MASTER

(In,Ga)N heterostructures in self-assembled GaN nanowires grown on TiN by molecular beam epitaxy

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Abstract

Semiconductor nanowires are promising candidates for future applications in opto-electronic devices and therefore have been the focus of intensive research over the last years. The topic of this thesis is the growth of (In,Ga)N heterostructures in self-assembled GaN nanowires on TiN by molecular beam epitaxy. Significant progress has been made in this field in the last years, but mainly based on (In,Ga)N/GaN NW ensembles on silicon. However, even for the established growth on Si, most of the fundamental physics of these structures is still poorly understood and the development of such NW technologies is still in its early stage. In this thesis two studies are carried out, concerning the growth of axial and radial (In,Ga)N heterostructures on thin and well-separated GaN NWs. The first atom-probe-tomography (APT) results on such NW heterostructures is a key novelty of this thesis as well. In general, the aim was to obtain a better understanding of the fundamental processes going on during growth and investigate the structural and optical properties of the NW heterostructures.

In the first study, we have obtained axial (In,Ga)N/GaN NW heterostructures on TiN grown by molecular beam epitaxy. These NWs are thin, uncoalesced and show a well-defined morphology after (In,Ga)N growth of the active region. The (In,Ga)N QWs show as well a structure which is well-defined having sharp interfaces with a disk-like morphology. This achievement is a good basis for fundamental investigations of the formation and strain relaxation of such structures. At the same time, the emission properties of these heterostructures do not seem to be influenced much by the growth parameters. These growth experiments have led to the first atom-probe-tomography measurements on axial (In,Ga)N/GaN NW heterostructures, which paves the way to an in-depth analysis of the In distribution in such structures. Compositional analysis shows an average In content in the QWs between 15 and 30% as measured by high-resolution transmission electron microscopy (HRTEM) and 17% as measured by APT. However, we have to be aware of the low statistics and NW to NW fluctuations.

For the second study, GaN/(In,Ga)N core-shell heterostructures were attempted to be grown under various growth conditions. In all the samples, shell growth was obtained to a greater or lesser extent. The NW morphology showed a widening of the NW diameter at the top for the NWs grown under locally metal-rich conditions, whereas the NW defined shape remained after (In,Ga)N growth under N-rich conditions. Calculations showed that the NWs are partly shadowed from nearest neighbours, however not enough to hamper shell growth. From the emission spectra obtained in NW ensemble room-temperature photoluminescence measurements as well as single-wire low-temperature cathodoluminescence measurements, the presence of In in the shell could not be observed. Therefore, we have to conclude that it is very difficult and not realized so far to incorporate In in a shell for GaN/(In,Ga)N core-shell NW heterostructures. The systematic growth experiments aiming at (In,Ga)N shell growth around very thin GaN NWs have demonstrated the strong influence of sidewall diffusion, which complicates the In incorporation at the NW sidewalls.
Abstract
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>cathodoluminescence</td>
</tr>
<tr>
<td>DX</td>
<td>donor-bound exciton</td>
</tr>
<tr>
<td>$E_{g}^{WZ,ZB}$</td>
<td>band gap energy of the wurtzite or zinc-blende phase</td>
</tr>
<tr>
<td>FX</td>
<td>free exciton</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>LED</td>
<td>light-emitting diode</td>
</tr>
<tr>
<td>PA-MBE</td>
<td>plasma-assisted molecular beam epitaxy</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>NW</td>
<td>nanowire</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>$P_{sp}$</td>
<td>spontaneous polarization</td>
</tr>
<tr>
<td>$P_{pz}$</td>
<td>piezoelectric polarization</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high-energy electron diffraction</td>
</tr>
<tr>
<td>QCSE</td>
<td>quantum-confined Stark effect</td>
</tr>
<tr>
<td>QW</td>
<td>quantum well</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SF</td>
<td>(basal plane) stacking fault</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>VLS</td>
<td>vapor-liquid-solid</td>
</tr>
<tr>
<td>WZ</td>
<td>wurtzite</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffractometry</td>
</tr>
<tr>
<td>ZB</td>
<td>zincblende</td>
</tr>
</tbody>
</table>
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1. Introduction

Booming integrated circuit technologies based on semiconductors have been accomplished during the past five decades resulting in electronic devices with higher integration densities and a reduced energy consumption. The scientific world as well as industry have been continuously pushing the limits of the conventional silicon-based semiconductor devices. However, at a certain point the physical limits of these concepts are reached and technological and fundamental challenges have to be overcome. A route to overcome these difficulties is to employ structures with their size in the range of 1 - 100 nm at least in one dimension, the so-called ‘nanostructures’ \[^1\]. One approach to integrate new designs of nanostructures with a high-quality material in semiconductor devices, are nanowires (NWs). The growth of semiconductor crystals in the shape of a nanowire, with diameters in the order of 10 to 100 nm and lengths in the order of \(\mu\)m, was reported already in the 1960’s \[^2\], but nanowires were not envisioned as building blocks for devices until the 1990’s \[^3\]. The possibility to grow high quality crystals on foreign substrates, the large surface-to-volume ratio and size effects resulting in unique quantum-mechanical and electrostatic properties, make NWs very interesting candidates for future technologies and devices.

