can be achieved by several approaches, depending on the required density of dispersed nanowires:

(i) *Press and pull:* A piece from the nanowire sample is placed upside down on a piece of bare wafer (e.g. silicon) and then pulled over this wafer in one direction using tweezers while at the same time being slightly pushed down. During this process, nanowires will break off the substrate and adhere to the bare wafer in a well aligned fashion along the direction of pulling. The resulting nanowire density is relatively high. For dense arrays of GaN nanowires, this can lead to a significant clustering of the dispersed nanowires. This method is well suited for sparser arrays of GaAs nanowires and was used for the samples discussed in Chapter 5. A similar procedure was used to disperse GaN microcrystals for μ PL measurements in Chapter 6.

(ii) *Dabbing*: A corner of lintless cloth is first dabbed on the nanowire sample and subsequently on a piece of bare wafer. Some nanowires will break off and thus can be transferred to the wafer. This yields a slightly lower density of nanowires, but without preferential alignment. The control over the placement of the nanowires on the wafer is also improved. This procedure is more suited for GaN nanowires as it results in less clustering and is used for some of the single nanowire measurements in Chapter 7.

(iii) *Wet dispersion:* A piece from the nanowire sample is immersed in a solvent (e.g. 2-propanol or acetone). The beaker is then placed in an ultrasonic bath. The vibration will cause nanowires to break off and float in the solvent. A μ l-pipette is used to transfer a few drops of the solvent onto a wafer or a TEM finder grid. Upon drying of the solvent, a very low density of nanowires will be deposited. By using less solvent, a longer time in the ultrasonic bath or more droplets of solvent, the nanowire density can be increased. This procedure is particularly suited to place nanowires on a TEM grid allowing for an identification of individual nanowires and thus subsequent measurements by different techniques on the same nanowire. This procedure was used for the correlation between CL and TEM as well as for μ PL measurements in Chapter 7.

SEM imaging at low magnifications can give an overview of the nanowire placement and density. It also allows for the identification of those quadrants of a TEM finder grid containing nanowires prior to μ PL measurements.

4.3. Additional experimental methods

In the last part of this chapter, experimental methods used in this thesis, apart from luminescence spectroscopy, are briefly reviewed. Besides electron beam-induced current measurements and energy-dispersive X-ray spectrometry in an SEM, transmission electron microscopy as well as Raman spectroscopy and X-ray diffractometry were employed to complement the analysis of emission properties.

Electron beam-induced current measurements (EBIC)

Electron beam-induced current measurements are closely related and complementary to cathodoluminescence spectroscopy. Likewise, EBIC relies on the generation of electron hole pairs in semiconductors irradiated by the electron beam in an SEM. Thus, the spatial resolution is determined by the same factors as for CL measurements. In addition, EBIC requires an electric field, e.g. from a p-n-junction or Schottky junction, to separate electrons and holes. The signal generation is governed by the diffusion of minority carriers to the depletion region of the junction and their collection by drift in the electric field. When the sample is contacted at the p- and n-side, the resulting current can be measured in an external circuit. In principle, this parallels the photovoltaic principle with the incident photons replaced by the electron beam. Therefore, EBIC is particularly suited for the investigation of the current collection in solar cells at a high spatial resolution.

An image of the EBIC signal may be recorded simultaneously with SEM and CL images. In measurements on the cross section of diode structures, the position of the junction can be identified, whereas top-view images allow for an assessment of the homogeneity of planar junctions. While the CL contrast is governed by the ratio of the radiative and non-radiative recombination probabilities, the EBIC contrast results from a combination of both types of recombination. Additionally, an external bias voltage may be applied to the samples through the current amplifier used in the detection circuit. A reverse bias will widen the depletion region of the junction.

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The EBIC measurements on a nanowire-based LED structure in Appendix A were performed with a system integrated with the Gatan CL setup. An SR570 low-noise current preamplifier is employed in the detection and for the application of a bias voltage.

Energy-dispersive X-ray spectrometry (EDX)

Another type of signal created in an SEM by the interaction of the electron beam with the sample are X-rays [cf. Fig. 3.6(b)]. These include characteristic X-rays and bremsstrahlung. The former can be used for an identification of elements and for a compositional analysis in an SEM equipped with an EDX detector.

The transfer of energy from an accelerated incoming electron to a secondary electron from an inner shell of an atom can result in the ejection of the latter. Then, a third electron from a higher electronic level will relax to this inner level, as the excited state is unstable (see Fig. 4.4). During this transition from a high- to a low-energy level, a photon carrying the corresponding excess energy $hv = E_i - E_f$ is emitted. Here, E_i stands for the energy of the initial and E_f for that of the final electronic state. For transitions involving the inner electron shells, hv usually lies in the X-ray domain of the electromagnetic spectrum. Transitions are named according to the involved energy levels as indicated in Fig. 4.4. The energies for each of these transitions are characteristic for every element.^[194]

Energy-dispersive detection indicates that the electronic pulses created in the detector are sorted according to their intensity in a multichannel analyzer. This process yields a spectrum of X-ray energies specific to the sample which then allows for an identification of the elements present. To reliably excite certain X-ray lines, V_{acc} needs to correspond to about 2hv. The detection limit lies in the range of 0.1–1% depending on the specific element and measurement conditions. For samples homogeneous over the excitation volume, the sample composition can be quantified from the EDX spectra. However, the diameter of the nanowires investigated in this work is too small to meet this criterion. The volume fraction of the (In,Ga)N insertions discussed in Chapter 7 is so small compared to the excitation volume that In is hardly detectable at all.

The Zeiss Ultra55 SEM used in this work [cf. Fig. 3.5(a)] is fitted with an EDAX Apollo XV silicon-drift-detector with a super ultra-thin window for EDX measurements.



Figure 4.4: Scheme of secondary electron ejection and characteristic X-ray emission with line types usually observed in EDX spectra (level multiplicity of inner shells is omitted for clarity).

Raman spectroscopy

Raman spectroscopy is a method based on the inelastic scattering of laser light by elementary excitations such as phonons in a crystal structure. This process leads to a Stokes shift of the scattered light which can then be detected in a spectrometer. This shift corresponds to the energy of the involved phonon mode and is characteristic for every crystal structure. The determination of the crystal structure and strain state of a sample are among the applications of Raman spectroscopy. The Stokes shift Δw is usually expressed in wavenumbers (cm⁻¹) where $\Delta w = (1/\lambda_0 - 1/\lambda_1)$ in terms of the excitation wavelength λ_0 and the shifted wavelength λ_1 . Two types of phonons can be distinguished: acoustic and optical phonons. The latter denote the additional vibrations possible in compound solids with more than one atoms in the unit cell. Optical phonons are in the focus of Raman spectroscopy. Depending on the direction of the displacement in relation to the direction of propagation, transverse and longitudinal phonon modes are distinguished. As different selection rules apply for certain Raman active modes, their observation may be restricted to specific geometries and polarizations of both the excitation and the detection with respect to the crystal structure.^[195]

Wurtzite crystals have a larger number of possible phonon modes than zincblende crystals, which can be derived from the crystal structures. Therefore, the E_2 optical phonon mode labeled according to its symmetry is specific to the wurtzite crystal structure.^[196,197] This fact is used in Chapter 5 to identify the presence of the wurtzite phase in GaAs nanowires.

Micro-Raman measurements were performed for as-grown nanowires at a temperature of 10 K using the 413 nm line of a Kr⁺ ion laser for excitation. The same spectrometer as for the μ PL measurements was used. Raman spectra were recorded in backscattering geometry with excitation from the top of the nanowire ensembles. The elastically backscattered stray light was suppressed by a notch filter. The Raman signal was not analyzed for its polarization. The Raman measurements presented in Fig. 5.2(b) were performed by Manfred Ramsteiner.

Transmission electron microscopy (TEM)

Transmission electron microscopy was pioneered by Knoll and Ruska^[198] in the early 1930s. The electron beam of typically 40–400 keV passes through a sufficiently thin sample (only a few ten nm). Either the image or the diffraction pattern can be focused onto the detector plane. With a variety of operation modes and analytical tools, structural and compositional investigations as well as imaging down to the atomic level are possible.

The most common mode of operation is bright-field imaging, where the contrast is mainly formed by absorption of electrons in the specimen. Therefore, regions with heavier elements or thicker areas will appear darker. In a crystal structure, the electron beam also undergoes diffraction at the crystal planes. With the help of apertures in the backfocal plane, the imaging can be restricted to certain Bragg reflections. Together with an accurate control of the sample orientation, such measurements can be used to identify extended defects in the crystal as well as areas with different strain or composition.

High-resolution TEM or phase contrast imaging is a way to resolve the crystal structure with atomic resolution. The sample has to be prepared and oriented very accurately to image a certain crystal direction. The used contrast is a result of the interference of diffracted beams and the primary beam in the image plane. The image is not a one-toone representation of the crystal lattice in the imaged plane, because a bright spot might

4. Samples and experimental background

correspond to a column of atoms or the space between the atom columns depending on the exact conditions such as the sample thickness and defocus. This method is well suited to distinguish the stacking sequences of zincblende and wurtzite polytypes and to identify stacking faults.

The TEM used for the measurements related to this thesis is a JEOL JEM-3010 operated at 300 keV with electrons from a thermal LaB₆ emitter and fitted with a Gatan charge-coupled device as imaging detector. With the ultra-high resolution pole piece of the objective lens, a point resolution of about 0.17 nm is achieved in high-resolution imaging.^[199] The micrographs presented in Fig. 6.1 were measured by Claudia Roder on samples prepared by a standard process of mechanical polishing followed by ion-milling, while the micrograph correlated to a CL measurement in Fig. 7.15 was recorded by Esperanza Luna on a nanowire dispersed on a TEM finder grid.

High-resolution X-ray diffractometry (XRD)

The wavelengths of X-rays are of the same order of magnitude as crystal lattice constants, whereby their diffraction provides an optimal probe of lattice parameters. With the crystal atoms acting as diffraction centers, constructive and destructive interference will constrain the diffracted beam to certain angles. The angular relationship between incident beam θ_i and diffracted beam θ_d leading to constructive interference is given by the Bragg condition $n\lambda = 2d_{hkl} \sin \theta$, where *n* is an integer, $2\theta = \theta_i + \theta_d$, and d_{hkl} is the lattice plane spacing corresponding to a crystallographic direction $\langle hkl \rangle$.^[200]

The geometrical alignment of source, sample and detector needs to allow for the detection of diffraction maxima. During ω -2 θ scans in symmetric mode ($\theta_i = \theta_d$), either sample and detector or source and detector are moved to keep the correct angular relationship. The diffraction angles, at which a signal is detected, correspond to a lattice spacing d_{hkl} . Thereby, the crystal phases present and their orientation can be identified from known standards.

High-resolution XRD experiments were carried out using a Panalytical X-Pert PRO MRDTM system with a Ge(220) hybrid monochromator and a three bounce Ge(220) channel cut analyzer crystal. We used CuK_{α 1} radiation with a wavelength of $\lambda = 1.54056$ Å. The XRD measurements presented in Fig. 5.2(a) were carried out by Bernd Jenichen.

5. Polytypism and luminescence of GaAs nanowires

GaAs nanowires often exhibit a mixture of different polytypes, i.e. they may contain segments of both the zincblende and wurtzite phases. Since the band gap differs between these two phases, GaAs nanowires represent heterostructures with complex optical properties, the interpretation of which is currently discussed controversially. In particular, the value of the band gap energy of wurtzite GaAs is under debate as reviewed in Section 2.3.5.

In this chapter, GaAs nanowires containing both phases are investigated. Depending on the growth conditions, luminescence is observed predominantly above or below the band gap energy of zincblende GaAs. To put this finding into context, the structural properties of the nanowires are investigated. After a closer analysis of the luminescence properties both by micro-photoluminescence and cathodoluminescence spectroscopy, a value for the band gap of wurtzite GaAs is derived from this data, and the results are discussed in the framework of a qualitative model for the band structure of polytypic nanowires.

5.1. Geometry and structure of polytypic GaAs nanowires

In a first step, the structure and geometry of the nanowires under investigation needs to be investigated. To this end, XRD measurements and Raman spectroscopy are employed besides SEM images.^[201]

Two samples of GaAs nanowires grown in the Ga-induced growth mode are investigated. To enhance the luminescence efficiency for the optical spectroscopy, the samples were overgrown with an (Al,Ga)As shell. Sample #1 was grown using a V/III flux ratio of one, while sample #2 was grown using half the Ga flux, i.e. a V/III ratio of two. Furthermore, as a reference sample (#Ref), bare nanowires grown in the Au-assisted growth mode are investigated. These are known to crystallize predominantly in the wurtzite (WZ) structure (see Section 4.1.1 for further details on the nanowire growth).

Figure 5.1 shows SEM images of single nanowires from samples #1 and #2 dispersed on a Si substrate. From these low- and high-magnification images representative for a number of nanowires of both samples, an average length of the nanowires on the order of 9–10 μ m can be estimated. Their average diameter amounts to 150 and 80 nm for samples #1 and #2, respectively. The spheres visible on top of sample #1 are Ga droplets as confirmed by EDX [see Fig. 5.1(c)]; for sample #2 the droplets were consumed at the end of the growth or when the shell growth was initiated. The core diameters were estimated assuming negligible axial lengthening during shell growth and considering that the GaAs volumes deposited for the core and the shell were equal. Thus, the nanowire core diameters of samples #1 and #2 are approximately 110 and 50 nm, respectively.

XRD ω -2 θ scans of all three samples are shown in Fig. 5.2(a). The reflection intensities are normalized to the one of the Si (111) reflection centered at 28.44° (not shown). The

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Figure 5.1: (a) SEM images of single nanowires from sample #1 and #2. In (b), the magnified top part of corresponding nanowires is shown. (c) EDX maps indicating the high Ga and low As content in the droplets on top of the nanowires of sample #1.

observed maxima centered at 27.13° and 27.30° correspond to lattice plane distances of 0.3288 and 0.3264 nm and, therefore, can be assigned to the wurtzite GaAs (0002) and zincblende GaAs (111) reflection, respectively. This assignment is consistent with the assumption that the nanowires of the reference sample, for which the narrow peak at 27.13° is most pronounced, crystallize predominantly in the WZ structure. The large width of the GaAs (111) reflection is caused by the fact that parasitic growth leads to an evolution of a highly defective and probably strained GaAs layer between the nanowires, which contributes to the zincblende (ZB) reflection. Most importantly, samples #1 and #2 exhibit a weak but distinct peak near the wurtzite GaAs (0002) reflection indicating that the nanowires contain segments of wurtzite GaAs. The small shift toward lower angles with regard to the GaAs (0002) reflection of the reference sample is probably caused by the presence of the (Al,Ga)As shell, which is not existent in the reference sample.

This result is confirmed in Fig. 5.2(b), where Raman spectra of the three samples are depicted. The Raman intensities are normalized to the peak intensity of the transverse op-



Figure 5.2: (a) ω –2 θ XRD scans and (b) Raman spectra of the as-grown samples #1 and #2 as well as of the reference sample. In (b), E₂ and TO (LO) indicate the corresponding phonon lines of GaAs where the E₂ phonon mode exists only in the WZ phase. [measurements by Bernd Jenichen (a) and Manfred Ramsteiner (b)]^[201]



Figure 5.3: (a) μPL spectra of as-grown nanowires from samples #1 and #2 as well as of the reference sample measured at 10 K. E^{ZB}_g marks the band gap energy of zincblende GaAs. (b) Histogram of peaks found in the μPL spectra of 30 nanowires from samples #1 and #2 dispersed on Si(111) as a function of the respective spectral position. D⁰-C⁰ and CB-C⁰ mark the energy position of the donor-acceptor pair and conduction-band-acceptor transition with carbon acting as acceptor. The corresponding μPL spectra have been measured at 10 K. (μPL data acquired by Carsten Pfüller)^[201]

tical (TO) phonon mode of zincblende GaAs centered at about 270 cm⁻¹. The E_2 phonon mode, which is most pronounced for the reference sample, is characteristic only for wurtzite GaAs.^[197] It is also present for samples #1 and #2, indicating that the nanowires of both samples contain segments of wurtzite GaAs in accordance with the XRD results of Fig. 5.2(a). The shift of the E_2 phonon line with regard to the reference sample as well as the broadening of the TO and longitudinal optical (LO) phonon resonances toward smaller wave numbers can be explained again by the presence of the (Al,Ga)As shell for samples #1 and #2.

Summarizing, the structural similarity of samples #1 and #2 containing comparable portions of wurtzite GaAs should be emphasized. As the measurements were performed on the nanowire ensembles including a parasitic interlayer, they do not allow for a further quantification of the ZB to WZ ratio.

5.2. Luminescence of polytypic GaAs nanowires

Turning to the optical properties of these GaAs nanowires, first μ PL and then CL spectroscopy were performed at low temperatures on single nanowires dispersed on Si substrates to investigate the detailed emission characteristics. Rather complex spectra are expected from the presence of different polytypes in these nanowires.^[18]

5.2.1. Micro-photoluminescence of individual GaAs nanowires

Figure 5.3(a) depicts the μ PL spectra of the as-grown samples #1 and #2 as well as of the reference sample recorded at a temperature of 10 K. At the low excitation density used to excite the nanowires of samples #1 and #2, the spectra consist of narrow lines, which

5. Polytypism and luminescence of GaAs nanowires

appear unchanged for repeated measurements at the same position on the sample. The spectrum of the reference sample is broad and does not show any spike-like structures. For this sample, an excitation density higher by about four orders of magnitude was necessary to obtain a PL intensity comparable to that of samples #1 and #2 as a consequence of the lack of an (Al,Ga)As shell and the Au-induced growth mode.^[165] The peak energy of this spectrum exceeds the band gap energy of zincblende GaAs ($E_g^{ZB} = 1.519$ eV at about 10 K)^[202] by more than 10 meV. The µPL spectra of samples #1 and #2 differ in the spectral distribution of the sharp lines. In case of sample #1, a significant part of the spectrum is found at energies above E_g^{ZB} as in the reference sample. In contrast, sample #2 exhibits a spectrum completely at energies below E_g^{ZB} . The origin of these sharp lines lies in the complex heterostructure formed by the alternating WZ and ZB segments, as will be discussed in more detail in Section 5.4. To confirm the observation concerning samples #1 and #2, the μ PL spectra of 30 nanowires of each of these samples dispersed on Si(111) were analyzed, and a histogram of the number of narrow lines observed as a function of the respective spectral position is plotted in Fig. 5.3(b). For sample #1, an essential portion of the narrow lines of the μ PL spectra clearly appears within the spectral range above 1.519 eV, and the highest observed emission energy amounts to 1.547 eV. This observation is in disagreement with the experimental results reported by Spirkoska et al.^[18] and Heiss et al.^[107], where GaAs nanowires with WZ structure do not show any luminescence for energies exceeding E_g^{ZB} ; a situation similar to what is seen for sample #2: almost all the sharp μ PL lines appear below E_g^{ZB} . Note that, especially for sample #2 [cf. bottom part of Fig. 5.3(b)], a considerable number of sharp PL lines pile up at energy values matching the transition energies of defect-related PL, namely the donor-acceptor pair and conduction-band-acceptor transitions related to carbon as an acceptor in zincblende GaAs.^[134]

Summarizing, it can be established that although the nanowires of both samples #1 and #2 contain segments of wurtzite GaAs with similar volume fraction, their optical emission characteristics differ substantially. While the spectral distribution of sample #1 resembles the one of the reference sample, for which a significant part of the spectrum appears above E_g^{ZB} , the spectra of sample #2 coincide with several literature reports in not exceeding E_g^{ZB} .^[18,103,107,116]

At this point, it is appropriate to add a comment on the lateral confinement of carriers in one-dimensional structures as a possible reason for a blue-shift of the corresponding transition energies. Despite the (Al,Ga)As shell, such a quantum effect can be ruled out for the nanowires under investigation since the estimated values of the nanowire core diameters are too large to cause a relevant confinement-related shift of the transition energy above E_g^{ZB} . Moreover, the nanowires with a larger core diameter (sample #1) and not those with a smaller diameter (sample #2) exhibit µPL lines exceeding E_g^{ZB} .