One important research field is the integration of III-nitride structures in semiconductor devices like LEDs \[^4\]. GaN-based LEDs are usually fabricated by growing thin films of GaN and (In,Ga)N alloys onto foreign substrates \[^5\]. The importance of GaN-based LEDs was quite recently emphasized by the awarding of the Nobel Prize in Physics 2014 "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources" to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura. Despite the tremendous progress in this field during the last years, conventional planar (In,Ga)N/GaN structures are still facing high dislocation densities and a rapidly decreasing efficiency for emission wavelengths in the green spectral range. Hence, innovative approaches are required. Due to their properties, nanowires might not only allow the growth of high quality structures on silicon, but they can also be grown on a wide variety of substrates as for instance on metals like titanium-nitride (TiN), without unfavorable effects for their optical and structural properties. Consequently, GaN nanowires have attracted great interest for the fabrication of nanoscale devices such as light emitters, solar water splitting cells, chemical sensors and photovoltaic cells on inexpensive and large area substrates \[^1\][\(^6\)][\(^7\)][\(^8\)]. However, the development of (In,Ga)N/GaN NW based devices is hampered by the still incomplete understanding of the fundamental physics and growth control of these structures.

This thesis contains two main studies making use of the self-assembled growth of GaN nanowires on TiN. These nanowire ensembles are used as a starting point for the growth of (In,Ga)N/GaN axial and core-shell heterostructures by molecular beam epitaxy (MBE).

First, in the second chapter some general concepts of semiconductor physics as well as the GaN/(In,Ga)N material system will be introduced. In addition, the established growth of GaN NWs on TiN will be introduced as a starting point for the growth of (In,Ga)N heterostructures in GaN NWs in the follow-up chapters. The key benefits of this approach, the growth on TiN, to the growth of NW heterostructures are the formation of
1. Introduction

rather thin, uncoalesced and well-separated NWs in a self-assembled way. So far, there have no reports been found in literature on the growth of such NW heterostructures by MBE.

In the third chapter, the growth of axial (In,Ga)N/GaN NW heterostructures will be discussed. The main goal of the growth of these NW structures is to study their structural and compositional properties by atom probe tomography (APT). These heterostructures are grown for the first time in rather thin, uncoalesced and well-separated NWs, with the aim to obtain better structural properties as seen in previous samples. Furthermore, APT results on (In,Ga)N/GaN NW heterostructures have not been reported in literature so far and thus will be shown for the first time. For this purpose, a temperature series of axial (In,Ga)N/GaN NW heterostructures is grown and subsequently the structural and optical properties are investigated.

The MBE growth as well as the morphology and optical analysis of the nanowires in this thesis was carried out at the Paul-Drude-Institut für Festkörperphysik (PDI) in Berlin, Germany. The structural and compositional analysis by APT was done at the Eindhoven University of Technology (TU/e). The majority of this thesis was carried out at PDI.

The fourth chapter contains the growth and characterization of GaN/(In,Ga)N core-shell NW heterostructures. The larger surface in comparison to planar structures is an important advantage in order to exploit an enhanced emission. In literature, only shell growth by both MBE and MOCVD around fairly thick GaN NW cores was reported in the past. The growth of core-shell NWs requires well-separated nanowire arrays. As we will see, this can be achieved under certain growth conditions for GaN NW ensembles on TiN, which is the main reason for growing on this metal. We first attempt to grow a well-defined shell around the rather thin and spontaneously grown GaN NWs, by exploring several growth conditions for shell growth, for different growth temperatures and V/III ratios. In addition to shell growth, the incorporation of In in the shell is a main goal for these growth experiments. By analyzing the final NW morphology and carrying out photoluminescence as well as cathodoluminescence experiments, (In,Ga)N shell growth is investigated.
2. The (In,Ga)N material system for nanowires

In the following chapter some general concepts of semiconductor physics as well as the GaN/(In,Ga)N material system will be introduced. Furthermore, the growth of GaN-based nanowires will be introduced and the conceptual advantages of NWs over planar films as well as possibilities towards new opto-electronic application will be discussed. Towards the end of this chapter, the established growth of thin and well-separated nanowires on titanium nitride will be presented, used as a starting point for the growth of (In,Ga)N nanowire heterostructures in Chapter 3 and 4.

2.1. Semiconductor materials

Semiconductor materials are widely studied because of their specific and very useful electrical and optical properties. A large range of devices is based on semiconductors, such as transistors, switches, diodes, detectors, photovoltaic cells and light emitting diodes (LEDs)\textsuperscript{[1]}. New applications of semiconductors can be found nowadays even in quantum cascade lasers\textsuperscript{[6][7]} and solar water splitters\textsuperscript{[8]}.

In a classical way, a semiconductor material at zero Kelvin has a fully filled valence band up to the energy $E_v$ and empty conduction band, which makes it an insulator at very low temperatures. As the temperature is increased, states in the conduction band above the conduction energy level $E_c$ will be filled and states in the valence band become vacant which is also shown in Fig. 2.1. These thermally excited electrons from the valence band to the conduction band, where they become mobile, are called the "intrinsic" carriers. Therefore, the intrinsic conductivity and carrier concentration are largely controlled by the Boltzmann factor $E_g/k_b T$, the ratio of the band gap energy ($E_g = E_c - E_v$) over the temperature. A large ratio means that the intrinsic carrier concentration is low and consequently the conductivity\textsuperscript{[10]}.

![Figure 2.1: Band diagram for an intrinsic semiconductor. At 0 K (a) the conductivity is zero because of all states in the valence band are filled and all states in the conduction band are vacant. As the temperature is increased (b), electrons are thermally excited from the valence into the conduction band, where they become mobile. Such carriers are called ‘intrinsic’.](image-url)

The band structure of a semiconductor determines if radiative recombination of elec-
2. The (In,Ga)N material system for nanowires

trons and holes is a likely process. Since the dispersion relation of electrons and holes is parabolic, as shown in Fig. 2.2, electrons will thermalize to the minimum of the conduction band and holes to the maximum of the valence band. During this process, the free electrons and holes attract each other by the Coulomb force, and eventually form quasiparticles of excitation, called excitons. Excitons in III-V and II-VI semiconductors have typically a low binding energy and thus a large radius, which means their wavefunction extends over many unit cells of the crystal. These excitons can move freely inside an ideal crystal and are called Wannier excitons\(^{[11]}\). The total energy of the exciton in the \(n\)th state in momentum space (\(k\)-space) is given by\(^{[12]}\)

\[
E = E_g + E_{\text{kin}} - E_{\text{FX}} = E_g + \frac{\hbar^2 k^2}{2(m_e^* + m_h^*)} - \frac{\mu e^4}{32\pi^2 \hbar^2 e^2 n^2}.
\]

Here, \(E_{\text{kin}}\) denotes the kinetic energy of the exciton and \(E_{\text{FX}}\) the reduced exciton binding energy, with \(\mu\) the reduced exciton mass, \(\hbar\) the Planck constant divided by \(2\pi\), \(k\) the wavevector and \(m_e^*, m_h^*\) the effective mass of the electrons and holes resp. Using isotropic masses \(m_e^* = 0.2m_0, m_h^* = 1.1m_0\) and a dielectric constant \(\epsilon = 9.5\) for GaN, we find \(E_{\text{FX}} = 25\) meV\(^{[5]}\)\(^{[12]}\).

Besides thermally excited electrons in the conduction band, it is also possible to excite electrons to higher states by absorption of photons (optical absorption). Two processes can be distinguished, namely direct absorption and indirect absorption as shown in Fig. 2.2a and b, respectively\(^{[10]}\)\(^{[13]}\). It depends on the energy landscape of the material if direct or indirect absorption is likely to happen. The (In,Ga)N material systems always have a direct bandgap which is needed for optical applications\(^{[5]}\).

![Diagram of direct and indirect optical absorption](image)

**Figure 2.2:** Direct (a) and indirect (b) absorption processes in a semiconductor material. For optical applications, a direct bandgap material is needed. The indirect bandgap material only absorbs (or emits) lights with the help of e.g. phonons. Thus transitions occur generally between almost all points of the two bands for which the wavevectors and energy can be conserved.

In a direct bandgap semiconductor, Fig. 2.2a, the maximum of the valence band and the minimum of the conduction band have the same \(k\)-value in the reciprocal space (\(k\)-space). For indirect bandgap semiconductors, Fig. 2.2b, these two points are shifted relative to each other by a substantial wavevector \(k_p\) which can be called the phonon wavevector. Here a direct photon transition at the energy of the minimum gap cannot satisfy the requirement of conservation of wavevector, because photon wavevectors are negligible at the energy range of interest. But as noted, if a phonon of wavevector \(k_p\) and frequency
2.1. Semiconductor materials

$\omega_p$ is created in the process, then it is possible to have:

$$k_{\text{photon}} = k_{\text{gap}} + k_{\text{phonon}} \approx 0.$$

(2.2)

as required by the conservation law and shows immediately the origin for the need of a direct bandgap material in optical applications.

As mentioned, electron-hole pairs can be created by photoexciting the semiconductor, which is done in photoluminescence spectroscopy (PL). The PL experiments are used as characterization tool in this thesis to analyze the optical properties of the grown nanowire ensembles.

For nanowire LED devices, it is of great importance to improve the light-output intensity. To do so, the semiconductor structure possesses one or more quantum well(s) (QWs) in the so-called ‘active region’ and the heterostructure is formed. The QW is formed by introducing a material of lower bandgap; in a GaN-based nanowire LED this is typically In$_x$Ga$_{1-x}$N. The heterostructure creates an energy potential well for the carriers to be trapped into. This drastically increases the carrier density and thus recombination efficiency $R$, since $R \propto np$, with $n$ and $p$ the negative and respectively, positive charge carrier densities. For deeper wells, more carriers are captured into the QW and the light output is increased\cite{14}. High In concentrations lead to deep QWs and thus brighter emission. In Fig. 2.3 the bandstructure of a QW is shown, as well as the carrier distribution in the conduction band within the QW.