5.2.2. Cathodoluminescence of individual GaAs nanowires

The luminescence distribution of the nanowires can be further elucidated using CL measurements at low temperatures. Figure 5.4 shows a CL spectrum acquired at 10 K from a set of dispersed nanowires of sample #1 over a wide spectral range. This spectrum consists of a broad intense luminescence band centered at 1.52 eV and a three orders of magnitude weaker band centered at 1.70 eV. The former corresponds to the μ PL emission in Fig. 5.3 and therefore can be assigned to the GaAs core, while the latter is attributed to the (Al,Ga)As shell. The assignment to the shell emission is suggested by its peak



Figure 5.4: CL spectrum of a set of nanowires from sample #1 measured at 10 K showing the dominant luminescence band from the GaAs core and an additional weaker emission from the (Al,Ga)As shell (logarithmic intensity scale).



Figure 5.5: Top: CL spectral line scans along the axis of single nanowires from (a) sample #1 and (c) sample #2. The insets show SEM images of the corresponding nanowires with the scan direction indicated by the dashed arrows. Bottom: SE images of different nanowires from (b) sample #1 and (d) sample #2 superimposed by monochromatic CL images. For sample #1, images obtained for detection energies above (top) and below (bottom) E_g^{ZB} are shown, while for sample #2 the energies of both depicted detection windows lie below E_g^{ZB} . The CL spectra and images were acquired at 10 K.

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position, which corresponds to an Al content of 12% in reasonable agreement with the nominal value of 10%. Moreover, the low CL intensity of the high-energy band is consistent with an efficient loss of carriers excited in the shell due to both carrier capture within the GaAs core and non-radiative recombination at the shell surface.

Further details can be obtained from measurements on single nanowires at 10 K. Figure 5.5 shows the spatial and spectral distribution of the GaAs core emission along the axis of individual nanowires. The CL spectral line scan from sample #1 shown in Fig. 5.5(a) was obtained by scanning the electron beam along the axis of the depicted nanowire. Clearly, the spectral contributions centered near and significantly above E_g^{ZB} are spatially separated from each other along the nanowire axis. While the upper part of the nanowire under investigation emits light predominantly near the band gap of zincblende GaAs, the CL spectra of the lower nanowire section are found between E_g^{ZB} and 1.55 eV. Figure 5.5(b) shows SE images of another nanowire from the same sample superimposed by monochromatic CL images acquired for CL detection energies below and above E_g^{ZB} . The CL obtained at 1.540 eV is found within well separated segments. Due to carrier diffusion along the nanowire axis, the segment structure of the CL image is smeared out for the image obtained at the lower detection energy (1.512 eV). These observations demonstrate that the WZ part of the nanowires detected by XRD and Raman (cf. Fig. 5.2) is indeed distributed segment-like along the nanowire axis and that $E_g^{WZ} > E_g^{ZB}$.

Similar spectral line scans were collected along the axis of individual nanowires for sample #2 as exemplified in Fig. 5.5(c). Again, the spectral position of the CL varies along the nanowire axis within a wide range. However, for a large portion of each individual nanowire, the emission is found at the spectral positions assigned to carbon-related defects, in agreement with the μ PL data of Fig. 5.3(b). In contrast to sample #1, the emission energies usually do not exceed E_g^{ZB} . Figure 5.3(d) shows monochromatic CL images at two detection energies for another nanowire from sample #2. The depicted energies both lie below E_g^{ZB} , however, again the segmented distribution of the emission along the nanowire axis can be observed.

In summary, the low-temperature CL measurements confirm the μ PL results concerning the different emission ranges of the two samples and their distribution further demonstrates the segmented nature of the crystal structure along the axis of the nanowire.

5.3. Band gap of wurtzite GaAs

The spectroscopic results at low temperatures, i.e. the observation of luminescence at energies larger than E_g^{ZB} , already indicate that $E_g^{WZ} > E_g^{ZB}$. However, the energy of the near-band edge luminescence should reflect the actual value of the band gap when measuring at 300 K rather than at low temperatures, since shallow defects such as impurities and stacking faults are ionized at higher temperatures. Thus, to obtain a quantitative estimate of the actual difference $E_g^{WZ} - E_g^{ZB}$, CL spectral line scans along the axis of single nanowires from sample #1 were performed at 300 K. Such a spectral line plot for a representative nanowire is shown in Fig. 5.6(a). Again, one section of the nanowire emits at energies centered at E_g^{ZB} , but others emit light at energies significantly exceeding E_g^{ZB} . The variation of the peak energy of the emission with the position along the axis of the nanowire depicted in Fig. 5.6(a) is plotted in Fig. 5.6(b). According to this graph, the maximum energy variation along this nanowire amounts to 58 meV. For a more accurate estimate of the variation of the band gap energy along the nanowire, Fig. 5.6(c) compares



Figure 5.6: (a) CL spectral line scan along the axis of a single nanowire from sample #1 acquired at 300 K. The inset shows an SEM image of the corresponding nanowire, where the dashed arrow marks the path of the scan. (b) Peak energy of the CL spectra in (a) as a function of scan position. (c) CL spectra showing the lowest and highest peak position among the spectra of (a). E_g^{ZB} is marked by dashed arrows in all plots. On the high energy side of the spectra, the exponential tail reflects the thermal distribution of the carriers at the band edge. The spectral shift of this exponential decay when measured at different positions along the nanowire axis is assigned to the band gap difference $E_g^{WZ} - E_g^{ZB}$. (Line scan acquired by David Stowe, Gatan Inc.)

the spectra with the highest and lowest peak energy. Note that the CL intensities are displayed on a logarithmic scale. The thermal distribution of carriers at the band edge is reflected by an exponential tail of the CL intensity on the high-energy side of the spectra. The slope of this tail is the same for all spectra shown in Fig. 5.6(a) and indicates the actual temperature of the free carriers under the chosen excitation conditions. Thus, the energy shift of the exponential tail between the spectra of Fig. 5.6(c) represents the maximal energy difference measured along the nanowire. This difference, amounting to 55 meV, can be taken as the lower bound for the band gap difference between wurtzite and zincblende GaAs.

Very recent experimental studies employing surface photovoltage spectroscopy,^[102] resonant Raman scattering,^[110] and magneto-PL,^[203] as well as DFT calculations^[71] converge on the conclusion that $E_g^{WZ} > E_g^{ZB}$. The reported experimental values for the band gap difference range between $35^{[110]}$ and 70 meV.^[102] The discrepancy between different experimental values may reflect the presence of different hexagonal polytypes. In fact, the 4H-polytype has been observed for both GaAs and InAs nanowires.^[58,59,204] For the partially hexagonal 4H- and 6H-polytypes of III-V semiconductors, calculations by DFT predict band gaps intermediate to those of the zincblende 3C- and wurtzite 2H-polytypes.^[71,205] Another explanation for the scatter in the experimental data could lie

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Figure 5.7: Qualitative illustration of the band structure for samples #1 and #2. WZ and ZB mark the position of the conduction band (CB) and valence band (VB) of the respective polytype. $CB-C^0$ and D^0-C^0 indicate conduction-band-acceptor (carbon) and donor-acceptor (carbon) transitions in ZB GaAs, respectively. The long diffusion length in GaAs allows carriers to reach confined states in ZB segments for electrons and in WZ segments for holes as a consequence of the type-II band alignment. The presence of very thin ZB segments in sample #1 would explain the observed emission at energies above E_g^{ZB} .

in a contribution from transitions involving the second valence band. Under the strong excitation in CL, the Γ_{7V} (lh)-band in wurtzite GaAs could become relevant [in addition to the Γ_{9V} (hh)-band].^[77] However, the experimentally observed valence band splitting of 65–103 meV^[109,110] is too large for such an explanation to be credible. Concerning higher conduction bands, the splitting between the lowest Γ_{7C} and second lowest Γ_{8C} conduction bands is expected to be even larger.^[71,77] In addition, the optical matrix element should be lower for transitions involving the Γ_{8C} state that arises from an L state back-folded from the ZB Brillouin zone than for those involving the Γ_{7C} state.^[109,206,207]

Given 1.424 eV as the band gap energy of zincblende GaAs at 300 K, the lower bound for the band gap difference obtained above translates into $E_g^{WZ}(300 \text{ K}) \ge 1.479 \text{ eV}$. Assuming this difference to be independent of temperature yields a low-temperature band gap of $E_g^{WZ}(10 \text{ K}) \ge 1.574 \text{ eV}$.

5.4. Qualitative model for polytypic nanowires

The observation of sharp lines in the μ PL spectra can be understood within the framework of a quantum well model for heterostructures consisting of wurtzite and zincblende GaAs (cf. Section 2.3.3). According to the calculations of Murayama and Nakayama^[77] and a more recent work by Belabbes et al.,^[71] such a heterostructure establishes a type-II band alignment in the case of GaAs with positive WZ conduction and valence band offsets. Thus, for nanowires consisting of alternate zincblende and wurtzite GaAs segments, electrons captured within the ZB segments recombine with holes of the neighboring WZ segments as illustrated in Fig. 5.7. For low *T*, this results in excitons bound to the ZB/WZ interface. The corresponding transition energy *E_t* depends on the degree of confinement of the electrons and can span the range between E_g^{WZ} and $E_g^{WZ} - \Delta E_C$, where ΔE_C denotes the conduction band offset. Values for *E_t* exceeding E_g^{ZB} , as observed for sample #1, are possible for very thin ZB segments as a result of confinement. For simplicity, the possibility of an additional confinement of holes in thin WZ segments of a more complicated



Figure 5.8: Calculated transition energy of a WZ/ZB/WZ GaAs quantum well structure as a function of the ZB segment thickness, where the confined electron of the ZB layer recombines with a hole of the neighboring wurtzite GaAs. The energy is plotted both for the two cases of $P_{\rm sp} = 0$ (squares) and $P_{\rm sp} = 0.002 \,\mathrm{Cm}^{-2}$ (circles).

heterostructure is not considered in the following, although it might well be present in the investigated nanowires. However, such a structure would be part of a sequence of closely spaced ZB and WZ segments where electronic coupling of the quantum wells would counteract the additional confinement. Otherwise, it could be argued that transition energies exceeding E_g^{WZ} could become possible for type-II heterostructures even for $E_g^{WZ} = E_g^{ZB}$. Such an effect was explicitly ruled out by dedicated calculations.^[208]

In order to obtain an estimate of E_t as a function of the thickness t_{ZB} of the zincblende GaAs segments, self-consistent Poisson-Schrödinger calculations^[209] were performed using the low *T* band gap energies. This yields the ground state of electrons in a WZ/ZB/WZ GaAs quantum well structure, where the confined electron of the ZB layer recombines with a hole of the neighboring wurtzite GaAs. Details on the parameters used in this calculation can be found in Appendix D. The results of these calculations are depicted by squares in Fig. 5.8, where E_t is shown as a function of t_{ZB} . The calculated data of Fig. 5.8 predict values for E_t ranging between E_g^{WZ} ($\approx 1.57 \text{ eV}$) and 1.43 eV when t_{ZB} varies between 3 and 30 bilayers^a. It becomes evident that emission energies higher than E_g^{ZB} are expected only for very thin ZB insertions, i.e., $t_{ZB} < 9$ bilayers.

Thus, the occurrence of WZ and ZB segments of different thickness leads to the observation of distinct sharp luminescence lines, as in the μ PL spectra shown in Fig. 5.3(a). However, a direct comparison of the energy of these sharp lines with the calculated values of $E_t(t_{ZB})$ in Fig. 5.8 is not conclusive because of the simplifications made in the calculation. In the framework of the above model, the different emission properties of samples #1 and #2 can be explained by assuming a higher probability for the occurrence of very thin ZB sections or stacking faults for sample #1, whereas for sample #2 the ZB sections are in general thicker than 9 bilayers. For the former, the electron confinement leads to values of E_t exceeding E_g^{ZB} . Whereas for sample #2, the electron confinement is small and E_t is generally found below E_g^{ZB} .

^aA bilayer is one layer of Ga as well as one of As amounting to t = c/2, with *c* being the WZ *c*-lattice constant

5. Polytypism and luminescence of GaAs nanowires

5.4.1. Spontaneous polarization of wurtzite GaAs

As interest in the WZ polytype of GaAs has only recently come up with the advent of nanowire growth, the possibility of a spontaneous polarization in wurtzite GaAs has not been treated in the literature. While Spirkoska et al.^[18] explicitly mention that effects of strain and spontaneous polarization at the WZ/ZB interface are neglected in their calculations of the band structure, Dayeh et al.^[210] assume a lower bound of 10¹³ cm⁻² for the sheet charge density resulting from P_{sp} in the case of InAs nanowires with WZ/ZB structure (this corresponds to $P_{sp}(InAs) \ge 0.016 \text{ Cm}^{-2}$). They discuss the transport properties of pure ZB and ZB/WZ nanowire field emission transistors in light of these polarization charges at the interfaces. However, their assumption is that P_{sp} is of the same order of magnitude as in the group-III nitrides and ZnO. Considering that the bond ionicity of group-III arsenides is clearly lower than that of group-III nitrides, it is more sensible to assume that the spontaneous polarization of GaAs is about one order of magnitude lower than that of GaN (cf. Section 6.2). The deviation of the internal parameter *u* is comparable – but opposite in direction – to that of GaN, $^{[22,23]}$ leading to a sign reversal of P_{sp} . Therefore, $P_{sp} = 0.002 \text{ Cm}^{-2}$ can be considered a reasonable estimate.^[201] In fact, recent DFT calculations arrive at exactly this value.^[32]

The results of the calculation of $E_t(t_{ZB})$ as a function of t_{ZB} taking into account the impact of the spontaneous polarization is also plotted in Fig. 5.8. This shows that already such a small value of P_{sp} leads to a significant increase of the slope of $E_t(t_{ZB})$ and, consequently, to a larger reduction of E_t with increasing thickness of the ZB insertion than for $P_{sp} = 0$. Accordingly, energies higher than E_g^{ZB} should actually be observable only for $t_{ZB} < 7$ bilayers.

A derivation of an experimental value for P_{sp} , as done for GaN (cf. Section 6.2), is unfortunately not possible from these data. Due to the expected lower value of P_{sp} , larger ZB segments and a more detailed knowledge about their actual width would be necessary to attribute shifts in the emission energy to a difference in ZB thickness and discriminate the contributions from P_{sp} and a change in confinement.

5.5. Conclusions

In this chapter, GaAs nanowires consisting of wurtzite and zincblende segments were analyzed. Their luminescence is spread over a wide spectral range, which can be explained in terms of a type-II band alignment of the ZB/WZ heterostructure sequence. Depending on the growth conditions, the nanowires exhibit either luminescence exclusively below or also clearly above the band gap energy of zincblende GaAs. The latter indicates a wider band gap for the wurtzite as compared to the zincblende modification of GaAs. The thickness of the zincblende insertion controls the energy of the transition between electrons confined in this insertion and holes of the neighboring wurtzite sections. This energy can exceed E_{q}^{ZB} for zincblende insertions as thin as a few bilayers, a result of the confinement of the electrons. Obviously, this condition is fulfilled for sample #1 investigated in this study, while for sample #2 the thickness of the zincblende segments of the nanowires must be generally larger than the critical value, even though the total amount of zincblende and wurtzite in the two samples is comparable according to the results from XRD and Raman measurements. Thus, these results clarify why in some previous work luminescence was not observed at energies above E_g^{ZB} , [18,103,107–109,116] while in other publications luminescence was also observed in this range.^[104–106]
At low temperatures (10 K), defect-related optical transitions contribute to the observed diversity of luminescence lines and the high probability to measure emission below E_g^{ZB} . In particular for sample #2, an accumulation of emission lines at energies corresponding to the donor-acceptor pair and conduction-band-acceptor transition are observed, where carbon acts as an acceptor. Acceptors exhibit a large carrier capture cross section and thus can effectively bind holes within the zincblende segments, namely preventing the hole diffusion toward the wurtzite segments. Therefore, an absence of emission lines above E_g^{ZB} is very probable especially for low temperatures, but does not mean an absence of higher energy states. The possible range of energies for the optical transitions increases if the spontaneous polarization of wurtzite GaAs is taken into account.

From CL measurements at 300 K, a value of 55 meV was estimated for the lower bound of the difference $E_g^{WZ} - E_g^{ZB}$.

6. Stacking fault luminescence and the spontaneous polarization of GaN

In contrast to GaAs, the equilibrium phase of GaN and the other group-III nitrides is the wurtzite crystal structure. For GaN, the growth of nanowires can again lead to polytypism, i.e. the stabilization of the zincblende phase^[75] or the formation of stacking faults.^[81] However, the appearance of basal plane stacking faults is known not only from nanowire growth. Especially the growth of non-polar and semi-polar GaN layers^[67,68,82,211,212] as well as epitaxial lateral overgrowth^[213–218] or the coalescence overgrowth of nanowires^[187,219,220] are associated with the formation of basal plane stacking faults. Again, stacking faults act as quantum wells with their emission energy determined by the thickness of the zincblende segment. However, this chapter will show that the spontaneous polarization plays the decisive role in governing the emission energy, in contrast to confinement as in the case of GaAs.

The spontaneous polarization of GaN is a fundamental, but elusive parameter. There has been only one attempt, based on an indirect thermodynamic approach, to arrive at an independent estimate of the spontaneous polarization of GaN from experiment.^[221] Other experimental studies have investigated ternary (Al,Ga)N/GaN quantum wells, where the contributions from the spontaneous and piezoelectric polarizations are not easily disentangled.^[42,95-98] As sketched in Section 2.3.4, stacking faults can serve as a model system for a determination of the spontaneous polarization in a crystal with a large ionicity such as GaN. Therefore, this chapter aims at systematizing the luminescence energies associated with the different stacking fault types in GaN in order to experimentally determine a value for the spontaneous polarization of GaN.

First, literature reports on the emission energies associated with stacking faults in GaN are briefly reviewed. Then, the presence of stacking faults in the microcrystals under investigation is confirmed in transmission electron micrographs. For stacking fault luminescence from these microcrystals recorded at 10 K, properties such as the linewidth, bundling of stacking faults, as well as the manifestation of the quantum-confined Stark effect in the measurements are discussed. Based on these issues, a careful statistical analysis of the peak energies is compiled to identify emission from individual stacking faults. This analysis confirms literature values for the intrinsic I_1 and I_2 stacking faults and establishes an emission energy related to the extrinsic E stacking faults. The difference in emission energies between the three types of stacking faults is used to derive values for the spontaneous polarization both from a plate capacitor model and from Poisson-Schrödinger calculations of these wurtzite/zincblende heterostructures. The results are then compared to the literature reports based on calculations using density functional theory. Finally, the last part of the chapter turns to thicker zincblende quantum wells: the Poisson-Schrödinger calculations are extended to thicknesses of the zincblende segments beyond those categorized as stacking faults, and room-temperature luminescence spectra from these heterostructures are discussed.

6.1. Stacking faults and their luminescence

Basal plane stacking faults in GaN are a local deviation from the hexagonal wurtzite (WZ) to the cubic zincblende (ZB) crystal structure. For WZ crystals, three main types of stacking faults (SFs) are distinguished, the intrinsic I₁ and I₂ as well as the extrinsic E SFs (cf. Section 2.3.2). These WZ/ZB heterostructures constitute optically active quantum wells as detailed in Section 2.3.3. The first experimental assignment of emission at 3.40–3.42 eV to I₁ SFs was by Albrecht et al.^[222] and Salviati et al.^[223] using PL/CL spectroscopy and TEM. In the meantime, this emission energy is well established after being confirmed by several groups^[82,215,224–226] with a direct correlation of CL and TEM in Ref. 215.

For I₂ SFs, Sun et al.^[68] reported emission at 3.356 eV and Paskova et al.^[69] at 3.355 eV for *M*- respectively *A*-plane GaN with a high density of this type of SFs. A direct correlation between CL and high-resolution TEM was carried out in Ref. 227. However, their value of 3.32 eV is redshifted by 0.02 eV through tensile strain as the excitonic near-band edge (NBE) emission in this region of their sample is also found at 3.45 eV (instead of the strain-free value of 3.47 eV).

Recently, Jacopin et al.^[81] also reported luminescence from thicker ZB segments in GaN nanowires. Note that for GaN, luminescence from the ZB polytype in bulk form has also been reported both from layers^[27] and nanowires,^[75] but this chapter will focus only on ZB segments acting as quantum wells.