![Figure 2.3: Carrier distribution in the conduction band of a QW with barrier height $\Delta E_C$. A double heterostructure active region can form a quantum well (QW).](image)

The efficiency of light (photon) creation in the active region depends on the carrier capture in the QW. Fig. 2.3 also shows the carrier distribution in the conduction band within the QW.

The (layer) growth and e.g. LED fabrication of different materials with various bandgap energy in order to create a heterostructure, have to be obtained by successive epitaxial crystal growth. Two well-known and established methods for the growth of crystal heterostructures are metal-organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE)\cite{15}. In one of the upcoming sections, the MBE growth will be discussed in more detail, as it is the growth technique used in this thesis.
2. The (In,Ga)N material system for nanowires

2.2. Properties of III-nitrides

The III-V compound semiconductor crystals are often used in applications due to their beneficial optical and electrical properties. For optoelectronics a direct bandgap material is essential, making widely used Si having an indirect bandgap not suitable for optoelectronic devices.[14]. In this regards, III-V compound semiconductors are dominating due to their direct bandgap and flexibility in band gap and lattice engineering. Especially optical applications (e.g. LEDs) are of interest since a suitable electronic band structure fitting the application can easily be found. In Fig. 2.4 the bandgap as a function of the lattice parameter is shown. While changing the composition of the material the lattice constant changes and therefore the bandgap \( E_g \) can be tuned. The spectral range reaches from the near-ultraviolet (UV) to the near-infrared (IR) as shown in Fig. 2.4, with GaN having a bandgap of \( \sim 3.4 \, \text{eV} \) and InN \( \sim 0.7 \, \text{eV} \).[5] [16]. Since \( \text{In}_x\text{Ga}_{1-x}\text{N} \) is able to cover this wide range of wavelengths, it makes the material extremely interesting for LED devices and laser applications in the visible range[17][16].

Figure 2.4: Bandgap as a function of the lattice constant for different compound semiconductors. The (In,Ga)N material system can be found more towards the left, ranging from about 0.7 to 3.4 eV. Image replotted from Ref.[18]

In this thesis the focus will be on GaN and \( \text{In}_x\text{Ga}_{1-x}\text{N} \) with \( x \) the relative In content in the material. Therefore, in the following parts the main discussion will cover these materials and other nitride compositions will be left out.

For group III nitrides it is possible to appear in the hexagonal \textit{wurtzite} (WZ) or cubic \textit{zinc blende} (ZB) crystal structure (i.e. \( \alpha \)-GaN and \( \beta \)-GaN respectively). Under ambient conditions the thermodynamically stable one is the wurtzite structure for bulk GaN and InN[5][19]. In general all the nanowires examined in the scope of this work are crystallized in the WZ structure. However, as we will see later on, during the growth of (In,Ga)N it is possible that material in the cubic phase is formed[5][12] and we will mention explicitly if the discussion also includes ZB material.

The wurtzite structure has a hexagonal unit cell which can be described by the lat-
2.2. Properties of III-nitrides

(a) GaN wurtzite structure with highlighted C- and A-plane. Representation of the two different polarities along the c-axis, (b) Ga-polarity and (c) N-polarity. Images taken from Ref.[5].

Figure 2.5: (a) GaN wurtzite structure with highlighted C- and A-plane. Representation of the two different polarities along the c-axis, (b) Ga-polarity and (c) N-polarity. Images taken from Ref.[5].

Table 2.1: Theoretical calculated and experimentally obtained lattice parameters for GaN and InN[5].

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal a [Å]</td>
<td>3.199</td>
<td>3.199</td>
</tr>
<tr>
<td>Exp. a [Å]</td>
<td>3.199</td>
<td>3.585</td>
</tr>
<tr>
<td>Ideal c/a</td>
<td>1.633</td>
<td>1.634</td>
</tr>
<tr>
<td>Exp. c/a</td>
<td>1.633</td>
<td>1.618</td>
</tr>
</tbody>
</table>

The lattice constant changes gradually with varying indium composition of the alloy, as shown in Fig. 2.4 and Table 2.1. When growing epitaxially materials of different indium composition, the lattice mismatch induces strain in the heterostructure which has consequences for the indium incorporation and can lead to unwanted defects[20]. Furthermore, the In incorporation also depends on the different crystal facets[21][22]. Since the wurtzite structure has no inversion plane perpendicular to the c-axis, the crystal structure in the ⟨0001⟩ direction is different than in the ⟨000¯1⟩ direction. In Fig. 2.5 and c this difference in polarity is shown. The two different polarities are called Ga-polar in the ⟨0001⟩ direction and N-polar in the ⟨000¯1⟩ direction. Due to the big difference in electronegativity of Ga and N, this specific configuration induces a spontaneous polarization field \( P_{sp} \) along the c-axis of the crystal[5][23]. Laehnemann et al.[24] determined experimentally a value of \( P_{sp}^{GaN} = -0.022 \pm 0.007 \) C/m² in relaxed GaN.

Besides this spontaneous polarization, another polarization called piezoelectric polarization \( P_{pz} \) is present. This \( P_{pz} \) is induced by strain, for instance at the hetero-interfaces.
2. The (In,Ga)N material system for nanowires

between GaN and InGaN in quantum well structures. Since the In\(_x\)Ga\(_{1-x}\)N QWs are compressively strained, \(P_{yy}\) and \(P_{pz}\) are opposite in sign. The resulting polarization is dominated by the strong piezoelectric fields \(P_{pz}\) since the lattice constants of GaN and InN have a mismatch of about 11\%\[5\]. This leads to an internal field in the \(\langle 000\bar{1} \rangle\) direction for the Ga-polar case as sketched in Fig. 2.6c and modifies the electronic band structure\[25\].

2.2.1. Optical properties

Light emission from the In\(_x\)Ga\(_{1-x}\)N alloy depends on the available optical transitions. Confinement of charge carriers in the QW, called quantum confinement, can separate the electron and hole energy states by more than the bandgap \(E_g\) as shown in Fig. 2.6a. It implies that the energy states are quantized within the well, which means that the ground state for electrons lies a bit above the conduction band and for the holes a bit below the valence band, inducing a blueshift of the emission wavelength\[13\][14].

The exact photon energy depends also on the type of e-h recombination. At low temperatures, excitonic recombination is dominant, and the photon energy is the bandgap energy less the exciton binding energy. It can be bound to an impurity, such as a donor, which will further reduce the optical transition energy. The luminescence behaviour at low temperatures is irrelevant for LED operation, but can be used for sample characterization as we will see later on. At room temperature, where the characteristic thermal energy \(k_b T\) is higher than the exciton binding energy for GaN, free e-h recombination dominates, and the thermally activated filling of the energy band broadens the emission spectrum\[12\].

The bandgap of In\(_x\)Ga\(_{1-x}\)N depends on several parameters: the composition, temperature and the strain in the active region of the heterostructure\[12\][14]. If In\(_x\)Ga\(_{1-x}\)N is under biaxial strain, like in the case of planar devices, an approximation for the bandgap is given by\[26\]

\[
E_g(x, \epsilon) = xE_{InN} + (1 - x)E_{GaN} - bx(1 - x). \tag{2.3}
\]

Here the bandgap energies for InN and GaN are 0.7 eV\[20\][27] and 3.4 eV\[20\] at room-temperature (RT), with a bowing parameter \(b\) of 1.43\[28\]. In, for instance, photoluminescence experiments the QW transition energy of radiative recombination will always deviate from the calculated value in eq. 2.3 due to several reasons:

(i) Localization of the wavefunction in the QW \(\rightarrow\) blueshift,
(ii) The quantum confined Stark effect (QCSE) \(\rightarrow\) redshift,
(iii) Local alloy fluctuations resulting in In-rich clusters \(\rightarrow\) redshift.

The first effect is the relative simple ‘particle in a box’ idea where the energy states are proportional to \(\sim \frac{1}{d_{QW}}\), with \(d_{QW}\) the quantum well thickness\[29\]. So for smaller QWs, the blueshift of the transition energy will become stronger. This is also sketched in Fig. 2.6b.

The second effect is the well known QCSE\[30\], which is induced due to the spontaneous and piezoelectric fields that draw the electron to the Ga-face of the QW, and the hole to
2.3. (In,Ga)N nanowire heterostructures and their advantages

Figure 2.6: Change of energy transition due to several effects. (a) The ground states of the electron (holes) are located a bit above (below) the bandgap. (b) Due to quantum confinement, the width of the QW determines the position of the energy states and $d_{QW}$ can be used as a tuning parameter. (c) Illustration of the quantum-confined Stark effect (QCSE) with consequent bandprofile and polarization field. (d) Compositional fluctuations lead to variations in the bandgap.

2.3. (In,Ga)N nanowire heterostructures and their advantages

As discussed before, heterostructures are needed for a higher light output and more efficient operation regarding LED devices and other applications. The focus of this thesis is the growth and characterization of (In,Ga)N nanowire heterostructures. Furthermore, these heterostructures are not grown on widely used silicon substrates, but on metal titanium (Ti) substrates. This section will cover the main advantages of nanowire heterostructures grown on Ti.

Nanowires can be seen as quasi one-dimensional (1D) crystal structures possessing a high aspect ratio (length-to-width ratio), similar to a wire or pillar with a diameter in the nanometer range. Due to their large surface-to-volume ratio and size effects, these properties make them a good choice for fabrication of quantum devices within nanometer scale suchs as field-effect transistors, single-electron transistors, light-emitting devices, chemical sensors and THz detectors. Nanowires are also a promising candidate for nanophotonics, where they can be employed as waveguides, point-like emitters and...
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even single photon emitters\textsuperscript{[34]}. All in all very exciting and new (applied) physics which, unfortunately, cannot be treated in this masters thesis.

Moreover, these novel one-dimensional III-V nanostructures also provide a good model system for investigating the dependence of electronic transport, optical and mechanical properties on their confinement effects and are therefore of great interest, besides device fabrication, for simulations and theoretical calculations\textsuperscript{[22][35]}.