Naturally, there is a variety of other luminescence lines of different origin in the spectral range associated with emission from SFs. Notably, concerning extended defects, Liu et al.^[215] found that *A*-plane prismatic stacking faults connecting basal-plane SFs of the I₁ type give rise to luminescence at around 3.33 eV, while partial dislocations terminating the I₁ SFs are related to emission at 3.29 eV. The luminescence at dislocations might be a result of impurity decoration of the dislocation cores.^[215] Similar results were reported by Mei et al.^[228] with an emission energy of 3.30 eV related to *A*-plane prismatic stacking faults. Furthermore, different point defects or sample contamination can lead to luminescence in this spectral range.^[229]

6.1.1. Structural confirmation of the presence of stacking faults

The sample used in this study was obtained by pendeoepitaxial overgrowth of selfinduced GaN nanowires as described in Section 4.1.2. The resulting GaN microcrystals are unique with respect to two important properties: they are free of strain and dislocations^[149] and contain all three types of SFs. The measurements in this chapter were performed on various microcrystals, all from the same sample. To confirm the presence of the SFs, Fig. 6.1 shows TEM images of microcrystals from the investigated sample. The overview in Fig. 6.1(a) illustrates that the formation of the SFs occurs in the region of lateral expansion from a single nanowire to a microcrystal and that the SFs can appear either isolated or in closely spaced "bundles". High-resolution transmission electron micrographs of this transition region are shown in Figs. 6.1(b) and 6.1(c) for two GaN microcrystals. All three types of SFs are observed in these micrographs. The presented images were chosen to also show that the SFs are often separated by only a few layers of WZ GaN. In the next section, the influence of this "bundling" on the emission properties of the SFs will be discussed.



Figure 6.1: Transmission electron micrographs revealing SFs of all three types and the bundling of such SFs with only thin WZ interlayers taken on crystals from the same sample used for the spectroscopic analysis. The bright-field micrograph in (a) shows an overview of the faulted region in a microcrystal. The different types of SFs can be identified in the high-resolution micrographs (b) and (c) which both contain I₁ SFs. In addition, micrograph (b) contains the I₂ and micrograph (c) the E SF. The overlaid ball-and-stick model (note that bright spots correspond to tunneling positions) illustrates the stacking sequence as also indicated explicitly for each SF type. (TEM images recorded by Claudia Roder)

6.1.2. Luminescence signature of stacking faults

Figure 6.2(a) presents a CL spectrum recorded on the crosssection of a GaN microcrystal. At high energies, emission from bound (D^0,X) and free (FX) excitons is observed at the positions expected for strain-free GaN. The spectrum is dominated by several lines at lower energies. Figures 6.2(b) and 6.2(c) show a cross section of this crystal, superimposed with monochromatic CL images acquired at different emission energies. These images show that the near-band edge luminescence originates from the upper part of the microcrystal. Additional and spatially highly localized transitions corresponding to the peaks at lower energies seen in the spectrum are observed within the spatial region of lateral expansion from a single nanowire to a microcrystal, where SFs were seen in the TEM images. All these low-energy lines appear as stripes running along the basal plane indicating their common origin [see also Fig. B.1(b) in Appendix B]. This spatial distribution of the luminescence intensity together with the wide spectral range across which such features can be observed rule out origins (e.g. point defects) other than the luminescence associated with zincblende quantum wells in wurtzite GaN. The broadening along the *c*-axis demonstrates the limit of the spatial resolution of the CL images resulting from the scattering volume of the electron beam and the diffusion of carriers to the SF quantum wells. Note that the narrowest peak in the CL spectrum corresponds to a single feature in the CL images, while for the wider peaks several positions show luminescence at these energies.

To begin with a closer analysis of the SF-related emission, normalized CL spectra of SF peaks recorded at 10 K are shown in Fig. 6.3(a). These were recorded in spot mode at different positions on the cross sections of two microcrystals. The contributions to a single spectrum come only from the SFs or bundles of these which lie within the spatial



Figure 6.2: (a) CL spectrum integrated over the cross section of an individual GaN microcrystal. (D⁰,X) and FX are at the position of strain-free material, while individual SFs and SF bundles emerge as additional lines. The emission corresponding to the I₁, I₂ and presumably the E SF is indicated. The remaining two lines are attributed to bundles of SFs. (b) and (c) False-color monochromatic CL maps of this microcrystal superimposed on the corresponding cross-sectional scanning electron micrograph with the detected energies denoted in the respective colors. The CL related to SFs shows a characteristic elongation along the basal plane.

resolution of the CL measurement. The linewidth (full width at half maximum) of these peaks is in the range of 20–25 meV, in accordance with previous measurements of the I_1 SF employing CL spectroscopy.^[85] For CL spectra, the linewidth is usually broader than in µPL measurements, possibly related to the high excitation intensity induced by the focused electron beam. Therefore, the low-excitation μ PL spectra recorded at 10 K on five microcrystals—detached from the sample and dispersed upside-down [cf. inset to Fig. 4.2] on a Si carrier—are displayed in Fig. 6.3(b). Each of the microcrystals contains several SFs of different types, bundles of these or even thicker cubic segments. The exact peak position varies. This variation in emission energy is attributed mainly to the formation of bundles of SFs exhibiting a random distribution of distances. The "bundling" of SFs will modify the transition energy associated with a specific SF arrangement. For larger spatial separations, the electric fields within the aggregate of SFs will be redistributed such as to blueshift the transitions with respect to an isolated SF,^[230] while a small separation will lead to a coupling of the associated electronic states, resulting in a redshift of the transitions.^[82] Hence, the random separation of SFs of different types as observed in Fig. 6.1 leads to a (potentially) continuous distribution of the transition energies, explaining the multiple peaks observed in Fig. 6.3. The transition energy of isolated SFs is, in contrast, well-defined and is thus expected to dominate statistically.

Not all spectra from microcrystals displayed in Fig. 6.3(b) show a contribution from the NBE luminescence in WZ GaN, which demonstrates the effective capture of carriers by the SF quantum wells. Where observed, the NBE emission is always found at its strain free position. Figure 6.3(b) further demonstrates that a linewidth down to 2 meV can be observed in low excitation μ PL spectra for individual emission lines, which is close to the spectral resolution of 1 meV for the used spectrometer settings. Note that the linewidth obtained for the donor-bound exciton in the microcrystals investigated here amounts



Figure 6.3: (a) Normalized CL spectra of SF emission extracted from spectral line scans (cf. Figs. 6.4 and B.1) on GaN microcrystals. Contributions from more than one SF or bundle in a single spectrum are due to carrier diffusion. The minimum linewidth observable in CL is 20 meV. (b) Normalized low-excitation μPL spectra of different individual microcrystals containing several SFs each. Peaks group around 3.42, 3.35 and 3.29 eV, but can be found also at intermediate energies. The linewidth of individual emission lines can be as low as 2 meV.



Figure 6.4: CL spectral line scan acquired on the cross section of a microcrystal along the arrow indicated in the scanning electron micrograph to the right. For each position along this line, a spectrum is recorded, which is displayed in the spectral line scan with its intensity color-coded as a heat map on a logarithmic scale. Note that the energy is blue-shifted by ΔE (26 meV for the marked case) due to a screening of the polarization field, when the electron beam approaches the SFs.



Figure 6.5: (a) Comparison of CL spectra recorded with the electron beam away from (noisy) and directly on the ZB segments (smooth). The peaks are blueshifted by a partial screening of the spontaneous polarization field under the increasing excitation. Note that the FWHM and shape of the peaks are not affected by the screening process. (b) Arrow plot of the maximum blueshift of the peaks due to screening of the polarization fields observed in the CL maps marked at the respective (unscreened) emission energies which increases from 3 meV at 3.42 eV to 88 meV at 3.09 eV.

to 1 meV.^[149] For an ideal quantum well, a similar linewidth should be obtained, but slightly broader peaks are observed. In another study, Jacopin et al.^[81] even measured a linewidth down to 0.8 meV for ZB/WZ quantum wells in nanowires. These small linewidths suggest that the coupling between SFs and donors in their vicinity is less pronounced than predicted by Corfdir et al.^[87] A possible reason is that the calculations in Ref. 87 neglect the influence of the spontaneous polarization fields.

6.1.3. Quantum-confined Stark effect and screening of the polarization fields

Prior to compiling a statistics of the emission energies related to SFs, it is crucial to ensure that the internal electrostatic fields we are intending to determine in Section 6.2 are not screened due to high excitation densities. The CL spectral line scan presented in Fig. 6.4 shows that screening may indeed occur: the crescent-shaped features reflect that the transition energy is lowest with the electron beam far off the SFs, but steadily increases with the electron beam closing in. The maximum blueshift is observed with the electron beam situated directly on the SF. The origin of this behavior is the increase in carrier density with increasing proximity of the electron beam due to diffusion and eventually direct excitation. This increased carrier density leads to a partial screening of the polarization fields in the SF quantum wells. Therefore, the observed shift in emission energy with excitation intensity is direct evidence for the quantum-confined Stark effect (QCSE). A similar shift for SF emission has been reported in Refs. 81 and 226 and is also known for stacking faults in SiC.^[231] The screening can only be partial, as it is accompanied by an increase in overlap of the electron and hole wavefunctions and thus a reduction of the radiative lifetimes. As a consequence, the screening of the polarization fields will saturate at a certain point. Figure 6.5(a) exemplifies a comparison of the unscreened and partially screened spectra for two emission peaks related to ZB quantum wells. The normalized spectra are rigidly blueshifted under the increased excitation, i.e. the FWHM of the peaks is not affected, and the symmetric profile is upheld. This property rules out state filling effects as an alternative origin of the blueshift. In Fig. 6.5(b), a compilation of the



Figure 6.6: Histogram compiled of peak energies from low-excitation μPL and of the lowest (unscreened) energies in CL (excluding phonon replica). The Gaussian fit further illustrates the energies around which the peaks assigned to the different SF types are grouped.

maximum shifts in energy observed as a result of the screening is given. The shifts are marked at the unscreened (onset) energy of the respective peaks in the CL spectral maps. As expected, the blueshift achieved as a result of the screening of the fields increases with the ZB thickness. The blueshift of about 45 meV observed for the peaks around 3.29 eV amounts to a screening of a fifth of the polarization fields according to the calculations presented later in this chapter.

Further evidence for the QCSE is given by the wide spectral range spanned by the observed emission peaks related to ZB segments: The lowest observed emission energies are 3.16 eV in Fig. 6.3(b) and an unscreened emission energy of 3.0 eV in the CL spectral line scan in Fig. B.2 in the appendix. Neglecting the aforementioned evidence for the polarization fields and assuming flatband conditions, the lowest emission energy observable for a ZB quantum well in a WZ matrix with type-I band alignment would be that of an exciton in the ZB phase, i.e. 3.276 eV.^[27,75] For a type-II band alignment, the conduction band offset ΔE_C between the ZB and WZ phase determines the maximum redshift with respect to the excitonic emission in WZ GaN. Even with the largest theoretical value for ΔE_C reported in the literature,^[65] a type-II band alignment leads to an emission energy of 3.2 eV, which is well above the observed energies.

Early models for the emission of excitons at SFs,^[76] but also more recent calculations^[84,87] and experimental studies^[227] have neglected the role of the spontaneous polarization fields. For the I₁ SFs, it might be possible to thus obtain a satisfactory agreement between calculations of the quantum well energies and experimentally observed emission energies. However, this approach fails as soon as the other types of SFs or thicker ZB segments are taken into account. In fact, as this chapter will show in the following, the emission energy is governed by the spontaneous polarization fields.

6.1.4. Statistical analysis of the emission related to stacking faults

After discussing factors which can shift the emission energy related to excitons at SFs, it is now possible to compile a statistics of these energies. To rule out excitation-induced shifts, exclusively (i) low-excitation μ PL spectra such as those depicted in Fig. 6.3(b) as

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Figure 6.7: (a) Microscopic electrostatic potential V_{es} for the E SF calculated by DFT. From the envelope of the potential, estimates can be given for the thickness (3.7 bilayers) and $\Delta V_{ESF} = 0.21$ eV resulting from the polarization field. (b) Transition energies for all three SF types from the Poisson-Schrödinger calculations with varied P_{sp} and for two different conduction band offsets ΔE_C corresponding to a type-I (red squares) and a type-II (purple stars) alignment. The vertical lines denote the values of P_{sp} for which the spectroscopically observed *differences* in the transition energy between the SF types are reproduced best; the *absolute* emission energies from experiment (including error bars) are shaded in gray for comparison. (DFT calculation by Abderrezak Belabbes, Universität Jena)

well as (ii) the low-energy onsets obtained for each of the transitions in CL spectral line scans are used. Figure 6.6 shows a histogram of SF-related emission energies compiled from spectra and spectral line scans recorded on several dozen microcrystals. The energies associated with the isolated SFs emerge in this statistical analysis of the peak energies: three peaks can be observed at 3.42 ± 0.01 , 3.35 ± 0.01 and (3.29 ± 0.015) eV.^a In order of appearance, these peaks are associated with the I₁, I₂ and E SF, respectively, as expected from the thickness of the SFs (ZB segments) increasing in this order. While this confirms the above mentioned literature reports on the emission associated with the I₁ and I₂ SFs, this is the first time that luminescence around 3.29 eV can be clearly attributed to excitons bound to E SFs.

6.2. Determination of the spontaneous polarization

Taking the coherent set of experimentally determined emission energies for all three types of SFs, it is now possible to derive the spontaneous polarization as proposed in Section 2.3.4. As sketched in Fig. 2.7, the crucial point in this analysis is that differences in the emission energies rather than their absolute values are employed. The difference in thickness between each of the SFs is a single (111) bilayer (or molecular monolayer) of ZB GaN, i. e., $\Delta d = 0.259$ nm. The differences in the emission energies are $\Delta E_{I_1 \rightarrow I_2} = (70 \pm 15)$ meV and $\Delta E_{I_2 \rightarrow E} = (60 \pm 18)$ meV; thus the mean energy difference for adding a bilayer to the quantum well is $\overline{\Delta E} = (65 \pm 23)$ meV. Now let us assume that the spontaneous polarization is sufficiently strong so that the single particle energies (relative to the respective

^aApart from the bundling of SFs, the error margins may contain additional effects such as localization of electrons by donors in the vicinity of the SFs.^[87]

band) are governed by the triangular potential and thus remain basically the same for all SFs, while the change in confinement remains negligible. In this case, the polarization sheet charges at the interface between the ZB and WZ modifications essentially represent a plate capacitor, for which the addition of a slab of dielectric of the width Δd results in the potential difference $\Delta V = \overline{\Delta E}$. From these elementary considerations, we can directly calculate the polarization sheet charge density using Eq. (2.8):

$$\sigma = |P_{\rm sp}| = \frac{\Delta V \epsilon \epsilon_0}{\Delta d} = (0.021 \pm 0.007) \,\mathrm{C/m^2},\tag{6.1}$$

where $\epsilon = 9.5$ is the static dielectric constant for GaN and ϵ_0 is the permittivity of free space. Note that the corresponding electric field within the SF amounts to 2.5 MV/cm.

The same argument also applies to the microscopic electrostatic potential calculated by density functional theory and depicted in Fig. 6.7(a) for the E SF (DFT calculation by Abderrezak Belabbes, for details see Ref. 79). Tracing the triangular envelope of the potential in one supercell [cf. Fig. 6.7(a)], an energy difference $\Delta V_{\text{ESF}} = 0.21$ eV for a thickness of $d_{\text{ESF}} = 0.96$ nm or 3.7 bilayers can be estimated. Using Eq. (6.1) this yields a value of $P_{\text{sp}} = -0.018 \text{ C/m}^2$.

To confirm the validity of the assumption inherent in the plate capacitor model used above, self-consistent Poisson-Schrödinger calculations^[209] for the quantum wells formed by the I₁, I₂ and E SFs are performed (see Appendix D for the applied material parameters). In light of the ambiguity in defining the stacking fault thickness discussed in Section 2.3.3, the effective electronic thickness of the E SF is set to 3.7 bilayers as motivated from the DFT results displayed in Fig. 6.7(a). The thickness of the I₂ and I₁ SF is then taken to be 2.7 and 1.7 bilayers, respectively, in accordance with their differences in structural thickness. In order to examine to which extent the transition energy depends on the respective band offsets, two extremes suggested in the literature are considered, namely, $\Delta E_C = 0.27 \text{ eV}^{[65]}$ and $\Delta E_C = 0.15 \text{ eV}^{[79]}$ resulting in a type-II and a type-I band alignment, respectively. The chosen values for the band gaps contain a correction for the excitonic nature of the transition.^b A value of $N_d = 5 \times 10^{16} \text{ cm}^{-3}$ was taken as the residual donor density in our samples.^c

Next, we varied $P_{\rm sp}$ across the range of values found in the literature (cf. Tab. 6.1) for both band alignments. The resulting transition energies for all three SF types are shown in Fig. 6.7(b). Evidently, the limiting values either under- or overestimate the differences in transition energies. The observed $\Delta E = (65 \pm 23)$ meV is best reproduced for $P_{\rm sp} = -(0.023 \pm 0.007)$ C/m² in the case of a type-I band alignment and for $P_{\rm sp} = -(0.022 \pm 0.007)$ C/m² in the case of a type-II band alignment. The fact that both band alignments result in essentially the same value for $P_{\rm sp}$ signify that the assumption made in our initial analysis is valid: the influence of confinement is indeed small compared to

^bThe exciton binding energy was taken to be equal to the wurtzite bulk value (26 meV) for all SF types. This assumption is justified since both the impact of confinement and the internal electrostatic field (enhancing and lowering the binding energy, respectively) are weak primarily due to the fact that the SF thickness is well below the excitonic Bohr radius with the exciton wavefunction largely extending into the wurtzite matrix. Furthermore, these two effects counteract each other, and both become stronger with increasing SF thickness. We thus expect little change of the exciton binding energy for the three types of SFs. This has recently been corroborated by calculations of the exciton binding energy for ZB/WZ quantum wells of different thickness.^[84]

^cThis value is an upper limit of the O concentration in the samples from our institute as measured by secondary ion-mass spectrometry. Independent optical studies of our samples arrive at even lower values.^[232]

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Method	$P_{\rm sp}~({\rm C}/{\rm m}^2)$
DFT (Berry phase) ^[36,37]	-0.029, -0.034
DFT (electrostatic) ^[234]	0.074
DFT (electrostatic/Berry phase) ^[32,79]	-0.014, -0.018
Bond-orbital model ^[235]	-0.029
Thermodynamics ^[221]	-0.022
This work (plate capacitor)	-0.021 ± 0.007
This work (EM, type-I)	-0.023 ± 0.007
This work (EM, type-II)	-0.022 ± 0.007

Table 6.1: Values for the spontaneous polarization P_{sp} derived from theory and experiment.EM stands for effective mass and denotes the self-consistent Poisson-Schrödinger
calculations.

that of the electric fields, and the stacking faults essentially behave as plate capacitors. For an example of the band profile, the ground states, their wavefunctions and the resulting transition energy for the E SF assuming a type-I band alignment see Fig. 6.8(a).^d

6.2.1. Comparison to values reported in the literature

All values for the spontaneous polarization of GaN obtained in this work and those available in the literature are summarized in Tab. 6.1. Considering the uncertainty of the former, we recommend $P_{\rm sp} = -(0.022 \pm 0.007) \text{ C/m}^2$. This value agrees exactly (probably fortuitously) with the only other experimental estimation of $P_{\rm sp}$ as reported by Yan et al.^[221] from a thermodynamic approach.

Concerning the theoretical calculations of $P_{\rm sp}$ using DFT, the standard value used in the literature is that given by Bernardini et al.^[36] who corrected his values a few years later.^[37] These values were calculated using the Berry phase approach.^[33] Another early report of DFT calculations for the group-III nitrides using the electrostatic method^[236] was given by Bechstedt et al.^[234] and largely overestimated $P_{\rm sp}$ as a result of using far too large values for (u - 3/8), i.e. the deviation of the internal parameter u from its ideal value. A very recent study by Belabbes et al.^[32] compares the two computational methods and a point-charge-model of the spontaneous polarization (cf. Appendix C). With the functionals used in this study, the resulting values for $P_{\rm sp}$ are smaller than the earlier reports. The value of $P_{\rm sp} = -0.018 \text{ C/m}^2$ calculated for GaN using the electrostatic method is in fair agreement with the experimental value determined in this work. Therefore, the set of spontaneous polarizations of the group-III nitrides from the latter computation can be considered to be the most accurate one available. In fact, Belabbes et al.^[32] have extended their calculations to all III-V semiconductors.