![Diagram of GaN, TiN, Sapphire, and (In,Ga)N nanowires](image)

\textbf{Figure 2.7:} Advantages of nanowires: defects can relax elastically towards the side facets, shown in the left nanowire (a). The middle and right nanowire of (a) show the embedded axial and core-shell heterostructure respectively. (b) Elastical strain relaxation in an (In,Ga)N quantum well. Figure by M. Hanke, PDI.

Another advantage of growing nanowires is the high crystal quality one can achieve on foreign substrates, e.g. silicon, since the dislocations are propagating from the substrate interface to the sidewalls\textsuperscript{[36]}.

When considering axial (In,Ga)N NW heterostructures, the strain which results from the difference in lattice parameter of the alloys can relax elastically towards the side facets as shown in Fig. 2.7b. Due to this elastic strain relaxation, the NW heterostructure can be grown defect-free\textsuperscript{[22][37][38][39]}. Moreover, it reduces the piezoelectric fields due to strain and therefore a reduced QCSE, which enables higher efficiencies at higher In contents in the active region of the NW\textsuperscript{[40]}.

Regarding core-shell structures, a further advantage is the larger surface in comparison to planar layers and thus a possible larger active region. This argument is connected to the increase of LED efficiency for lower current densities. Flowing a current through a larger region means decreasing the current density, which improves the LED light output. Secondly the non-polar character of the $M$-planes of the (In,Ga)N nanowires reduces the QCSE effect\textsuperscript{[41][42]}.

Besides the many different advantages of growing nanowires and using the III-V material system, also the substrate plays an important role in the production, characterization and eventually device fabrication of i.e. LEDs. Growing on a metal has also advantages, since the metal substrate can be used as a back contact for LED or solar cell devices. Fur-
thermore, the reduction of the so-called ‘coalescence’ for GaN NW plays an important role in choosing a Ti substrate\cite{43}. The term coalescence means here the bundling or attachment of two or more wires with each other. Due to the relative low density and thin NWs, the GaN NWs possess a low degree of coalescence. The ensemble of thin wires are well-separated. This is a big achievement in comparison to other established growths of GaN NWs and has several advantages. One of the advantages is the decrease of shadowing due to neighboring NWs and thus the possibility for radial growth along the whole NW length, allowing growth of core-shell structures, as will be more extensively discussed later on.

2.4. Crystal growth by molecular beam epitaxy

For this thesis, the GaN NWs were grown by molecular beam epitaxy (MBE). One of the main differences of this technique, in comparison with other growth techniques like MOVPE, is the ultra-high vacuum. Therefore the mean free path is long enough for atoms to reach the substrate by a straight-line path. Secondly, due to this long mean-free path it is possible to use \textit{in-situ} surface analysis by electron diffraction (RHEED) and \textit{in-situ} desorption by line-of-sight QMS.

This section will give a brief introduction to general physical concepts of crystal growth and the MBE growth technique to give a little better general understanding of crystal growth.

2.4.1. Basics of crystal growth

The nucleation and growth of crystal films in general can be divided into three different mechanisms\cite{15}\cite{17}\cite{19}:

- atomic layer-by-layer growth of a thin film, also known as the ‘Frank-van der Merwe’ (FM) growth,
- the formation of three-dimensional islands, known as ‘Volmer-Weber’ (VW) growth,
- and layer growth up to a critical thickness, followed by roughening and three-dimensional island growth, the ‘Stranski-Krastanov’ (SK) mechanism.

These three scenarios can be physically understood in terms of thermodynamics by looking to the different energy terms involved. If we use our ‘gezond boeren verstand’ (English: common sense) it is easy to see that each of these growth modes can be thermodynamically motivated by considering the net energy difference of (i) the crystallization from the vapor to the solid phase, (ii) the free surface energy of the adlayer and (iii) the interface energy of the adlayer and substrate. The formation of an adlayer can lead to strain, associated with strain energy, which is dependent on the lattice parameter mismatch. The strain energy increases with increasing lattice mismatch.\cite{19}\cite{17}

The interface surface energy \(\gamma\) plays an important role here. If \(\gamma\) is small compared to the (free) surface energy of the adlayer, FM growth is probably to occur. In contrast, high interface energy on a foreign substrate prevents a so-called wetting layer and leads to VW growth. The SK growth mode is something in between and the growth mode is
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switched from FM to VW. This situation can happen when a solid film on a foreign substrate possessing a lattice mismatch, initially wets the substrate surface and then strain may build up with increasing thickness of the wetting layer, making further layer growth unfavourable due to increasing strain energy, and thus leading to island growth by the SK mechanism\cite{15}.

2.4.2. Molecular beam epitaxy

The typical aspect of MBE is the low deposition rate (typically less than 1 µm per hour) that allows the films to grow epitaxially. The UHV conditions and the absence of carrier gases result in the highest achievable purity of the grown crystals. Furthermore, low growth temperatures can be used and smooth growth surfaces with steps of atomic height can be achieved\cite{15}.

The growth of crystals and their quality depends on several parameters. Most important are the temperature of the substrate during growth \(T_{\text{sub}}\) and the impinging fluxes and their, in our case, V/III-ratio. These parameters can be adjusted for controlling the growth. Other, less significant influences are the pressure in the growth chamber \(P_{\text{ch}}\) and stability of the substrate heater and effusion cells to obtain a constant \(T_{\text{TC}}\) and flux.

![Figure 2.8: Vertical cross-section of the growth chamber of MBE9, which is similar to the MBE2 system at PDI. Most samples covered in this thesis are grown in MBE2. The main parts of the system and the installed components are shown. The effusion cells, QMS as well as the plasma source (not shown in picture) are all under the same angle \(\alpha = 37.5^\circ\) for MBE2 and \(\alpha = 30.0^\circ\) for MBE9.](image)

Most MBE systems are equipped with a reflection high-energy electron diffraction (RHEED) system, in order analyze the crystalline surface of the sample, and routinely used in the MBE to investigate growth mode, growth rate, flatness, crystal structure, adlayer formation, facet angles and epitaxial relations of heterostructures. The RHEED system consists of a RHEED gun acting as the electron source generating an electron beam striking the sample. The fluorescent screen acts as a detector of the diffracted electrons\cite{44}. Although the high added value of RHEED data during the growth and
afterwards for the analysis, the RHEED system in MBE 2, which was used for the growth of most of the samples covered in this thesis, was broken or not working properly during the period of growth experiments discussed in this thesis.

Besides RHEED, another powerful in-situ tool is the line-of-sight quadrupole mass spectrometry, or shortly, QMS system. The spectrometer is arranged in line-of-sight from the substrate and can identify the rate and species of atoms desorbing from the substrate. Therefore, the QMS is used to quantitatively study the growth kinetics, i.e. nucleation, decomposition and desorption. During MBE growth experiments, a drop in the desorption can indicate nucleation and the beginning of crystal growth. In this way, QMS has been used to study the nucleation of planar GaN films and GaN NWs\textsuperscript{19}\textsuperscript{44}\textsuperscript{45}.

In the same fashion, the QMS is used in our experiments to be reproducible with the growth temperature in an indirect way. The QMS signal shows a typical behaviour for the growth of GaN nanowires, with a peak followed by a drop and then a second rise of the desorption level again. By monitoring the time and signal height between the two different peaks, originating from the NW nucleation, an indication of the growth temperature can be obtained. In other words, if the second rise of the signal is too fast, the growth temperature is probably too high since a lot of atoms are desorbing very fast from the substrate.

A more technical detailed explanation about the working principle of the QMS can be found in Appendix B.

\section*{2.5. Growth of GaN nanowires by molecular beam epitaxy}

One of the main aims of this thesis is to understand and explore new formation approaches of In\textsubscript{x}Ga\textsubscript{1−x}N heterostructures on GaN nanowires, making use of thin and well-separated nanowires on metal. This last property of the NWs results from the growth on Ti and is the main reason for choosing this material as a substrate in this thesis. Well-separated nanowires enable the growth of core-shell heterostructures, which is much more difficult for dense NW arrays on e.g. Si.

To introduce and prepare the study of heterostructure synthesis, the established concepts and knowledge about the GaN NW growth are presented in this section.

In contrast to other III-V NWs grown mostly according to the well-known vapor-liquid-solid (VLS) mechanism, GaN NWs can originally be grown catalyst-free within the self-assembled approach. This ‘self-assembled’ term points out that GaN NWs spontaneously form without the help of any catalyst or Ga droplets, and should not be confused with self-assisted or self-catalyzed terms used for other III-V semiconductors, for which III-element droplets are typically employed\textsuperscript{19}.

This chapter introduces the growth fundamentals and established growth models as known from MBE growth of In\textsubscript{x}Ga\textsubscript{1−x}N/GaN NW heterostructures on Si and GaN NW growth on Ti by M. Wölz\textsuperscript{43}.

\subsection*{2.5.1. Kinetic description of nanowire elongation}

To understand the (axial) C-plane growth of the NWs, we need to include kinetic effects, since the NW morphology is very complex resulting in local flux variations. This section introduces these kinetic effects, in order to describe later the growth conditions and
2. The (In,Ga)N material system for nanowires

The evolution of the GaN nanowires.

**Figure 2.9**: Schematic diagram representing the different physical processes involved in the NW elongation from stable nuclei during the growth phase. Two main contributions are depicted: the direct incorporation from the impinging Ga flux $\phi_{Ga}^{imp}$ and the Ga adatom surface diffusion on the substrate surface through the NW vertical sidewalls to the NW top. The growth temperature dependent distance $d_{CR}$ represents the average critical length from which Ga adatoms cannot reach the NW bottom. Taken from Ref. [19]

The growth models of GaN nanowires include the following main processes going on at and around the wires, namely:

(i) adsorption
(ii) desorption
(iii) surface and sidewall diffusion
(iv) incorporation
(v) decomposition