^dNote that the small electric field in the barriers is a consequence of the low donor concentration and the large separation of SFs chosen in the calculation to exclude proximity effects. At these low doping densities, charge redistribution and Fermi level pinning did not noticeably affect the calculations, even for SFs close to the surface in accordance with analogous calculations for (In,Ga)N/GaN quantum wells.^[233]



Figure 6.8: (a) Exemplary band profiles for the E SF and a ZB segment which is 5 bilayers thicker in a WZ matrix calculated in the effective mass approximation. A type-I band profile is assumed in the two cases. The first electron and hole states and their wavefunctions are displayed. The vertical arrows indicate the resulting transition energies. (b) Transition energies related to cubic (ZB) quantum wells of different thicknesses. As in Fig. 6.7(b), two different band alignments have been assumed. Over the displayed range, the overlap of the electron and hole wavefunctions is reduced by one order of magnitude.

6.3. Luminescence associated with thicker ZB segments

In the first part of this chapter, the focus was on the luminescence from the I_1 , I_2 and E stacking faults. These SFs are the three thinnest possible zincblende quantum wells in a wurtzite semiconductor. As mentioned in the discussion on the QCSE, thicker ZB segments can lead to emission at energies below the zincblende NBE emission at 3.27 eV. The histogram in Fig. 6.6 evidences emission energies down to 3 eV. However, apart from the SFs, the histogram does not permit the identification of emission energies associated with quantum wells of a specific thickness.

6.3.1. Calculation of the emission energies

When the thickness of the ZB segments is increased above that of the extrinsic SFs, the QCSE leads to a further redshift of the emission. Taking the polarization fields of 2.5 MV/cm (0.022 C/m²) determined above, the Poisson-Schrödinger calculations are extended for cubic segments up to a thickness of 3 nm. Again, a type-I alignment of the valence bands is compared with a type-II alignment, and the excitonic transition energies of the ZB and WZ phase have been used in place of the real band gap to account for the exciton binding energy. The results are presented in Fig. 6.8. The band diagram of two exemplary ZB quantum wells-the E SF and a thicker segment-are shown in Fig. 6.8(a), while the evolution of the emission energy with ZB thickness is given in Fig. 6.8(b). As above, a negligible change in excitonic binding energy is assumed, which is reasonable as the change should be less than 5 meV across the displayed thickness range according to calculations in Ref. 84. Note that our calculated transition energies agree with those of Ref. 84 when taking into account the polarization fields and our definition of an effective electronic thickness of the SF quantum wells. The different band alignments lead to a relatively small difference in absolute energies that increases slightly with increasing ZB thickness (from 10 to about 35 meV). Across the thickness range displayed in Fig. 6.8(b),

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Figure 6.9: (a) Normalized room-temperature CL spectra recorded with spot mode excitation on GaN microcrystals also show SF-related emission. The indicated emission energies assume that both the band edge and the SF emission are shifted by 70 meV from their low-temperature values. (b) Monochromatic false-color CL images for two microcrystals recorded at the specified energies superimposed on the corresponding SEM images. The spatial distribution of the emission along the basal plane can be resolved at room temperature for thicker ZB segments.

the wavefunction overlap of the electron and hole decreases by one order of magnitude. Our lowest observed emission at 3.0 eV would correspond to an effective electronic thickness of the ZB segment of 8.7 bilayers, i.e. five bilayers more than the E SF.

Another interesting feature in Fig. 6.4 and the two additional line scans given in Appendix B concerns the peak intensities. From the continuous reduction of the wavefunction overlap with increasing ZB thickness (further separation of electrons and holes), one would expect the emission intensity to continuously decrease from the I₁ SF onwards. Instead, the peak intensities are strongest for intermediate energies (e.g. at 3.28 eV in the case of Fig. B.1) and lower both for the thinnest SFs as well as for thicker cubic segments. When looking at the band profiles displayed in Fig. 6.8(a), it becomes clear that the confinement provided by the triangular potential in the conduction and valence band as well as the capture efficiency of the quantum wells increases with the thickness of the ZB segment. Therefore, carriers will be localized more efficiently with increasing ZB thickness. This trend is opposite to that of the wavefunction overlap, and the superposition of both trends can explain the observed development of the peak intensities.

6.3.2. Luminescence of ZB segments at room temperature

Only few reports include measurements of the emission related to SFs at elevated sample temperatures.^[82,83,223,225] These reports concentrate on the I₁ SFs and tend to see a quenching of this emission with increasing temperature. However, the temperature dependent measurements in Refs. 83 and 223 indicate that the peak might indeed be shifted together with the NBE luminescence, and as a result of the thermal broadening of the latter, ends up as a mere shoulder of this emission at room temperature.

Also for the microcrystals investigated in this chapter, room-temperature luminescence at energies both between the WZ and ZB band gaps as well as below that of the ZB phase can be observed in the CL spectra in Fig. 6.9(a) with peaks in the range between 2.9 and 3.4 eV. Again, spot mode CL measurements provide a way to selectively excite these

WZ/ZB quantum wells. However, the peak broadening at elevated temperatures hinders the identification of a peak shift related to the screening of polarization fields as seen at low temperatures. Therefore, it is not possible to compile a peak histogram of emission energies and thus to identify the energies related to specific SF types. Assuming that the SF emission shifts by a similar degree as the NBE luminescence when going from 10 to 300 K (-70 meV), emission energies of 3.35, 3.28 and 3.22 eV can be expected for the I₁, I₂ and E SFs, respectively. These energies are marked in Fig. 6.9(a) by grey dashed lines, while the NBE emission energies of ZB and WZ GaN at 300 K are marked by dot-dashed lines. Note that in fact two of the peaks in Fig. 6.9(a) coincide with the emission energy of ZB GaN, which could point to the presence of bulk-like (thick) segments of ZB GaN.

This discussion highlights the advantage of the spatially resolved spectral measurements: While it is possible to identify the ZB segments in spot mode CL spectra, the identification is more difficult in spectra integrated over a larger area^[83,223] or in maps of the monochromatic CL intensities (CL images). The identification in CL images of the microcrystals was only possible for thicker ZB segments, e.g. for emission energies around 3.16 and 3.04 eV as displayed in Fig. 6.9(b). This result indicates a less efficient capture of carriers by the SF quantum wells compared with low temperatures, but is in part also due to the increased linewidth and the more pronounced LO phonon replicas at elevated temperatures. Therefore, for spatially integrated luminescence spectra, the emission related to SFs might easily be merged into a shoulder of the WZ peak, making it hard to identify these peaks and to distinguish them from the phonon replicas. Furthermore, in CL images, detection windows centered on the SF emission energies will also contain an additional signal from the phonon replicas of WZ GaN making a distinction impossible.

6.4. Conclusions

Since the first identification of luminescence attributed to I₁ stacking faults,^[76,222,223] a quite comprehensive picture on the emission related to stacking faults and zincblende segments in GaN has emerged. Stacking faults in wurtzite semiconductors act as quantum wells which collect charge carriers from the surrounding crystal in a very efficient way. Therefore, luminescence spectroscopy offers a sensitive way to assess the presence of stacking faults in GaN layers without the need for TEM investigations.^[237] For high SF densities, the associated luminescence will even dominate the optical emission at low temperatures.^[82,215]

Particularly, this chapter has shown that the coalescence overgrowth of nanowires is accompanied by the formation of SFs during the lateral growth and that the luminescence associated with these SFs exhibits a quite distinct distribution along the basal plane in monochromatic CL images. Consequently, it is likely that so far not clearly identified emission observed in similar structures is also related to SFs or cubic segments. Notably, emission at 3.4 eV was observed in Ref. 238 and related to the N polarity of the sample, emission at 3.32 and 3.42 eV in Ref. 239 was attributed to the Y2 and Y6 defect peaks,^[229] and room-temperature luminescence at 3.19 eV in Ref. 240 was attributed to the donoracceptor pair transition. Also, the emission at 3.4–3.42 eV related to defects close to the nanowire substrate interface in Ref. 241 is likely related to I₁ SFs. Emission around 3.35 and 3.29 eV without clearly identified origin is quite commonly observed also in other samples, some of which are known to contain SFs.^[82,216,218,242,243] However, a distinction from other structural defects, such as prismatic stacking faults, will not always be possible without additional structural characterization.

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By µPL at low excitation densities, it was confirmed that luminescence from individual SFs can indeed give rise to narrow emission lines with a linewidth down to 2 meV. Furthermore, our results emphasize the role of the spontaneous polarization fields for the emission energy of ZB segments in WZ GaN. This role is evidenced both by the wide emission range covered by such ZB segments spanning down to energies well below that of the NBE emission in ZB GaN and by the blueshift of the emission energy arising from the partial screening of the polarization fields achieved under high excitation. In fact, the comparison of Poisson-Schrödinger calculations for two completely different valence band alignments shows that the emission energy of excitons at the SFs is governed primarily by P_{sp} . Thereby, the sheet charge densities equivalent to the absolute value of P_{sp} can be determined through a parameter-free plate capacitor model. From the comparison of this model and the Poisson-Schrödinger calculations, an experimental value for the spontaneous polarization of WZ GaN of -0.022 C/m^2 is obtained. This experimental value for P_{sp} agrees fairly well with the most recent DFT calculations by Belabbes et al.^[32]

The calculations of the emission energies related to SFs were further extended to ZB segments of up to 3 nm thickness. At room temperature, the efficiency of the carrier localization at the SFs is reduced, but the related emission can still be observed. CL spectra under local excitation indicate that the emission energy of the SFs is shifted by a similar degree as that of the NBE emission. For thicker ZB segments, the CL distribution along the basal plane could be imaged also at 300 K.

The core point of this chapter is that the spectroscopic fingerprint of stacking faults in GaN allows for the determination of the strength of the spontaneous polarization in an inherently parameter-free way. This approach may also be used to determine the spontaneous polarization for other important wurtzite materials such as ZnO.

Polarization fields and carrier localization in (In,Ga)N/GaN nanowires

When going from polytypic heterostructures to those including other elements, e.g. the ternary alloy (In,Ga)N, the picture becomes more complicated. Strain and the resulting piezoelectric polarization as well as compositional fluctuations affect the emission properties. These effects have been intensely studied for planar quantum well structures used for optoelectronic applications.^[117,126,244] To overcome some of these drawbacks, the integration of (In,Ga)N insertions into GaN nanowires has received a significant amount of attention in recent years. Considering only the studies employing molecular beam epitaxy, more than half a dozen groups have already reported the growth of (In,Ga)N insertions (axial heterostructures) in nanowires.^[8,245–254] Some of these studies report an absence of the quantum-confined Stark effect,^[14,249–251] thus concluding that the internal piezoelectric fields in the (In,Ga)N insertions are "not significant".^[14,250,251] The efficient strain relaxation in the nanowire geometry is suggested as a possible origin for such a drastic reduction in the piezoelectric polarization.^[14,250] At the same time, it was shown that localization centers play a role in the luminescence of nanowire heterostructures,^[14] like they do for planar quantum wells.^[126]

As already pointed out in Chapter 5, the emission from a nanowire ensemble represents a superposition of spectra from single nanowires. To truly understand the origin of the observed luminescence, it is necessary to examine the emission of individual nanowires. Only few reports of such measurements for (In,Ga)N insertions in GaN nanowires have been presented so far.^[13,14]

In the current chapter, cathodoluminescence and micro-photoluminescence measurements on single GaN nanowires with embedded (In,Ga)N insertions are combined with time-resolved photoluminescence measurements on the ensemble to learn more about the mechanisms governing the luminescence of these heterostructures. Conclusive evidence is presented that, in addition to localization phenomena, polarization fields still play an important role in these (In,Ga)N/GaN nanowire heterostructures.

Two sets of samples will be discussed: (*A*) a sample where six (In,Ga)N insertions with a thickness of about 3 nm are separated by 7 nm *wide* GaN barriers (Section 7.1), and (*B*) a sample where two (In,Ga)N insertions of about 11 nm thickness are separated by an only 2–3 nm *thin* GaN barrier (Section 7.2).

7.1. (In,Ga)N insertions separated by wide barriers

In the first part of this chapter, a sample (*A*) of nanowires containing six (In,Ga)N insertions is studied. Their composition and dimensions can be assessed from the superlattice fringes of the stack of (In,Ga)N insertions in XRD profiles, ^[255–257] which yields 3 ± 2 nm for the thickness of the (In,Ga)N insertions and 7 ± 2 nm for the thickness of the GaN barriers. Their average In content is $x = 0.26 \pm 0.1$. Note that these are ensemble averages, and the large error margins reflect the statistical distribution of dimensions and



Figure 7.1: (a) CL spectra recorded in top-view geometry at 300 K and 10 K on nanowire ensemble *A* with larger barriers and six (In,Ga)N insertions. (b) Cross-sectional false-color CL images of the (In,Ga)N luminescence of the same sample recorded at 300 K superimposed on the corresponding SEM image. Two spectral windows centered at 2.2 eV (green) and 2.5 eV (red) are shown. The emission at both energies overlaps leading to the yellow color. For the CL images, a wide spectral bandpass of 50 nm (\approx 200 meV) was selected to accomodate the rather wide band. It is evident that carriers diffusing to the insertions recombine at lower energies whereby the emission at higher energies seems to originate from a spatially more confined region.

composition between different nanowires of the nanowire ensemble. TEM reveals that the insertions are laterally embedded in a GaN shell and further confirms that the barriers are indeed significantly wider than the insertions.^[257] The specific sample was selected for the detailed analysis using luminescence spectroscopy by virtue of its high luminescence yield.

With device applications in mind, the room-temperature luminescence of the nanowire ensemble is of interest. A comparison of the CL spectra from this nanowire ensemble measured at temperatures of 300 and 10 K is given in Fig. 7.1(a). The area scanned by the electron beam of 360 μ m² includes around 20 000 nanowires. Both the emission from the GaN nanowires and the (In,Ga)N insertions are visible. The latter is centered in the green spectral region at 2.24 eV for 300 K and at 2.25 eV for 10 K. The full widths at half maximum (FWHM) are 340 meV and 380 meV, respectively. Hereafter, this emission is referred to as the (In,Ga)N band. The rather large FWHM compares well with literature reports of PL or EL from other MBE grown (In,Ga)N insertions in GaN nanowires, the reported central energies in these studies spanning the range of 1.9-2.8 eV (roughly corresponding to wavelengths of 450–650 nm).^[8,245–254] The spectrum at 10 K shows an additional contribution around 2.8 eV that will be discussed in Section 7.1.3. The GaN luminescence originates from the excitonic near-band edge (NBE) emission, but includes an additional contribution from the donor-acceptor pair (DAP) transition for the measurement at 10 K. Figure 7.1(b) shows room-temperature CL images of the (In,Ga)N band superimposed on the corresponding cross-sectional SEM image. They were recorded in spectral windows around the center (2.2 eV) and the high-energy side (2.5 eV) of the (In,Ga)N band. These images already confirm that the luminescence indeed comes from the area where the (In,Ga)N insertions are located. At the lower of the two energies, the signal originates from a larger area. While carriers diffusing to the insertions tend to recombine at the lowest available energy states or potential minima, a direct excitation of the insertions can lead to recombination at higher energies. Probably, the latter is due to a filling of

the lowest states under the high excitation. As a consequence, the spatial resolution in the images is actually enhanced when detecting on the high energy side of the (In,Ga)N band.

As in the previous chapters, the advantages of CL come into effect most prominently when looking at spectral mappings of individual nanowires. For the nanowires with (In,Ga)N insertions, the spectral resolution combined with the spatial resolution along the nanowire axis allows for the identification of several interesting effects. They will be discussed first with a focus on the near-band edge and defect-related emission and subsequently for the luminescence of the (In,Ga)N insertions. For each displayed CL line scan, several spectra extracted from the positions marked in the respective colors are displayed above the color maps to highlight spectral features.

7.1.1. Influence of defects on the luminescence of the nanowires

It is a common notion to talk of "defect-free" nanowires. Indeed, dislocation densities are significantly reduced compared to planar heteroepitaxy,^[189,258] and also the emission related to native point defects might be less significant.^[9,259] However, already the coalescence of neighboring nanowires in dense arrays might introduce stacking faults and dislocations.^[260] Furthermore, reduced growth temperatures are required for the incorporation of In. This change may increase the point defect density and can facilitate the nucleation of zincblende (ZB) segments.^[75,81] The manifestation in the luminescence spectra of both intrinsic and extrinsic point defects as well as ZB segments will be presented in the following paragraphs.

Luminescence related to zincblende segments

The luminescence associated with stacking faults and zincblende segments in GaN was already discussed in detail in Chapter 6. However, it can also play a role for nanowires containing (In,Ga)N insertions as can be seen in Fig. 7.2(a) for measurements at room temperature and in Fig. 7.2(b) for 10 K. The peak at 3.05 eV in Fig. 7.2(a) originates from a region just below the (In,Ga)N insertions. For sample *A*, only some individual nanowires exhibit this spectral feature, while for other samples containing (In,Ga)N insertions even the ensemble spectra at room temperature show a prominent peak around 3 eV.^[257]

At 10 K, the contribution from ZB segments should be more pronounced. However, when looking at spectra integrated over one or more nanowires, it can be masked by the band formed by the DAP emission of GaN at 3.27 eV and its phonon replicas [cf. Fig. 7.1(a)]. The CL line scan in Fig. 7.2(b) shows that under local excitation the emission from zincblende GaN segments stands out quite clearly against the DAP luminescence. For the depicted nanowire, several ZB contributions in the range between 3.3–3.0 eV are observed, which corresponds to ZB thicknesses of 1-2 nm (4-8 bilayers) according to Fig. 6.8. The emission is spectrally shifted, and its intensity is stronger in comparison to the DAP band. The positions of these peaks along the nanowire indicate that the ZB segments are located both below and between the (In,Ga)N insertions. In contrast to the measurements in Section 6.1.3, the background provided by the DAP prevents the observation of a peak shift related to a screening of the polarization fields in the ZB segments under direct excitation in CL. However, the actual excitation density might also be lower because the excited carriers are distributed among the (In,Ga)N insertions, ZB segments and DAP transition, and further non-radiative recombination might play a different role than for the GaN microcrystals.



Figure 7.2: CL spectral line scans collected at (a) 300 K and (b) 10 K on single nanowires from sample *A* with the intensity plotted with heat map coloring on a logarithmic scale. The SEM images of the nanowires are set beside the line scans. Several spectra extracted from the line scans at the positions marked by colored arrows are plotted above. The line scans highlight that the reduced substrate temperature necessary for the growth of the (In,Ga)N insertions also results in the formation of ZB segments.

The formation of such ZB segments is related to the reduced substrate temperature during the growth of the (In,Ga)N and the GaN barriers, which is necessary to avoid In desorption. Hence, also the probability for the nucleation of the ZB phase of GaN is increased. The presence of the ZB polytype has been confirmed for similar samples both in reflection high-energy electron diffraction during the growth of GaN segments in nanowire-based heterostructures^[257] and in a post-growth TEM study.^[261] Other groups have likewise investigated the luminescence properties of zincblende GaN^[75] or segments of this polytype^[81] in GaN nanowires. In contrast, a few reports attribute luminescence in the range above 3 eV to (In,Ga)N insertions.^[262–264] This attribution contradicts the general trend that the luminescence is well below 3 eV for such MBE grown insertions in nanowires.^[8,245–254] Even studies dedicated to a variation of the emission energy do not get beyond 2.8 eV.^[8,250,255] The detailed characteristics presented in the reports with luminescence above 3 eV suggest that luminescence from the DAP transition^[262] and from ZB segments^[263,264] was probably misinterpreted as (In,Ga)N emission. This controversy, together with the discussion on yellow defect luminescence in the next paragraph, highlights the power of CL spectral line scans (or maps) to disentangle the contributions from point defects and quantum wells-be it intended (In,Ga)N insertions or unintentional ZB segments. This question could be addressed neither by spectra integrated over a larger area nor by monochromatic CL images where one spatial, respectively spectral, dimension is lacking.

Luminescence related to point defects

The strong contribution from the DAP transition^[229] in low-temperature spectra of sample A has already been mentioned. The DAP luminescence is typical for samples from the used MBE as a result of a Mg memory effect in the growth chamber from experi-



Figure 7.3: CL spectral line scan collected at 300 K on a single nanowires from sample *A* with the intensity plotted as a color map on a logarithmic scale. The SEM image of the nanowire is depicted on the right hand side. Several spectra extracted from the line scan at the positions marked by colored arrows are displayed above. Furthermore, the inset of the spectra shows linear intensity line profiles extracted around 2.2 eV (turquoise circles) and 3.4 eV (pink squares). While the emission at 2.2 eV is constant up to the (In,Ga)N insertions, the NBE luminescence at 3.4 eV is reduced both towards the bottom and the top of the nanowire.

ments including this dopant which acts as an acceptor in intrinsically n-type GaN.^[265] The low-temperature CL measurements in Chapter 6 (e.g. Fig. 6.4) show that this peak is completely absent for samples from a different MBE system.

A common feature of the CL spectral line scans of sample A both at 300 K and 10 K is an emission band between 2.0–2.4 eV that is visible all along the nanowire base (cf. Figs. 7.2, 7.3 and 7.6). Its energy position seems uncorrelated to that of the (In,Ga)N band. The extracted spectra in the top part of Fig. 7.3 show that the emission intensity is about 2 orders of magnitude lower than for the (In,Ga)N band. A line profile of the emission intensity from the spectral map in Fig. 7.3 was extracted at around 2 eV and is displayed as an inset. The spectral position is chosen as far as possible from the center of the (In,Ga)N band to reduce the influence from the latter. The CL intensity remains almost constant until the (In,Ga)N band sets in. Such an emission at slightly lower energies than the main peak could stem from carriers diffusing to the (In,Ga)N insertions, but then a gradual increase of its intensity should be expected. Therefore, it is likely related to the vellow luminescence band which is quite widespread for GaN layers grown by a variety of methods.^[229] It is generally attributed to intrinsic point defects, but their exact nature is under dispute.^[229] A likely candidate is a transition between shallow donors and Ga vacancies acting as deep acceptors.^[266] These results are in contrast to other nanowire samples, for which an absence of this luminescence band in PL measurements was reported and taken as a proof of a low density of native point defects.^[9,259] While the nanowire base was grown at temperatures optimized for GaN, the appearance of the yellow luminescence might depend sensitively on factors such as the detailed growth conditions or defect interactions.



Figure 7.4: (a) Conduction band profile (E_C) and (b) electric field strength across a GaN nanowire having a diameter of 80 nm for different donor concentrations N_d given in units of cm⁻³. For comparison, E_C and the electric field are also plotted for a layer with $N_d = 5 \times 10^{16}$ cm⁻³. The band profiles are obtained from self-consistent Poisson-Schrödinger calculations.^[209]

Luminescence quenching towards the foot of the nanowires

Turning to the NBE emission of GaN at around 3.4 eV in the CL line scan of Fig. 7.3 recorded at room temperature, it is clearly complementary to the emission from the (In,Ga)N insertions which dominates the top part of the nanowires. Thus, there is no significant contribution from the barriers because carriers excited in these will reach the insertions prior to radiative recombination, if they do not recombine non-radiatively. However, towards the foot (bottom) of the nanowires, the intensity of the GaN luminescence is also reduced (compare also Fig. 7.2). This reduction of the luminescence efficiency η_{GaN} is further highlighted by the line profile extracted for the emission at 3.4 eV and again displayed in the inset of the spectra in Fig. 7.3. For the first 280 nm, the intensity of the GaN emission increases continuously. This trend cannot result from CL quenching with time (cf. Section 3.3.4), as the electron beam was scanned from the foot to the top of the nanowires. Because the nanowires were dispersed, non-radiative recombination at the substrate interface can also be ruled out. As detailed in the following, Si indiffusion from the substrate during the growth of the nanowires is a more likely explanation for the reduced GaN luminescence towards the foot of the nanowires. In nanowires, the surface depletion region usually spans the complete cross section.^[19] With a pinned Fermi level, the additional n-type doping would increase the lateral band bending across the nanowire to a degree where excitons are broken up by the electric fields in the lateral direction. Thus, electrons would be confined in the center and holes at the perimeter of the nanowire. Figure 7.4(a) illustrates the development of the band profile in a GaN nanowire with increasing donor concentration when the Fermi level is pinned at about 0.6 eV below the conduction band edge,^[19,160] while Fig. 7.4(b) gives the resulting strength of the electric field. The ionization field for excitons in GaN is around 15 kV/cm for donorbound and 90 kV/cm for free excitons.^[135] Even at typical intrinsic doping densities of $N_d = 5 \times 10^{16}$ cm⁻³, the excitonic NBE luminescence in GaN nanowires will be partially quenched due to a dissociation of excitons in the lateral electric field. The calculations show that a very modest indiffusion of Si can increase these fields to a degree where the luminescence will be quenched completely. The gradual increase in emission intensity is consistent with such a process of Si indiffusion. Also note, that the intensity remains constant along the nanowire base for the luminescence related to point defects, i.e. the



Figure 7.5: Comparison of the CL ensemble spectrum from sample *A* at 10 K with spectra from single nanowires of the same sample, which illustrates that the (In,Ga)N band is the result of a superposition of the emission from individual nanowires.

DAP and the yellow luminescence. The strong binding of holes to the acceptors prevents them from being affected by the depletion process.

7.1.2. Variation of the indium content among insertions in a single nanowire

In the following, the focus will lie on the (In,Ga)N band. From the spectra measured on the ensemble [Fig. 7.1(a)], a rather large FWHM of more than 300 meV was determined. In Fig. 7.5, the low-temperature spectrum of the ensemble is compared with spectra recorded on single dispersed nanowires. The emission energy of the (In,Ga)N band varies from nanowire to nanowire in the range of 2.1–2.4 eV. This scatter in emission energies proves that the (In,Ga)N band of the nanowire ensemble is a superposition of these peaks and shows that it clearly dominates with respect to the yellow luminescence in the same spectral region that does not shift between nanowires. Fluctuations of the insertion dimensions and foremost of the In content between nanowires, evidenced by the large error bars in their assessment by XRD,^[255] explain the observed variation in emission energy. However, the individual bands remain rather broad with a FWHM of 200–300 meV. Some nanowires have an additional contribution between 2.6 and 2.8 eV. Together, these features call for a closer investigation of the (In,Ga)N luminescence of single nanowires in the CL spectral line scans.

Figure 7.6(a) shows another CL line scan recorded at 10 K. Looking at the emission energy in more detail, the three extracted spectra at the top of Fig. 7.6(a) highlight that the peak of the (In,Ga)N band shifts to lower energies along the stack of six insertions. The dimensions of these insertions are at the limit of the spatial resolution and thus individual insertions are not clearly resolved in SEM-based CL, in contrast to TEM-based CL.^[267] Nevertheless, diffusing carriers should be trapped in the closest insertion,^[268] and therefore, the resolution is limited by the scattering volume of the electron beam of about 30 nm at $V_{acc} = 5$ kV. Hence, the observed shift in emission energy is probably related to the two uppermost insertions. In fact, this trend is representative for most investigated nanowires. As a confirmation, the emission energies at three points from the bottom to the top of the stack of (In,Ga)N insertions extracted from nine CL line scans are plotted in Fig. 7.6(b). Most nanowires exhibit a similar trend like in Fig. 7.6(a); two



Figure 7.6: (a) CL spectral line scan on a single nanowire from sample *A* acquired at 10 K with the intensity plotted on a logarithmic color scale and corresponding SEM image. The spectra extracted from the line scan at the positions marked by colored arrows and plotted above show a shift in the central emission energy along the axis of the stacked (In,Ga)N insertions. This trend to lower emission energies for the uppermost insertions is confirmed in (b), where the development of the peak energy from the bottom to the top of the stack of (In,Ga)N insertions is plotted for three points from all available line scans; the solid black line marks the data from (a).

nanowires show the trend with only a small change in energy and one shows the opposite trend.

A trend in emission energy along the nanowire axis was already observed by Tourbot et al.^[267] on a stack of three insertions, where the emission was resolved for individual insertions with the help of a TEM-based CL system. However, they see the larger redshift already between the first and second insertion. They even resolve that some insertions do not emit any light and that the lower part of the insertions shows a reduced luminescence intensity, which they relate to the presence of non-radiative recombination centers. The differences in energy both within a single nanowire and between nanowires are explained by the strain relaxation during growth resulting in the so-called compositional *lattice pulling* effect.^[267] To reduce the strain energy, a lower fraction of the available In atoms is incorporated initially. Therefore, the *lattice pulling* results in a gradual increase of the In content.^[269] This effect could induce a gradient in the In content both in individual insertions and along the stack of insertions.^[267] Also Knelangen et al.^[193] observed a higher In content at the top of the insertions (cf. Section 7.2.1), but their XRD measurements evidence a bimodal distribution of the In content instead of a gradient. It is possible that such a change in In content along the stack of insertions is indeed also the explanation for the redshift in emission energy presented in Fig. 7.6.

7.1.3. Indications for the presence of localization centers

Another interesting point is that the peak energy does not correlate with the nanowire diameter for the measurements on individual nanowires at 10 K. This effect is exemplified in Fig. 7.7 for two nanowires both with the (In,Ga)N emission centered at 2.33 eV,



Figure 7.7: (a) Comparison of the CL spectra of two nanowires from sample *A*, with similar peak energies but different diameters. Diameters of 50 and 120 nm can be determined for the two nanowires from their SEM images depicted in (b) and (c). The inset in (a) shows a plot of the emission energy versus diameter for 11 nanowires; the dashed line marks the emission energy of *NW* 4 and 5.

but with diameters of 50 and 120 nm, respectively. The point is further highlighted by the inset in Fig. 7.7(a) showing that there is no correlation between the peak energy of the (In,Ga)N emission and the nanowire diameter for 11 investigated nanowires. For a quantum well transition, a dependence on the diameter could be expected, because it has been observed that the height of the insertions depends on the diameter of the nanowires.^[270] Also the strain state should depend on the diameter. Therefore, the absence of a correlation between emission energy and nanowire diameter is a first indication that localization centers resulting from fluctuations of the In content within the insertions could play a prominent role in determining their emission properties.

For an even more detailed analysis of the (In,Ga)N emission, the results from a twodimensional CL mapping on the top of two nanowires are presented in Fig. 7.8. First, in Fig. 7.8(a), all the spectra from the CL maps are summed up both for *NW* 6 and *NW* 7, and displayed together with the ensemble spectrum. The mapped area is marked on the SEM images of the two nanowires in Figs. 7.8(b) and 7.8(c).

A graphical representation of the spectral maps containing various peaks at different energies and spatial positions is difficult. Therefore, a number of representative spectra are shown in Figs. 7.8(d) and 7.8(e) for *NW* 6 and *NW* 7, respectively, while the laterally integrated line scans from the maps are displayed in Figs. 7.8(f) and 7.8(g). The individual spectra from a single nanowire with six insertions show features that are common to several spectra as a result of the limited resolution. Still, quite distinct variations within a nanowire can be found. Among the individual spectra, those taken at the same height, i.e. separated only laterally, are plotted in the same color. This is the case for two pairs of spectra in Fig. 7.8(d) and for one pair in Fig. 7.8(e). These pairs of spectra should largely originate from the same insertions. Nevertheless, quite different contributions to the spectra can be seen which indicates that the emission from a single insertion can consist of several peaks, e.g. from localization centers. A deconvolution of the spectra yields linewidths of 50–100 meV for the individual peaks.

Another observed feature is the emission at slightly higher energy in the range between



Figure 7.8: (a) Comparison of ensemble spectrum (thick black line) with spectra measured at 10 K of two individual nanowires from sample *A* (thinner lines) containing six (In,Ga)N insertions each. The spectra of *NW* 6 and *NW* 7 were mapped over the area marked in the SEM images in (b) and (c). Their spectra in (a) are integrated over this mapped area. Representative spectra from individual points of these maps are displayed in (d) for *NW* 6 and (e) for *NW* 7 to illustrate the inhomogeneity of the emission within a single nanowire; spectra displayed in the same color are from points separated only in lateral direction, i.e. they highlight different contributions from the same (In,Ga)N insertion. To illustrate changes in the axial direction, line scans obtained by a lateral summation of the spectra are displayed in (f) for *NW* 6 and (g) for *NW* 7; note that these are plotted on a logarithmic color scale, while the other spectra are plotted on a linear scale. The direction of the line scans is marked by arrows in (f) and (g) as well as in the SEM images in (b) and (c).

Photon energy (eV)

Photon energy (eV)

2.6 and 2.8 eV. Such peaks are visible in the CL line scans in Figs. 7.6(a) and 7.8(f). They look quite similar to those of the ZB segments in Fig. 7.2, but they are redshifted by more than 200 meV and thus correspond to ZB thicknesses of more than 3 nm. The reduced wave-function overlap for these thicknesses renders this explanation unlikely. Instead, In clusters of very small dimensions and therefore with a strong confinement-related blueshift are a more likely origin of these peaks, further discussed in Section 7.2.5.

Concluding this section, the spatially resolved CL measurements point towards car-



Figure 7.9: Normalized PL transient of the spectrally integrated emission from the (In,Ga)N/GaN nanowire ensemble *A* at 10 K. The line shows a bi-exponential fit to the data with lifetimes $\tau_1 = 0.4$ ns and $\tau_2 = 7.1$ ns. The inset shows transient spectra at different delay times exhibiting only a minor shift of the peak energy with time. (TRPL measurements by Timur Flissikowski)

rier localization as a major factor affecting the (In,Ga)N emission. This question will be elucidated in more detail for sample *B*.

7.1.4. Time-resolved luminescence of the nanowire ensemble

In the following, the discussion of CL measurements on sample *A* is supplemented by a brief look at time-resolved PL measurements on the nanowire ensemble. A more detailed treatment of the luminescence decay for sample *B* can be found in Section 7.2.3.

Figure 7.9(a) reveals a decay of the luminescence of sample A at 10 K that cannot be described by a single exponential. This is in line with the CL measurements pointing rather to an inhomogeneous (In,Ga)N insertion than showing luminescence of a well defined quantum well. The measurements of the low-temperature lifetime associated with (In,Ga)N insertions embedded into nanowires in Refs. 14 and 13 yield an ensemble lifetime of 550 ps and 4.3 ns for the slow component of a bi-exponential fit, respectively. For comparison with these studies, a bi-exponential fit to the transient is given in Fig. 7.9(a) (orange line). This fit returns $\tau_2 = 7.1$ ns for the slow component which compares quite well to the latter value from literature. Bardoux et al.^[14] observe an even faster decay for their NW ensemble. The dynamic range of their measurement is quite limited, so the existence of an additional slower component may not be ruled out. By µPL spectroscopy on single NWs, Bardoux et al.^[14] show that the localization of excitons plays a significant role in their sample. Thus, they motivate the bi-exponential decay by a transfer of carriers from high-energy states of the (In,Ga)N insertions to the localized exciton states. However, it has been shown that for disordered systems such as a ternary (In,Ga)N layer, the decay dynamics should follow a power law for long times.^[128,129] A discussion of physically more appropriate models will be given in the context of time-resolved PL measurements on sample *B* in Section 7.2.3.

The inset to Fig. 7.9(a) presents spectra of the (In,Ga)N band at different delay times during the luminescence decay. A spectral diffusion to lower energies (redshift) of only

16 meV is discernible. This shift should be more pronounced for the case of a screening of the piezoelectric polarization fields in the insertion under the strong excitation used for time-resolved measurements.^[47] Later, it will be shown that sample *B* shows a more significant spectral diffusion that can be related to differences of the heterostructures in the two samples.

7.2. (In,Ga)N insertions separated by a thin barrier

In the second part of this chapter, another nanowire sample with (In,Ga)N insertions is investigated. This sample contains only two insertions separated by a thin barrier and was again chosen for its outstanding luminescence. But foremost, the dimensions and composition of these (In,Ga)N insertions have been established through a detailed investigation by TEM.^[193] Therefore, after briefly reviewing the structural properties, the luminescence of the (In,Ga)N insertions can be interpreted in light of this knowledge. In this part, CL spectroscopy will be supplemented both by time-resolved PL measurements of the nanowire ensemble and excitation dependent µPL on single nanowires.

7.2.1. Structure and composition of the (In,Ga)N insertions

The structure and composition of sample *B* were deduced by Knelangen et al.^[193] from high-resolution transmission electron micrographs (using geometrical phase analysis) complemented by synchrotron-based high-resolution XRD scans. The two $In_xGa_{1-x}N$ insertions of height $h \approx 11$ nm are separated by a 2–3 nm wide barrier. They are fully embedded in GaN, i.e. they are surrounded by a GaN shell in the lateral direction. The insertions have an average In content of $x \approx 0.2$, but they are capped by a 1–2 nm thick layer with $x \approx 0.4$ which is attributed to the segregation of In. This structure is illustrated in Fig. 7.10 and shown schematically in Fig. 7.11(b). It should be noted that these are representative values for the dimensions and composition of the (In,Ga)N insertions. Within the nanowire ensemble, there is a scatter in the parameters between different nanowires. This statistical distribution is better represented in the superlattice fringe measurements by XRD employed for sample A, ^[255] a method not available for a stack of only two insertions.

Finite element simulations

The structure of sample *B* just described is visualized in Fig. 7.10 by plotting the spatial distribution of $|\vec{P}_{pz}|$, the absolute value of the piezoelectric polarization, which is the dominant cause of the quantum-confined Stark effect (QCSE) in (In,Ga)N/GaN quantum wells. The elastic strain tensor ϵ_{ij} was obtained by numerical finite element (FEM) simulations based on linear elasticity theory^[272] with the structural parameters from TEM and XRD as input parameters. The piezoelectric polarization \vec{P}_{pz} is related to ϵ_{ij} via the piezoelectric tensor e_{ij} for the space group P6₃mc according to Eq. (2.4). The quantity displayed in Fig. 7.10 is the absolute value of \vec{P}_{pz} , i.e.

$$|\vec{P}_{pz}| = \begin{vmatrix} e_{15}\epsilon_{xz} \\ e_{15}\epsilon_{yz} \\ e_{31}\left(\epsilon_{xx} + \epsilon_{yy}\right) + e_{33}\epsilon_{zz} \end{vmatrix}.$$
(7.1)



Figure 7.10: Spatial distribution of the absolute value of the piezoelectric polarization within the (In,Ga)N nanowire heterostructure for sample *B* as obtained by FEM simulations. The geometry and composition of the structure has been derived by TEM and XRD.^[193] (FEM simulations by Michael Hanke)^[271]

In contrast to the case of planar quantum wells, the shear components of ϵ_{ij} must not be ignored for the nanowire geometry. The theoretical piezoelectric constants for GaN given by Shimada^[39] were used ($e_{33} = 0.83 \text{ C/m}^2$, $e_{31} = -0.45 \text{ C/m}^2$, $e_{15} = -0.38 \text{ C/m}^2$). These values seem appropriate also for (In,Ga)N, as the values of e_{ii} for GaN and InN differ less than when comparing the values for GaN from different theoretical and experimental studies.^[39] Figure 7.10 shows that there is a considerable piezoelectric polarization in the (In,Ga)N insertions. In the center of the insertion, $|\vec{P}_{pz}|$ amounts to 0.018 C/m² compared to 0.021 C/m^2 for a planar quantum well with the same thickness and composition profile, i.e. it is reduced by only 15%. More importantly, even at the edge of the (In,Ga)N insertion, a value of 0.013 C/m^2 is observed. The elastic relaxation is actually not enhanced for an insertion extending to the nanowire sidewalls, which leads to a more complex strain distribution towards the surface including significant shear components. In any case, the piezoelectric polarization still dominates over the spontaneous polarization, the contribution of which amounts to 0.005 C/m^{2} ^[41] or 0.002 C/m^{2} ^[32] the latter being the result from a linear interpolation of the recent calculations by Belabbes et al.^[32] that are in better agreement with the value for the spontaneous polarization of GaN determined in Chapter 6.

7.2.2. Luminescence of the nanowire ensemble at room temperature

Based on the review of the structure and composition of the (In,Ga)N insertions of sample *B* and the prediction of the piezoelectric polarization in these structures, it is now interesting to correlate this knowledge with the optical emission of the insertions.

Figure 7.11(a) presents a room-temperature spectrum acquired by CL on the nanowire ensemble *B*. As for sample *A*, both the emission from GaN and the (In,Ga)N insertions are visible. The (In,Ga)N band is centered at 2.44 eV with a FWHM of 300 meV. These values compare well with PL measurements on this nanowire ensemble.^[193] The FWHM



Figure 7.11: (a) Room-temperature CL spectrum of the nanowire ensemble *B* containing (In,Ga)N insertions recorded in top-view geometry. The inset shows a cross-sectional monochromatic false-color CL image of the (In,Ga)N emission superimposed on the corresponding SEM image to illustrate the origin of the luminescence. (b) Poisson-Schrödinger calculation of the band structure and transition energies for the N-polar (In,Ga)N/GaN nanowire heterostructure. At the bottom of the plot, the layer sequence is given in a color representation corresponding to the inset sketch of the nanowire heterostructure. The transition energy observed in (a) for the (In,Ga)N insertions corresponds to the inter-well transition calculated in (b).

is a little lower than for sample *A*, while the emission energy is about 200 meV higher. It should be added, that as a result of temperature gradients across the wafer during growth the central wavelength of the (In,Ga)N emission can vary up to 200 meV for different positions on the same wafer. The inset in Fig. 7.11(a) shows a cross-sectional CL image of the (In,Ga)N band superimposed on the corresponding SEM image. Again, these images show that the luminescence comes from the area where the (In,Ga)N insertions are located, which will be elaborated in Section 7.2.4. Note that the vertical extent of the (In,Ga)N emission is reduced compared with sample *A* in agreement with the smaller number of insertions.

With the composition profile of the (In,Ga)N insertions known from TEM, it is possible to calculate the band structure of these insertions employing self-consistent Poisson-Schrödinger calculations.^[209] Details on the parameters used in this calculation can be found in Appendix D. Following recent reports that nanowires grown in the self-induced growth mode are always N-polar,^[183–185] this polarity was chosen. Additionally, the piezoelectric polarization^[41] has been reduced by 15% compared to a planar quantum well in light of the FEM calculations presented above. The one-dimensional band profile presented in Fig. 7.11(b) for the structure under investigation evidences the resulting strong internal electrostatic fields. Figure 7.11(b) shows that a "regular" quantum well transition across the 11 nm thick insertions would have a negligible wave-function overlap, and the calculated energy would be significantly lower than the observed emission energy. However, no emission could be detected for energies lower than 2 eV. In contrast, the observed transition energy is better reproduced by an inter-well transition across the 2–3 nm thick barrier. This range in barrier thickness corresponds to a range in transition energies of 2.35–2.52 eV in the calculations. Therefore, as already pointed out by Knelan-



Figure 7.12: PL transients of the spectrally integrated emission from (In,Ga)N/GaN nanowire ensemble *B* at 20 K and (inset) 300 K. Normalized transients for different excitation pulse intensities are plotted, where I_0 refers to the highest excitation density with 1.24×10^{13} carriers/cm² per pulse. The long time asymptote at 300 K indicated by the gray line in the inset corresponds to a decay time of 400 ns. (TRPL measurements by Timur Flissikowski)^[271]

gen et al.^[193], the observed green emission may be related to the inter-well transition between the two (In,Ga)N insertions. In any case, these one-dimensional calculations can give only a rough idea for such a complex three-dimensional, ternary heterostructure. As will be explained in Section 7.2.5, the observed transition energy is also compliant with emission from spatially localized excitons not affected by the polarization field, as the emission energy lies slightly below the band gap energy for $In_{0.2}Ga_{0.8}N$.

7.2.3. Time-resolved luminescence of the nanowire ensemble

An investigation of the carrier dynamics in time-resolved PL measurements can give further clues on the origin of the luminescence. Experimentally, the presence of piezoelectric fields in the nanowire ensemble under investigation predicted by the FEM simulations in conjunction with the band structure calculations should manifest itself in the PL transients measured at 20 K and presented in Fig. 7.12. The first notable feature is that the decay is rather slow, taking place over a timescale on the order of 1 µs. This long decay time is in contrast to the TRPL measurements on sample A for which the timescale was found to be on the order of 10 ns in Section 7.1.4, i.e. faster by a factor 100. Therefore, the much longer lifetimes observed for sample B suggest that a transition must play a role for which the wave-function overlap is significantly reduced, consistent with the assumption that the emission is related to a spatially indirect inter-well transition. For the present sample, the long decay time alone thus does not provide evidence for the presence of electric fields. However, the decay becomes faster with increasing excitation density (Fig. 7.12). Such a behavior would not be expected for a transition being merely spatially indirect, but may very well be caused by a progressive screening of electrostatic fields. Note that the carrier sheet density giving rise to $|\vec{P}_{pz}| = 0.018 \text{ C/m}^2$ is $n_s = 1.13 \times 10^{13} \text{ cm}^{-2}$ and therefore close to the maximum excitation density I_0 (cf. Fig. 7.12).

If the highest applied excitation screens the internal electrostatic fields, this effect should result in a characteristic spectral evolution of the peak energy with decay time.^[47]



Figure 7.13: (a) Evolution of the emission energy with decay time for the highest excitation density I_0 at 20 K (sample *B*). The line is a guide to the eye. The inset shows the corresponding transient spectra at different times as well as the Gaussian fits (solid lines) for obtaining the transition energies. (b) PL transient for the lowest excitation density $0.013I_0$ at 20 K in double-logarithmic representation. For clarity, only a fraction of the data are displayed. The power law decay is described well by a DAP recombination model (solid line). Two other models for disordered systems are given for comparison. (TRPL measurements by Timur Flissikowski)^[271]

As displayed in Fig. 7.13(a), this behavior is indeed observed: the emission band strongly red-shifts within the first 100 ns of the decay, followed by a much more gradual change. This strongly non-linear dependence of emission energy on time reflects the fact that the initial decrease of carrier density is fast because of the screening of the internal fields by the initially created carrier density. The decay of the carrier population progressively restores the internal fields, and the dynamics slows down correspondingly.^[47] At lower excitation densities, a spectral diffusion of the emission towards lower energies can still be observed (not shown here), but is slightly less pronounced than depicted above for the highest excitation. In contrast, sample *A* exhibits a significantly reduced spectral diffusion—though, of course, over a two orders longer time span. This difference in the spectral diffusion of the two samples can again be ascribed to the presence of an interwell transition in sample *B*. For sample *A*, without such a transition, the polarization fields seem to play a less significant role.

For all excitation densities depicted in Fig. 7.12, the decay remains strongly nonexponential. In the discussion of the transient from sample *A* (Section 7.1.4), it was already pointed out that a bi-exponential fit is not appropriate to describe the decay dynamics and that a model with a better physical motivation is needed. Figure 7.13(b) displays the low-excitation PL transient from sample *B* on a double-logarithmic scale. Clearly, the decay of the intensity *I* over time *t* essentially follows a power law, i.e. $I(t) \propto t^{-k}$. Here, *k* is a constant, usually between 1 and 1.5, but possibly smaller than 1 or as large as 2.^[273] This dependence is characteristic for disordered systems in general^[273,274] and for (In,Ga)N in particular.^[128,129] Regardless of the details, the interpretation of this peculiar decay type always relies on a spatial separation of charge carriers induced by an individual localization of electrons and holes in separate potential minima. Recombination is *not* excitonic in this case, but occurs between electrons and holes with varying spatial separation and thus varying wavefunction overlap similar to DAP recombination. The solid line in Fig. 7.13(b) is a fit to the data with the classical three-dimensional DAP model of Thomas et al.^[275] The intensity I(t) of the light emitted at time *t* is

$$I(t) = -\frac{d}{dt}N(t),$$
(7.2)

$$N(t) = \exp\left[4\pi n \int_0^\infty \{\exp[-W(r)t] - 1\} r^2 dr\right],$$
(7.3)

$$W(r) = W_{\max} \exp[-r/a]. \tag{7.4}$$

Here, *n* is the majority carrier concentration. This model includes an exponential distribution for the radiative recombination rate W(r) of an electron and hole at distance *r*, where W_{max} is a scaling factor and *a* related to the electron Bohr radius. Morel et al.^[128] have modified this model to an essentially two-dimensional case for quantum wells with a polarization field in which the electrons and holes are each confined to a layer at the respective interfaces. In this case, the exponential term for W(r) is replaced by a Gaussian distribution $\exp[-r^2/a^2]$. However, especially at short times, this latter model does not fit as good to our data—see dashed line in Fig. 7.13(b). This deviation indicates that we cannot strictly speak of a complete confinement of electrons and holes to the interface regions around the barrier which would result in a constant vertical, but varying lateral separation. Instead, we probably also have a certain vertical distribution of the electrons and holes within the insertions.

The DAP model of Thomas et al.^[275] yields a good fit over the available 1.5–2 orders of dynamic range in intensity, but the decay according to this model becomes faster than a power law for long times. A more complex version of the model intended for equal donor and acceptor concentrations would yield a power law also for a larger dynamic range. The same can be achieved with the more simple model for the recombination dynamics in disordered systems given by Huntley^[273] which is added to Fig. 7.13(b) as a dotted line. For the limited range available in our measurement, the fit of this model coincides with the fit using Eqs. (7.2)–(7.4). Huntley considers a random distribution of trap states and of recombination centers to which the trapped electrons can tunnel, with ρ being the density of the latter. This process slows down the recombination in a similar way as the varying overlap in the case of the DAP model. He arrives at the following equations:^[273]

$$I(t) \propto -\frac{dn(t)}{dt},\tag{7.5}$$

$$n(t) = \int_0^\infty 3(r')^2 \exp[-(r')^3] \exp(-t/\tau) dr', \tag{7.6}$$

$$r' = (4\pi\rho/3)^{1/3}r, \qquad \tau = s^{-1}e^{\alpha r}.$$
 (7.7)

Here, n(t) is the trapped electron concentration, r is the tunneling distance, τ is the mean lifetime for the tunneling process, α is a constant and $s \approx 3 \times 10^{15} \text{ s}^{-1}$ for an electron in an atom-sized box.^[273]

Recently, Cardin et al.^[276] have also investigated (In,Ga)N insertions in nanowires and shown that in their case the power law behaviour is upheld for up to four orders of dynamic range in intensity which they fit with another model based on the transfer of



Figure 7.14: Sketch of the lateral band profile across the (In,Ga)N insertions where the long range depletion field is superimposed by potential fluctuations in the ternary alloy. The localization of electrons and holes in separate potential minima at various distances leads to the DAP like behaviour. As a consequence of the depletion fields, a lateral Stark shift affects the transition energy.

carriers between a bright state and a dark trap state. [129,276]

The low-temperature decay may thus be interpreted as follows. At low excitation densities, the broad emission band observed in the inset of Fig. 7.13(a) stems from nonexcitonic transitions between individually localized electrons and holes, resulting in a very slow, power law decay of the emission intensity. These single particle states can be spatially separated in the vertical direction by the barrier between the two (In,Ga)N insertions. Then, the resulting emission energy will be affected by the vertical electrical field in the structure. Furthermore, there is a lateral electric field as the depletion region spans the whole nanowire (cf. Fig. 7.4). The strain relaxation in the insertions might also lead to an additional lateral band bending.^[277] Therefore, the lateral separation of the electrons and holes will not only influence the overlap, but might also have an effect on the transition energy. The electric fields may even result in a complete lateral separation of electrons and holes, inhibiting recombination entirely. However, these complications are attenuated through the localization of carriers by short range potential fluctuations in the ternary alloy which again highlights the importance of the latter for the luminescence of the insertions. The resulting band structure in the lateral direction is sketched in Fig. 7.14: Excitons might be localized in a single potential minimum, but due to the electric fields in the lateral and vertical direction, a fraction of the excitons will be ionized leading to the DAP-like localization of electrons and holes in separate potential minima that leads to the observed power law decay. The emission energy as well as the overlap will depend sensitively on the carrier density due to both a saturation of low-energy states and a screening of the internal fields at high excitation density.

Remarkably, the decay remains quite slow at elevated temperatures. The inset in Fig. 7.12 shows the PL transient obtained at room temperature. The long-time asymptote of the decay gives a lower bound of 400 ns for the non-radiative lifetime, significantly longer than values reported for state-of-the-art (In,Ga)N blue-to-green light-emitting and laser diodes.^[278,279] This result demonstrates the potential of such (In,Ga)N insertions in GaN nanowires for applications in light emitting devices and constitutes a major motivation to investigate the emission of this specific structure in more detail.

7.2. (In,Ga)N insertions separated by a thin barrier



Figure 7.15: (a) Superposition of SEM and (false-color) monochromatic CL images acquired at room temperature. (b) Bright-field TEM image of the same nanowire from sample *B* dispersed on a TEM grid. The strain-induced contrast from the heterostructure coincides with the location of the light-emitting region. (c) Comparison of normalized CL spectra from single nanowires (dashed lines) and from nanowire ensemble *B* (solid line) recorded at 10 K. The complete spectra exemplified for the ensemble and one nanowire exhibit additional contributions above 3 eV from the excitonic NBE luminescence and the DAP transition in the GaN nanowire base. (TEM image recorded by Esperanza Luna)

7.2.4. Cathodoluminescence of individual nanowires

To start with the investigation of single nanowires from sample *B*, images of the same single nanowire recorded successively by SEM/CL and TEM are displayed in Figs. 7.15(a) and 7.15(b), respectively. These experiments illustrate the spatial correlation of the green emission and the strain fields associated with the (In,Ga)N insertions. A complete CL spectrum measured at low temperature (10 K) on the nanowire ensemble is given in Fig. 7.15(c) (solid line) together with spectra from dispersed individual nanowires (dashed lines). The (In,Ga)N band in the ensemble spectrum has a similar FWHM (300 meV) as that measured at 300 K, while the emission center shifts to 2.5 eV when going to 10 K, i.e. by a similar magnitude as the 70 meV observed for the NBE luminescence. This analogy may, however, be fortuitous considering that, for example, some of the localization centers active at low temperatures might well be thermally depopulated at room temperature. In fact, a much lower shift of only 10 meV was seen for sample *A* [cf. Fig. 7.1(a)]. Again, the DAP transition of GaN is present in the low temperature spectra (cf. sample *A*).

For the individual nanowires, the emission energy of the (In,Ga)N band varies from nanowire to nanowire in the range of 2.3–2.7 eV. In analogy to sample *A*, this spread in emission energies confirms that the (In,Ga)N band of the nanowire ensemble is a superposition of these peaks. Considering the reduced number of insertions per nanowire compared with sample *A*, it is not surprising that the linewidth of the (In,Ga)N bands from individual nanowires is narrower for sample *B*. Nevertheless, the FWHM of around 160 meV is still rather broad. This considerable linewidth is consistent with the existence of a near-continuum of DAP-like localized states in line with the interpretation of the decay dynamics presented above.



Figure 7.16: Monochromatic false-color CL images at different detection energies recorded at 10 K on a cluster of nanowires from sample *B* superimposed on the corresponding SEM image. The energies are denoted in the respective colors used in the plot. Different nanowires dominate for different detection windows; a mixing of colors indicates that the emission is present for several detection energies.

The variation in emission energy of the (In,Ga)N band between different nanowires is further illustrated by a series of monochromatic CL images of a cluster of nanowires displayed in Fig. 7.16. For four detection windows separated by steps of 100 meV, the emission originates from different nanowires. Note that the linewidth of the (In,Ga)N band for a single nanowire is reflected in the overlap of emission in different detection windows also leading to a mixing of colors in the false-color representation. Variations of the mean In content of a few percent and of the barrier thickness (2–3 nm) observed between different nanowires in TEM (cf. section 7.2.1) readily account for the spread of the emission energy over 400 meV.

7.2.5. Photoluminescence of individual nanowires

To improve the spectral resolution and to reduce the excitation density, it is worth turning to μ PL measurements at 10 K on single dispersed nanowires. Figure 7.17(a) shows the μ PL spectra for an individual nanowire taken with excitation densities spanning two orders of magnitude. Over the entire range of excitation densities, the integrated intensity exhibits a strictly linear dependence on excitation density. At the same time, the (In,Ga)N band exhibits a significant blue-shift with increasing excitation density. Note that the spectra are basically *rigidly* blue-shifted, with little symmetric broadening and no asymmetric broadening towards higher energies except for the highest excitation density.



Figure 7.17: (a) μPL spectra for an individual nanowire with the excitation density increasing from bottom to top and (b) peak energy versus excitation power (logarithmic scale) of the (In,Ga)N band for different nanowires with the nanowire displayed in (a) highlighted by the thick line. (μPL measurements by Carsten Pfüller)^[271]


Figure 7.18: μPL spectra for a nanowire from sample *B* exhibiting additional sharp lines at energies above the main (In,Ga)N band. These lines do not shift with excitation power (increasing from bottom to top by approximately two orders of magnitude). (μPL measurements by Carsten Pfüller)^[271]

Also note that the low-energy tails of the spectra are parallel to each other. These findings rule out band filling as the cause of the blue-shift, render the saturation of localized states at lower energies unlikely, and thus leave the progressive screening of internal electrostatic fields as the most likely cause of the blue-shift observed.^[280,281] This conclusion is confirmed by power-dependent measurements for eight different single nanowires as shown in Fig. 7.17(b). The magnitude of the peak shift is very similar for all investigated nanowires. Looking at the more detailed measurement highlighted in this semilogarithmic plot, it is clear that the dependence is weaker than logarithmic. This peculiar dependence follows the behavior predicted by Kuroda and Tackeuchi^[282] and by Pinos et al.^[283] for free carrier screening of the QCSE. The saturation of the peak shift with excitation density simply arises from the fact that the lifetime decreases once screening is effective, thus requiring disproportionately higher excitation densities to further increase the carrier density. Contrary to expectation,^[283] a saturation of the transition energy for low excitation densities is not observed. This effect indicates that the carrier densities under continuous (cw) excitation remain rather high even for the lowest applied excitation density, which is presumably a consequence of the very long carrier lifetime. At the same time, this high carrier density could also explain the lack of any fine structure in the spectra due to individual localized states, which otherwise one would expect to emerge in single-wire spectroscopy. Note that the screening process for the piezoelectric polarization is equal to that of the spontaneous polarization discussed in Chapter 6.

However, besides the broad emission band visible on the low energy side of the spectrum, additional sharp PL peaks at a slightly higher energy appear in the spectra of many nanowires. An example of such a spectrum is shown in Fig. 7.18. The positions of these sharp PL peaks are insensitive to the excitation density as emphasized by the vertical lines. This fact and their small FWHM of down to 3–6 meV are fingerprints of zero-dimensional localized states. In fact, localized states originating from compositional fluctuations are known to manifest themselves in spectrally narrow transitions in planar (In,Ga)N/GaN quantum wells when measured using nano-apertures^[126] as well as for (In,Ga)N insertions in GaN nanowires.^[14]

Provided that the spatial extent of the associated potential minima is on the order of one nm, the resulting localization centers facilitate spatially direct transitions and are

thus not affected by the polarization field. Note that these direct transitions are related to localized *excitons*, in contrast to the individually localized electrons and holes (DAP-like) discussed in the framework of the time-resolved measurements. Due to their much longer lifetime, the latter dominate the PL transients. Taking into account the strong confinement in the nm-scale potential minima, the energy of the corresponding localized states would be only slightly below that of the surrounding (In,Ga)N matrix, which was measured to have an In content of 0.2. According to the In_xGa_{1-x}N band gap $E_g(x)$ (neglecting excitonic effects) of

$$E_g(x) = 3.51(1-x) + 0.69x - 1.72x(1-x)$$
(7.8)

with the parameters taken from Schley et al.^[284] corrected for temperature, this In content corresponds to an energy of 2.67 eV, i.e., right at the high energy cutoff of the sharp lines visible in Fig. 7.18. Note that while all investigated nanowires show the broad emission band, a few do not exhibit the additional sharp lines [cf. Fig. 7.17(a)]. In other words, the inter-well transition appears in all nanowires, while strong exciton localization within one insertion occurs in most but not all nanowires.

7.3. Conclusions

In this chapter, the luminescence from (In,Ga)N insertions embedded in GaN nanowires was investigated for two different samples: First, an ensemble with six (In,Ga)N insertions per nanowire, each 3 nm thick and separated by 7 nm wide barriers (sample *A*) was studied by detailed CL measurements. Second, the luminescence of nanowires containing two (In,Ga)N insertions of about 11 nm thickness separated by an only 2–3 nm wide barrier (sample *B*) was additionally investigated by μ PL and TRPL. The results stress the importance of polarization fields even for heterostructures integrated into nanowires and the prominent role of carrier localization for the emission properties, but also the influence of defects on the luminescence was discussed.

The analysis of sample *A*, presented in the first part of this chapter, reveals the presence of ZB segments in the upper part of the nanowire that exhibit luminescence in the range of 3–3.3 eV. The probability to form zincblende GaN is increased at the reduced substrate temperatures necessary to grow the (In,Ga)N insertions. Besides DAP emission at low temperatures, also the presence of a weak yellow luminescence band is revealed by the spatially and spectrally resolved CL scans. Furthermore, the GaN luminescence from the nanowire base decreases in intensity towards the bottom end of the nanowires. This trend might indicate the indiffusion of Si from the substrate during growth which would enhance the depletion of the nanowires by increasing lateral band bending and associated electric fields for a pinned Fermi level. Furthermore, these results highlight the power of spatially resolved CL measurements in distinguishing contributions to the luminescence which coincide spectrally, such as from (In,Ga)N insertions and segments of zincblende GaN versus emission from point defects in GaN, e.g. yellow luminescence and the DAP emission.

For both samples *A* and *B*, the (In,Ga)N emission originates from the upper part of the nanowires as verified in monochromatic CL images. Measurements on a single nanowire from sample *B* even allow for a clear spatial correlation of the CL to the strain contrast associated with the insertions in a corresponding TEM image. From the variation of the emission energy between single nanowires, the large FWHM of the (In,Ga)N band

amounting to 300–400 meV is partially explained. Nevertheless, the linewidth still remains rather broad for individual nanowires with more than 200 meV for sample *A* and around 160 meV for sample *B*.

This linewidth can be attributed to fluctuations of the In content that lead to the localization of carriers. The CL measurements on sample A already indicated a prominent role of carrier localization for the emission of the (In,Ga)N insertions in GaN nanowires, similar to what is known for planar quantum wells.^[126] The impact of carrier localization was confirmed by the results presented for sample *B* which additionally show that also the QCSE is of importance. Two types of localization need to be distinguished in the context of this work. First, excitons might be bound to a single potential minimum leading to zero-dimensional states not affected by the polarization fields. These states result in sharp emission lines insensitive to the excitation density which were evidenced in μ PL measurements on single nanowires. Second, individual electrons and holes may be localized in separate potential minima. The varying spatial distance leads to a power law decay in PL transients characteristic for disordered systems such as (In,Ga)N and similar in nature to that of the DAP emission. Both types of carrier localization are a result of the complex potential landscape induced by compositional fluctuations of the (In,Ga)N alloy and possibly also by a roughness of the interfaces of the insertions to the surrounding GaN.^[285] Additionally, the depletion fields at the surface that span the whole nanowire and possibly also the elastic relaxation of the insertions^[277] lead to a bending of the band edges in the lateral direction. This effect may inhibit recombination entirely through a complete *lateral* separation of electrons and holes. Thus, the localization of carriers is necessary in order to observe luminescence from these structures. In the full three-dimensional picture, the short-range potential fluctuations leading to the carrier localization are superimposed on the long-range gradients of the band edges induced by the polarization fields in the vertical direction and the depletion fields as well as elastic relaxation which mainly affect the lateral direction. The long-range fields might be strong enough to dissociate excitons, leading to the emission from individually localized electrons and holes seen in TRPL. The QCSE and the lateral Stark shift induced by these fields together with the essentially random distribution of carriers account for the large FWHM of the emission associated with individual insertions. Nonetheless, the sharp lines in µPL spectra evidence that a fraction of the excitons remain intact and are strongly bound in single potential minima.

The results discussed here should be of general significance for (In,Ga)N insertions embedded in GaN nanowires. Evidence for carrier localization was found on two samples emitting in the green spectral region, but with quite different dimensions of the (In,Ga)N insertions. The emission range for other such samples presented in the literature is quite comparable. Also, (In,Ga)N insertions similar to sample *B* of up to 10 nm thickness being embedded within the GaN nanowire are evident from the TEM images presented in at least three other studies.^[248,249,267] FEM simulations reveal the elastic relaxation of such structures to be marginal, causing strong piezoelectric fields to reside within the insertions. The associated drastic decrease of the electron-hole overlap renders a "regular" quantum well transition unlikely. In fact, for the green (In,Ga)N band observed for sample *B*, an *inter-well* transition could explain the clear experimental observation of the QCSE in this specific sample both by μ PL and TRPL. As it was shown that the emission energy of strongly localized excitons may be entirely insensitive to the excitation density even in the presence of a strong electrostatic field, the absence of an excitation-dependent

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blue-shift observed by other groups^[249–251] may be due to exciton localization and not to an absence of polarization fields. Even though we see a trend towards lower emission energies (redshift) from the bottom to the top of the stack of (In,Ga)N insertions which could be explained by lattice pulling as suggested by Tourbot et al.^[267], the localization processes seem to play the major role in the broadening of the emission from individual nanowires.

8. Summary and outlook

In this thesis, different heterostructures embedded into III-V semiconductor nanostructures were investigated by cathodoluminescence spectroscopy, supplemented by microphotoluminescence measurements with both continuous-wave and time-resolved setups. The aim was to systematically study the luminescence of these structures, but also to derive fundamental material parameters from these measurements.

The most notable results for the three types of structures studied in the course of this work are: (i) a contribution to the discussion concerning the band gap of wurtzite GaAs based on the luminescence of GaAs nanowires consisting of zincblende and wurtzite segments; (ii) an experimental determination of the spontaneous polarization of GaN from the luminescence of stacking faults in GaN microcrystals; and (iii), evidence for the co-existence of polarization fields and carrier localization in (In,Ga)N insertions embedded into GaN nanowires.

In the following, the three topics are recapitulated in more detail.

Bottom-up growth of semiconductor nanostructures may stabilize crystal phases not (i) readily obtainable in planar growth. Alternating segments of such crystal polytypes may form quantum well heterostructures. To begin with, GaAs nanowires, for which polytypism is commonly observed, were studied. The investigated nanowires contain both the zincblende and wurtzite polytypes as evidenced by X-ray diffraction and Raman spectroscopy. Two such samples grown using different V/III flux ratios were compared. One sample exhibited luminescence at energies both above and below the band gap of zincblende GaAs, while the other one emitted only at energies below the zincblende gap. This sensitivity of the luminescence spectra on the growth conditions could explain why many groups have reported only the latter situation. The observation of luminescence at energies exceeding the zincblende band gap, in line with a few other reports in the literature, [104-106] can be explained only for $E_g^{WZ} > E_g^{ZB}$. In fact, band structure calculations for zincblende segments in a wurtzite matrix indicate that luminescence at energies above E_{σ}^{ZB} is restricted to zincblende segments not thicker than a few bilayers. Therefore, the variation in the emission range can be explained by a different distribution of segment thicknesses in the two investigated samples.

Since standard routes to assess the band gap are not accessible for wurtzite GaAs due to the lack of bulk samples, luminescence spectroscopy is a commonly employed alternative. However, at low temperatures, the luminescence is dominated by bound states. An assessment of the difference between the band gap energies of the two polytypes was hence conducted at room temperature. In the context of luminescence measurements, the resulting 55 meV can be regarded as lower bound for the difference between the band gaps of the two polytypes.

(ii) Similar heterostructures formed by the wurtzite and zincblende polytypes were investigated in GaN microcrystals obtained by the lateral overgrowth of nanowires. The lateral growth regime is seen to be accompanied by modifications of the stacking se-

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quence. A particularity of the studied microcrystals is that all three types of stacking faults and even thicker zincblende segments can be found, whereas planar layers typically exhibit only the two types of intrinsic stacking faults. In cathodoluminescence line scans along the cross sections of microcrystals, stacking faults appear as a series of peaks at different energies. To address shifts of the emission energies induced by effects such as the bundling of stacking faults, the emission energies associated with individual stacking faults were obtained from a statistical analysis of the luminescence lines. This analysis resulted in emission energies of 3.42 and 3.35 eV for the intrinsic I_1 and I_2 stacking faults, respectively, in good agreement with previous literature reports. For extrinsic stacking faults, an emission energy of 3.29 eV could be established. Furthermore, various aspects of the emission from stacking faults were investigated, including their linewidth in micro-photoluminescence and luminescence at room temperature. The observation of emission from zincblende segments at energies down to 3.0 eV as well as a blueshift of the peak energies with increasing excitation in cathodoluminescence line scans are both evidence for the quantum-confined Stark effect, i.e. a manifestation of the polarization fields in the emission energies of these heterostructures.

In fact, it could be shown that the emission energies of the stacking faults are governed by the spontaneous polarization. Therefore, an experimental value for the spontaneous polarization could be derived by treating the stacking fault quantum wells as plate capacitors. In this picture, the additional potential drop induced by the polarization field when another layer of zincblende is added to the structure, i.e. by going from one type of stacking fault to the next, is directly reflected in the emission energies. This approach was verified by self-consistent Poisson-Schrödinger calculations taking the spontaneous polarization as a free parameter. Thereby, -0.022 C/m^2 is obtained as experimental value for the spontaneous polarization of GaN. To resolve the ambiguity of assigning a thickness to the stacking faults in the Poisson-Schrödinger calculations, an effective electronic thickness was introduced on the basis of computations of the stacking fault potential in the framework of density functional theory. Note that the calculations were performed both for a type-I and a type-II band alignment. Due to the polarization fields, type-I quantum wells are associated with similar indirect transitions as type-II quantum wells. Therefore, luminescence spectroscopy can not resolve the question of the band alignment between the polytypes when strong polarization fields are involved.

(iii) Turning to intentionally grown ternary heterostructures in group-III nitride nanowires, the emission of axial (In,Ga)N insertions in GaN was investigated. Again, significant polarization fields come into play. The significant mismatch of the lattice constants between GaN and (In,Ga)N results in a dominant role of the piezoelectric polarization. Some previous reports have argued that the effect of polarization fields should be negligible for the nanowire geometry due to a better relaxation of the strain at the free surfaces, but failed to substantiate this claim. Finite element calculations predict only a partial reduction of the piezoelectric polarization.^[271] Subsequently, evidence for the presence of polarization fields was found in continuous and time-resolved photoluminescence measurements. However, the localization of carriers was found to be another crucial factor controlling the luminescence of these heterostructures. First, the localization fields, which confirms previous reports.^[13,14] However, individually localized electrons and holes contribute to the emission as well. These transitions occur at varying spatial separation, which is reflected in the PL transients. Their emission energy can be affected

by polarization fields, but also by lateral depletion fields due to a pinning of the Fermi level at the nanowire surface. Essentially, the (In,Ga)N insertions will exhibit a complex band structure landscape influenced by these various aspects.

In consequence, the two major phenomena governing the luminescence from planar (In,Ga)N/GaN quantum wells, carrier localization as well as the quantum-confined Stark effect as a result of differences in the piezoelectric polarization, have been evidenced also for nanowire-based heterostructures. Both processes may result in a redshift of the emission and could be part of the reason why (In,Ga)N insertions in nanowires grown by molecular beam epitaxy emitting above 2.8 eV have not been reported. It is suggested that the inhomogeneities responsible for carrier localization are even more pronounced in the case of such three-dimensional heterostructures than for layers. As for the microcrystals, luminescence related to zincblende segments was detected in cathodoluminescence line scans. These segments are formed in some of the GaN nanowires probably due to the reduced growth temperature necessary for the integration of (In,Ga)N insertions.

Nanowire-based (In,Ga)N/GaN heterostructures have been proposed as building blocks for light emitting diode structures. Such a prototype device is investigated in Appendix A. The investigation indicates that the so far insufficient luminescence yield from only one percent of the nanowires is a direct consequence of the inhomogeneity of the nanowire ensemble concerning the conductivity of individual nanowires and injection barriers at the nanowire–substrate interface.

Apart from the main topics, an experimental issue was already covered in the course of the introduction to cathodoluminescence in Chapter 3. A quenching of the near-band edge luminescence in GaN nanowires under the electron beam irradiation can be observed, and its origin was attributed to an interplay of carbon contamination and the trapping of injected charges. Both carbon contamination and carrier trapping inhibit the radiative recombination of excitons in nanowires, and especially the former may also enhance the non-radiative surface recombination. Fortunately, this quenching does not significantly affect the luminescence from heterostructures, which are in the focus of this work.

Highlights from using cathodoluminescence This thesis has confirmed the necessity to look at individual nanostructures to truly understand the origin of their luminescence. Cathodoluminescence measurements in a scanning electron microscope allowed for a spatial resolution of the embedded heterostructures along the axis or cross-section of the investigated nanostructures. Both a monochromatic as well as a spectral imaging mode were employed: Either images of the CL emission in a specific spectral window were recorded using a photomultiplier, or the beam was stepped across the sample and a charge-coupled device detector was used to record complete spectra at each point. Some highlights emphasizing the advantages of cathodoluminescence spectroscopy include:

- Along the axis of GaAs nanowires, the segmented nature of spectral contributions below and above the zincblende band gap was resolved.
- The emission from stacking fault quantum wells was directly visualized as stripes extended along the basal plane in cross-sectional images of GaN microcrystals.
- In spectral line scans across such stacking faults, their spatial position could be determined to within 15 nm indicating the spatial resolution of the method. A spectral

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shift of the emission energy under the high excitation in cathodoluminescence was identified.

- Even at room temperature, emission from stacking faults and zincblende segments in GaN could be probed in spatially resolved measurements (spot mode). In spatially integrated spectra, this emission would be a mere shoulder, indiscernible from phonon replicas of the near-band edge emission.
- The location of (In,Ga)N insertions embedded along the axis of GaN nanowires could be identified. For a single nanowire, a direct correspondence to the strain contrast in a transmission electron micrograph could be established.
- Spectral line scans along the axis of nanowires allowed for the distinction between different contributions which would overlap in integral spectra. Namely, luminescence from zincblende segments could be distinguished from the donor-acceptor pair transition, and the (In,Ga)N emission band could be discerned from a weak yellow luminescence in the base of the nanowires.
- Concerning the (In,Ga)N emission band of the nanowires, evidence for a redshift between the lowest and the uppermost insertions was found. Also, a variation of the emission energy between the insertions in different nanowires was observed.

Outlook

At this point, it is appropriate to point out some questions that could become the focus of further studies.

For wurtzite GaAs, the spontaneous polarization has been largely disregarded in the literature. Indeed, the lower ionicity compared with the group-III nitrides implies a lower spontaneous polarization. The recent calculations by Belabbes et al.^[32] have confirmed our assumption in Ref. 201 of a spontaneous polarization opposite in sign and weaker by an order of magnitude for GaAs compared to GaN. In calculations of the band structure, the consideration of this polarization clearly leads to an additional reduction of the transition energies for zincblende quantum wells in wurtzite GaAs (Fig. 5.8). Still, this shift is too small to experimentally confirm the presence of the polarization fields from the luminescence of the random heterostructures of GaAs polytypes investigated in this work. For other III-V semiconductors, the growth of controlled heterostructures has been reported.^[286] Such structures may, in principle, enable an experimental determination of the spontaneous polarization in wurtzite group-III arsenides through a comparison of luminescence spectroscopy with band structure calculations, if the segment thicknesses are known from transmission electron micrographs. At least, it should thus be possible to verify the presence of polarization fields.

However, for other wurtzite semiconductors with a high ionicity and therefore strong spontaneous polarization, such as ZnO or the other group-III nitrides, the procedure employed in this work to obtain a value for the spontaneous polarization should be applicable. Concerning AlN and InN, this approach would be slightly more challenging as their respective emission in the ultraviolet and infrared spectral regions requires dedicated setups for luminescence spectroscopy. To our knowledge, stacking fault emission has been reported for ZnO,^[287] but not for AlN and InN. Nevertheless, a consistent set of experimental values for the spontaneous polarization of all group-III nitrides would be highly desirable. In the meantime, among the available calculations, the recent work of Belabbes et al.^[32] comes closest to the experimental value for GaN. Therefore, their set of values

may be regarded as a sensible choice for situations where different group-III nitrides are involved. The results in Chapter 6 show that zincblende segments in wurtzite GaN act as quite efficient quantum well structures emitting in the spectral range of 3.0–3.4 eV. So far, a control over the growth of these heterostructures has not been achieved. If this control could be attained, devices based on such lattice matched polytype quantum wells in nanowires could be imagined.

The investigation of (In,Ga)N insertions in GaN nanowires has revealed a quite significant scatter in the emission properties from nanowire to nanowire. Some groups have proposed to employ the resulting broad emission band for white light emitting diodes without the need for additional light conversion using a phosphor.^[249,250,288] However, Appendix A has shown that this inhomogeneity of the structures is in fact detrimental for the device performance. Instead, a better homogeneity of the nanowire ensemble than attained by the self-induced growth would be desirable. Selective area growth on predefined templates could be a route to more suitable nanowire ensembles. The interplay of three-dimensional relaxation, polarization fields and lateral depletion fields calls for detailed calculations of the band structure for (In,Ga)N insertions embedded in nanowires. However, the additional influence from carrier localization would not be reflected in such calculations. Even though this work has revealed details on the processes of light emission from nanowire based heterostructures, the luminescence yield could not be quantified by the available methods. This efficiency of the current to light conversion would need further clarification by dedicated measurements in order to pursue the goal of nanowire based light emitting devices.

A. Light emitting diodes based on nanowire ensembles

With their significant savings in power consumption, light emitting diodes based on the group-III nitrides are on the verge to revolutionize the general lighting sector. Different pathways are pursued to increase their efficiency and reduce the production costs. Among these, the integration of light emitting diode (LED) structures in nanowires lifts several constraints of planar growth such as the use of costly substrates and limitations on the color tunability.

LED structures were grown and processed based on heterostructures similar to those described in Chapter 7.^[12,184] However, only about 1% of the nanowires contribute to the observed electroluminescence of this device emitting in the green spectral region.^[184] This appendix is dedicated to an analysis of whether the origin of this low electroluminescence yield lies (i) in the contacting of the nanowires, or (ii) in the internal quantum efficiency of many nanowires being too low to detect their emission. To this end, both electron beam-induced current and cathodoluminescence measurements are employed.

A.1. The LED structure

The nanowire LED was grown by plasma-assisted MBE. Building on the heterostructures described in Chapter 7, a full LED structure was grown. The base was n-doped with Si, followed by an active region of four (In,Ga)N quantum wells, an (Al,Ga)N electron blocking layer and a cap p-doped with Mg.^[12,184] The resulting structure is sketched in Fig. A.1(a). The main segments are discernible in the CL spectral line scan recorded



Figure A.1: (a) Schematic representation of the nanowire-based LED structure. (b) CL spectral line scan acquired at room temperature along the path marked by the arrow on the depicted nanowire from sample *E*. The spectral image is plotted on a logarithmic scale using heat map colors. This measurement confirms the growth sequence; the main segments can be identified as indicated.

A. Light emitting diodes based on nanowire ensembles



Figure A.2: (a) Monochromatic false-color room-temperature CL image superimposed on a cross-sectional SEM image and (b) corresponding EBIC map with color-coded intensity (heat map scale), both under a reverse bias of -3.5 V. The dashed lines indicate the substrate-nanowire (white) and nanowire-top-contact (red) interface. The yellow arrows highlight broken nanowires that do not contribute to the EBIC signal. (c) & (d) CL images of the same region acquired unbiased and under reverse bias, respectively. All images taken on sample *D*.

along the axis of a nanowire from this sample and displayed in Fig. A.1(b). The base is dominated by near-band edge emission at 364 nm indicative of n-type GaN; the active region shows a broad emission band in the green spectral region. Finally, the cap exhibits luminescence peaked at 380 nm that is red-shifted compared to the emission of the n-type GaN as a consequence of the presence of Mg acceptors, i.e. confirming the p-doping of this segment.^[229,265]

This ensemble of nanowires was then processed into an LED device by planarization with spin-on-glass, back-etching to expose the nanowire tips and deposition of a semitransparent Ni/Au front contact as well as a back contact.^[12,184] The current-voltage characteristics and the electroluminescence (EL) data from this device are presented by Limbach et al.^[184] A striking feature in the EL mapping of the device is that only 1% of the nanowires seem to contribute to the EL signal. This low density of electroluminescent spots is congruent with observations by other groups.^[246,250,252]

A.2. Electron beam-induced current measurements

A cross-sectional SEM image of the nanowire-based LED is depicted in Fig. A.2(a). Superimposed is a monochromatic false-color CL image of the emission from the (In,Ga)N/GaN quantum wells recorded in a spectral window of 30 nm centered around 560 nm. This image visualizes the position of the quantum wells along the cross section of the nanowire. Most nanowires emit CL although the intensity varies significantly. This observation will be analyzed in more detail in Fig. A.3.

Our microscope facilitates the simultaneous acquisition of CL and EBIC signals. The EBIC map associated with the same SEM image is depicted in Fig. A.2(b). In EBIC, electron-hole pairs created in or diffusing to the depletion region of the p-n-junction are separated by the electric field. The resulting short-circuit current can be detected through an external current amplifier while the electron beam is scanned across the sample. The nanowires need to be contacted electrically in order to contribute to the EBIC signal. In the color-coded EBIC presented in Fig. A.2(b), the bright stripe in the middle of the

nanowires indicates the position of the p-n junction. An additional, but weaker, EBIC signal can be detected from the region of the top contact implying the presence of a slight band bending at the semiconductor-metal interface. The strong EBIC signal related to the p-n junction directly shows that all nanowires are contacted. Those nanowires not contributing to the EBIC signal in Fig. A.2(b) are broken and thus not connected to the back contact as highlighted by the yellow arrows. Note that a reverse bias of 3.5 V was applied through the current amplifier, which increases the width of the depletion region of the diode. At an acceleration voltage of 8 kV for the electron beam, most of the signal originates from the first row of nanowires. Consequently, the cross-sectional EBIC map directly visualizes that the majority of nanowires is contacted during the device processing.

The quantum well and the p-n-junction compete for the carriers excited by the electron beam. Under reverse bias, the drift of carriers to the contacts induced by the increased electric field dominates over the diffusion to the (In,Ga)N quantum wells. Therefore, only carriers excited directly at the quantum wells contribute to the CL signal, and the spatial resolution of the CL is thus improved as can be seen in the comparison of the CL images in Figs. A.2(c) and A.2(d), which were acquired at a bias of 0 V and -3.5 V, respectively. In the first case, electrons and holes can diffuse to the quantum wells and recombine radiatively even if they are excited by the electron beam outside the active region. In contrast, under reverse bias, the CL signal is only recorded when the electron beam directly excites the quantum wells. Therefore, Fig. A.2(a) precisely reflects the position of the quantum wells in the nanowires. This position coincides with the upper part of the depletion region visualized in the EBIC map.

A.3. Top-view cathodoluminescence maps

Since the contacting of the nanowires during the device processing does not seem to be the origin of the low EL yield for the presented device, the next point to look at is the internal quantum efficiency of the nanowires. To assess the homogeneity of the luminescence independently of the current path, CL is the method of choice. A top-view CL image of the as-grown (unprocessed) nanowire ensemble recorded with a wide spectral bandpass of about 50 nm is presented in Fig. A.3(a). This combination of three false-color images is dominated by luminescent spots with a diameter of 200–500 nm. The spots indicate luminescence centers which collect charge carriers excited by the electron beam. The number density of these spots of about 1×10^8 cm⁻² is one order of magnitude higher than observed in μ EL, but still one order of magnitude lower than the nanowire density. The electron beam interaction volume at an acceleration voltage of 8 kV contributes to the size of the spots. However, the major role in this spatial broadening is carrier diffusion within the partially coalesced p-type cap segment, i.e. between neighboring nanowires. Carriers excited in the cap may diffuse along local minima in the potential landscape to quantum wells even in neighboring nanowires and recombine there radiatively. However, the resulting emission is attributed to the position of the electron beam during their excitation. Recombination centers emitting at lower energies (green and red) typically collect carriers from a larger area, and thus, these spots have a larger diameter than for higher energies (blue). Hence, the CL image presented in Fig. A.3(a) is largely affected by the relaxation of charge carriers into potential minima and does not reflect the capability of the individual active regions to emit light.

The coalescence enabling the carrier diffusion between neighboring nanowires is a re-

A. Light emitting diodes based on nanowire ensembles



Figure A.3: Top-view false-color CL images taken at room temperature of (a) the nanowire-LED sample (unprocessed, sample *E*) and (b) an undoped reference sample (sample *C*). To cover the broad (In,Ga)N contribution, three monochromatic images were superimposed. Additional colors result from an overlap of the monochromatic images. The bandpass regions were slightly adjusted for the two samples to accommodate minor differences in the emission wavelengths of the quantum wells.

sult of the p-type doping with Mg in the topmost segment of the nanowires.^[245,264] Thus, to avoid this carrier diffusion, the CL of an undoped reference sample with similar quantum wells emitting at a slightly shorter wavelength, but with a similar PL intensity under resonant excitation is shown in Fig. A.3(b). Indeed, the spot diameter decreases with the reduced degree of coalescence, and the total number of luminescence spots now agrees fairly well with the nanowire number density. This result shows conclusively that the low percentage of emitting nanowires observed in μ EL is not caused by a low internal quantum efficiency for the majority of the nanowires.

At the same time, the emission intensity of a few nanowires is significantly higher than the mean, and their number density is similar to the one observed in Fig. A.3(a). Of course, differences in the internal quantum efficiency of individual nanowires will occur in a self-induced nanowire ensemble, in which fluctuations of the quantum well thickness and In content from nanowire to nanowire are essentially inevitable (cf. Chapter 7). However, an effect just as inevitable for a random array of nanowires is the fluctuation of the extraction efficiency. Whether we view the nanowire ensemble as a disordered photonic crystal in which multiple light scattering contributes to light extraction^[289,290] or as an inhomogeneous effective medium in the limit of very small nanowire dimensions and distances^[291] does not change the result: the spatially random arrangement of dielectric cylinders results in areas of incidentally enhanced extraction efficiency. A closely related subject is the random lasing observed upon optical pumping for GaN nanowire ensembles in which spatial light localization occurs by chance.^[292,293]



Figure A.4: Sketch to illustrate the filamentation of the current flow as a result of the inhomogeneity of the nanowire ensemble. The shades of blue indicate differences in the doping and thus in the series resistance. The SiN interlayer at the substrate interface acting as a tunnel barrier is represented by black bars. The current (red arrow) chooses the path of lowest series resistance and lowest tunnel barrier.

A.4. Conclusions

Summarizing the experimental results presented above, it can be ruled out for the investigated device that a large number of the individual nanowire LEDs is either not contacted or not able to emit light. Therefore, in an array of single nanowire LEDs contacted in parallel, a large inhomogeneity in local current densities in the individual nanowires must exist to explain why only so few nanowires contribute to the EL emission. This filamentation of the current flow is probably the decisive factor in determining how many nanowires contribute to the EL of the overall device. The situation for our case is sketched in Fig. A.4 where several factors can contribute to the filamentation. First, the self-induced growth of GaN nanowires on Si(111) leads to the formation of an amorphous SiN interlayer between substrate and nanowire, [181,294] which acts as a tunnel barrier. Fluctuations in thickness of this tunnel barrier from nanowire to nanowire can have a profound impact on the current flowing through the individual nanowires. Second, a variation of the doping of the nanowires and therefore of their individual series resistances is likely and would also contribute to such a filamentation of the current flow. Finally, the current densities of neighboring nanowires will not be independent, and nanowires carrying a high current density will likely be surrounded by nanowires with low current densities.

This highlights a problem inherent to devices based on nanowire ensembles in general. However, the inhomogeneity of self-induced GaN nanowire ensembles makes it even more pronounced. This necessitates the use of more homogeneous nanowire ensembles. Therefore, the use of selective-area grown nanowires would be desirable for further studies on device applications.

B. Additional CL spectral line scans for the GaN microcrystals

Complementary to the results presented in Chapter 6, this appendix shows CL results for two additional microcrystals from the same sample. Fig. B.1 displays another CL spectral map recorded along a line on the cross section of a microcrystal together with monochromatic CL images of this cross section superimposed on an SEM image. These measurements again demonstrate that the different peaks related to stacking faults originate from a single microcrystal, e.g. in μ PL, originate from different positions along the cross section of the crystal. In cross-sectional CL images (non-polar plane), the emission related to stacking faults or bundles of these shows a characteristic elongation along the basal plane. Their corresponding emission peaks in the spectral map are indicated by the horizontal arrows. Hardly any near-band edge luminescence is observed in the spectral map of the investigated crystal, while the emission from the stacking faults is quite intense, which highlights the efficient collection of charge carriers by the stacking faults.

Another such CL spectral map from a different microcrystal is shown in Fig. B.2 to demonstrate that emission down to 3 eV can be observed from zincblende segments in the investigated microcrystals. For these rather thick zincblende segments, the blueshift of the emission energy arising from a partial screening of the spontaneous polarization field in the heterostructure can amount to 80–90 meV.



Figure B.1: (a) CL spectral line scan along the cross section of another GaN microcrystal revealing luminescence from stacking faults and zincblende segments of different thickness. The CL intensity is color-coded on a logarithmic scale (heat map). (b) Corresponding SEM image of the GaN microcrystal with the path of the line scan marked by the dashed arrow. Superimposed are monochromatic false-color CL images recorded at the indicated detection energies. The corresponding emission peaks in the line scan are highlighted by horizontal arrows.

B. Additional CL spectral line scans for the GaN microcrystals



Figure B.2: CL spectral line scan from the cross section of a different GaN microcrystal and corresponding SEM image with the path of the scan marked by a dashed arrow. The CL intensity is color-coded on a logarithmic scale (heat map). Emission ranging down to 3.0 eV, corresponding to cubic segments of about 3 nm thickness, is observed. The blueshift resulting from the field screening under direct CL excitation can reach up to 80–90 meV.

C. Spontaneous polarization in the context of a point charge model

The derivation of Eq. (2.1) from a point charge model as proposed by Jerphagnon and Newkirk^[31] is briefly reviewed in this appendix. The sketch in Fig. C.1 shows the tetrahedral unit cell with the cation carrying a charge Q and the anions carrying the charges q_1 and q_2 .

The unit volume $\Omega = \sqrt{3a^2c/4}$ is marked by the grey box. Considering only the polar z-direction (the other components cancel each other), the distance from Q is $d_1 = uc$ for q_1 and $d_2 = -(c/2 - uc)$ for the q_2 . To satisfy the charge neutrality, $Q + q_1 + 3q_2 = 0$ must hold. Then the spontaneous polarization P_{sp} , defined as the dipole moment p = qd per unit volume, becomes

$$P_{\rm sp} = \frac{qd}{\Omega} = \frac{q_1d_1 + 3q_2d_2}{\Omega} = \frac{4}{\sqrt{3}a^2}[q_1u + 3q_2(u - 1/2)].$$
 (C.1)

For zincblende or an ideal wurtzite structure with u = 3/8 and $q_1 = q_2$, P_{sp} vanishes. Assuming that no quadrupole moments result from the slight deformation of the wurtzite tetrahedra, $q_1 \simeq q_2$ and Eq. (C.1) can be rewritten as^[31]

$$P_{\rm sp} = \frac{-4Q}{a^2\sqrt{3}} \left(u - \frac{3}{8}\right) \tag{C.2}$$

The remaining question is how to define the cation charge Q. This issue has been



Figure C.1: Point charge model of the tetrahedral unit cell with the cation carrying a charge Q and the anions carrying the charges q_1 and q_2 . The unit volume is indicated by the gray box. The dashed arrow signifies the displacement of the cation and anion along the polar axis from their ideal positions in a tetrahedron.

C. Spontaneous polarization in the context of a point charge model

resolved by Bechstedt et al.^[234] by taking $q_1 = eg_{\parallel}$ and $q_2 = eg_{\perp}$ in Eq. (C.1). The ionicity of the bonds is described via the charge asymmetry coefficients g_{\parallel} and g_{\perp} for the two different bonds, and e is the electron charge. For the wurtzite, structure the values of g deviate slightly from those of the zincblende structure, first introduced by García and Cohen^[295]. Using this approach, Belabbes et al.^[32] obtained a fair agreement between $P_{\rm sp}$ from the point-charge model and values calculated using density functional theory.

D. Poisson-Schrödinger calculations

At various points of this thesis, the band profile of heterostructures is calculated employing a self-consistent effective-mass Poisson-Schrödinger solver. To this end, the *1D Poisson* freeware written by Greg Snider of the University of Notre Dame is used.^[209] The numerical routines allowing for a nonuniform mesh used by this software are described by Tan et al.^[296] Note that in this framework electrons and holes are calculated independently and, therefore, excitonic binding energies (where applicable) are not included.

The parameters used in the band structure calculations are summarized in the following for the different material systems.

GaAs polytypic heterostructures

For GaAs, the wurtzite conduction band offset with respect to zincblende GaAs is assumed to be $\Delta E_C = +149 \text{ meV}$,^[71] and the experimental value found in Section 5.3 as the lower bound of the difference $E_g^{WZ} - E_g^{ZB}$, i.e. 55 meV, is taken into account. Standard values for the effective masses and for the dielectric constant are employed: $m_e^* = 0.063m_0$, $m_{hh}^* = 0.51m_0$, $m_{lh}^* = 0.082m_0$ and $\epsilon = 12.9$.^[29]

Stacking faults in GaN

For ZB/WZ heterostructures in GaN, the standard effective masses and dielectric constant of the wurtzite phase are applied to both polytypes: $m_e^* = 0.2m_0$, $m_{hh}^* = 1.6m_0$, $m_{lh}^* = 0.15m_0$ and $\epsilon = 9.5$.^[138] Reported values for the zincblende phase show a deviation among different studies, which is as large as their difference to the well established values of the wurtzite phase.^[138,297,298]

The low temperature band gaps^[297] of the two phases were corrected by the exciton binding energy of wurtzite bulk GaN to account for the excitonic nature of the investigated transitions and therefore set to $E_g^{ZB} = 3.27$ eV and $E_g^{WZ} = 3.48$ eV. Recently published calculations^[84] confirm the assumptions that the exciton binding energy for thin zincblende quantum wells in a wurtzite matrix is similar to that of bulk wurtzite (26 meV) and changes only insignificantly with zincblende thickness. These calculations resulted in deviations of no more than 4 meV for a thickness range of 0–2.5 nm at polarization fields of 2.5 MV/cm (as determined in this work).

Concerning the band alignment, there is a disagreement in the literature. Stampfl and Van de Walle^[65] give $\Delta E_C = 270$ meV corresponding to a type-II band alignment, while recently Belabbes et al.^[79] published a value of $\Delta E_C = 150$ meV corresponding to a type-I band alignment. Therefore, we performed the calculations for both band offsets.

(In,Ga)N/GaN heterostructures

As input for (In,Ga)N/GaN heterostructures, the standard effective masses and dielectric constant of GaN ($m_e^* = 0.2m_0$, $m_{hh}^* = 1.6m_0$, $m_{lh}^* = 0.15m_0$ and $\epsilon = 9.5$)^[138] were

D. Poisson-Schrödinger calculations

employed across the whole range of In compositions. This choice reflects the fact that the values for GaN are well established, while reported values for InN show a larger spread,^[298,299] and the bowing of these parameters for intermediate compositions is not clear.

For the bowed band gaps, the values at room temperature values published by Schley et al.^[284] are used, i.e.

$$E_g(x) = 3.45(1-x) + 0.68x - 1.72x(1-x).$$
 (D.1)

Note that in Eq. (7.8) these values were adapted to low-temperature band gaps. The ratio of the band offsets $\Delta E_V / \Delta E_C = 21/79$ is taken from King et al.^[300] and is assumed to stay constant over the whole compositional range, while a nonlinear bowing of ΔE_C similar to that of E_g is chosen. This yields a trend that agrees well also with calculations by Moses and Van de Walle.^[301]

Finally, the bowed polarization values of Fiorentini et al.^[41] were included by a quadratic fit to $P = P_{sp}^{In_{1-x}Ga_xN} + P_{pz}^{In_{1-x}Ga_xN}$ with

$$P_{\rm sp}^{\rm In_{1-x}Ga_xN} = -0.042x - 0.034(1-x) + 0.038x(1-x), \tag{D.2}$$

$$P_{\rm pz}^{\rm In_{1-x}Ga_xN} = x(-1.982\varepsilon(x)^2 - 0.455\varepsilon(x)) - 0.918\varepsilon(x) + 9.541\varepsilon(x)^2, \tag{D.3}$$

$$\varepsilon(x) = (-0.034955x)/(0.31876 + 0.034955x).$$
 (D.4)

For the case of the nanowire heterostructure calculated in Section 7.2.2, the piezoelectric polarization P_{pz} was reduced to 85% of its full value to reflect the finite element calculations in Section 7.2.1. Note that improved values for P_{sp} of the group-III nitrides have been reported recently.^[32] However, for the case of (In,Ga)N, P_{pz} is the more decisive factor and, therefore, the consistent set of values from Ref. 41 was used.

E. List of investigated samples

Table E.1: List of nanowire samples investigated in this thesis. All samples were grown on Si(111) substrates at the Paul-Drude-Institut für Festkörperelektronik in Berlin using molecular beam epitaxy (MBE). The column *growth run* denotes the running numbers of the samples grown in the respective *MBE* systems. In the text, the specified short identifier (ID) is used, when several samples are discussed in one chapter. When more than one value is given for the flux ratio and substrate temperature (T_{sub}), the first value corresponds to the base nanowire and the second one to the overgrowth or (In,Ga)N insertions.

MBE	Growth run	ID	Material/ geometry	V/III flux ratio	T _{sub} (°C)	Overall length/ thickness	NW density (cm ⁻²)
Section 3.3.4							
M8	m81087		GaN	5.1	780	570 nm	$1 imes 10^{10}$
Chapter 5							
M6	m6835	#Ref	GaAs Au induced	2	500	1.5µm	$7 imes 10^8$
M6	m6967	#1	GaAs/(Al,Ga)As core shell	1	580	10.5 µm	6×10^7
M6	m6966	#2	GaAs/(Al,Ga)As core shell	2	580	8.5 μm	6×10^7
Chapter 6							
M9	m9314		GaN NWs	3	800	1.9 µm	$5 imes 10^9$
			& overgrowth	0.75	740		
Chapter 7							
M8	m81310	Α	GaN/(In,Ga)N	8.7	780	500 nm	$6 imes 10^9$
			insertions	10	605		
M8	m8872	В	GaN/(In,Ga)N	7.6	778	500 nm	7×10^{9}
			insertions	11.8	617		
Appendix A							
M8	m81109	С	GaN/(In,Ga)N	5.1	780	750 nm	$2 imes 10^9$
			insertions	8.2	578		
M8	m81133	D	GaN/(In,Ga)N	5.1	780	750 nm	2×10^9
			LED (no EBL [†])	8.2	604		0
M8	m81146	Ε	GaN/(In,Ga)N	5.1	780	750 nm	2×10^{9}
			LED	8.2	604		

⁺ electron blocking layer

F. Conditions for cathodoluminescence measurements

Table F.1: Summary of the conditions used for the cathodoluminescence (CL) measurements presented in this thesis. For each figure including CL data, the measurement temperature as well as the beam parameters and spectrometer settings are summarized (cf. discussion in Section 3.3.2).

Figure	Т	$V_{\rm acc}$	Aperture	Slits	Grating, blazed at
	(K)	(keV)	(µm)	(mm)	(l/mm @ nm)
3.10	10	3	60 HC	0.25	1200 @ 500
3.11	10	3	60 HC	0.5	1200 @ 500
3.12	300	5	60 HC	0.1	300 @ 500
3.12-inset	300	5	60 HC	0.5	1200 @ 500
3.13	300	5	120 HC	0.5	1200 @ 500
5.4	10	3	60 HC	0.3	1200 @ 500
5.5(a)&(c)	10	5	30 HC	0.1	1200 @ 500
5.5(b)&(d)	10	5	30 HC	0.3	1200 @ 500
5.6 [‡]	300	3	5 nA	0.1	150 @ 300
6.2(b)&(c)	10	2	60 HC	0.1	1200 @ 500
6.3(a), 6.4(a), 6.5	10	3	60 HC	0.25	1200 @ 500
6.9	300	5	60 HC	1	1200 @ 500
7.1(a)	300	5	60 HC	1.0	300 @ 500
7.1(a)	10	3	60 HC	0.05	300 @ 500
7.1(b)	300	8	60 HC	5.0	300 @ 500
7.2(a)	300	5	60 HC	0.5	300 @ 500
7.2(b)	10	3	60 HC	0.2	300 @ 500
7.3	300	5	60 HC	0.5	300 @ 500
7.5, 7.6(a), 7.7(a), 7.8	10	3	60 HC	0.2	300 @ 500
7.11(a)	300	5	60 HC	0.5	1200 @ 500
7.11(a)–inset	300	3	60 HC	2	1200 @ 500
7.15(a)	300	5	60 HC	10	1200 @ 500
7.15(c), 7.16	10	3	60 HC	0.5	1200 @ 500
A.1(b)	300	5	60 HC	0.3	300 @ 500
A.2(a)& (c)& (d)	300	8	120 HC	5	300 @ 500
A.3	300	8	60 HC	5	300 @ 500
B.1(a), B.2(a)	10	3	60 HC	0.25	1200 @ 500

[‡] Measured at a different CL setup from the same manufacturer, by courtesy of David Stowe. Therefore, a beam current from the SEM is given in place of the aperture value usually reported.

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Selbständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe.

Berlin, den 02.05.2013

Jonas Lähnemann