In Fig. 2.9 and Fig. 2.10, these different processes and flux contributions to NW elongation are sketched for GaN NWs grown by MBE. Atoms from the impinging flux $\phi_{Ga}^{imp}$ can adsorb on the substrate or NW top facet and sidewalls and subsequently contribute to NW growth (incorporation of atoms, $\phi_{inc}^{top}$). The impinging flux of atoms can be divided into two. On one hand the flux impinging on the top-facet, $\phi_{imp,top}^{top}$, enabling direct axial growth. Secondly, the fluxes impinging at the substrate and sidewalls $\phi_{imp,side}^{imp}$, where the atoms start to diffuse over the substrate and sidewalls of the NW once they hit the sample, which is called substrate or sidewall diffusion respectively. For the growth of GaN, only Ga is diffusing, whereas the active N is not considered to diffuse. For surface diffusion on the substrate, a certain critical radius (denoted as $d_{CR}$ in Fig. 2.9b) has to be taken into account: atoms arriving within this critical radius can contribute to NW growth,
2.5. Growth of GaN nanowires by molecular beam epitaxy

which is especially important for very small NW lengths smaller than the Ga diffusion length on the substrate plus on the NW sidewall \( (\ll \lambda_{\text{sub, Ga}} + \lambda_{\text{sid, Ga}}) \). At higher temperatures the so-called adatoms have more energy and the diffusion length will be longer. However, one should be careful, since higher temperatures also increases the desorption rate of adatoms which eventually may reduce the diffusion length.

Above a certain NW length, sidewall diffusion \( \phi_{\text{diff, side}} \) is the most important diffusion contribution in describing NW growth. For convenience, we will write \( \phi_{\text{diff}} \) when discussing sidewall diffusion, disregarding substrate diffusion when not specifically mentioned. The same applies to the Ga diffusion length\[^{[19][46][44]}\].

Since N does not diffuse\[^{[36]}\], the positioning of the plasma cell (N-source) in the MBE system has a particularly strong effect on the growth and morphology of the NWs.

The last and less pronounced contribution to NW elongation, or actually NW shortening is the decomposition of the material. The atoms that were able to be incorporated in the material is decomposed, denoted as \( \phi_{\text{dec}} \). This happens of course at higher temperatures \( > \sim 830^\circ\text{C} \).[47]

2.5.2. Self-limiting radius mechanism

One consequence of the adatom supply towards the top facet via sidewall diffusion is that thick NWs grow slower than thinner NWs, since \( \phi_{\text{diff}} \sim \frac{1}{r} \) which will be shown here below. Furthermore it is important to realize that, however the NWs mainly axially grow, radial growth is generally not completely suppressed. Radial growth can be fed by atoms impinging on the sidewalls, if their diffusion length is too small to permit incorporation on the top facet, i.e. \( \lambda_{\text{Ga}} < \) the NW length, and shadowing of the NW lower parts does not occur\[^{[19][36][48]}\].

Radius dependence

To summarize and give a more quantitative image of all contributing fluxes, one can write down the growth rate of the NW as a sum of contributing fluxes at the NW top facet\[^{[36]}\] as also sketched in Fig. 2.10:

\[
\frac{dL}{dt} = R = \phi^{\text{imp, top}} + \phi_{\text{diff}} - \phi_{\text{des}} - \phi_{\text{dec}},
\]

(2.4)

with \( \frac{dL}{dt} \) the change in NW length per time interval which is per definition the axial growth rate \( R \). Additionally we can describe sidewall diffusion for a NW with radius \( r \) as follows: the impinging atoms contributing to axial growth are collected on an area as big as \( 2\pi r \lambda_{\text{Ga}} \) and will diffuse towards the top C-plane facet with an area of \( \pi r^2 \). So from simple geometrical arguments we can write for \( \phi_{\text{diff}} \):

\[
\phi_{\text{diff}} = \frac{\phi^{\text{imp, side}} 2\pi r \lambda_{\text{Ga}}}{\pi r^2} = \frac{2\phi^{\text{imp, side}} \lambda}{r} \sim \frac{1}{r}.
\]

(2.5)

Here we see clearly the \( \frac{1}{r} \) dependence of the diffusion flux towards the top facet and why thicker NWs grow slower than thin ones and the fact that diffusion is more pronounced for thin NWs. From a geometrical point of view it is easy to calculate the im-
2. The (In,Ga)N material system for nanowires

Impinging fluxes on the top and side facets of the NW using the $\cos(\alpha)$ and $\sin(\alpha)$ respectively, as shown in Fig. 2.10. We have to remark that the calculation here above is based on (at least) three assumptions:

- The NW is assumed to have a cylindrical geometry instead a hexagonal geometry containing six side facets.

- All the Ga atoms impinging within a distance of $\lambda_{Ga}$ from the NW top facet are able to contribute to the growth. In principle one could argue here not all the atoms will diffuse upwards, contributing to the axial growth, but some of the impinging atoms will diffuse downwards to be incorporated at the sidewall or to be desorbed again. However, due to a gradient in chemical potential, is it energetically favourable for atoms to diffuse towards the top facet\([37][49]\]

- Secondly, we assume due to rotation of the sample that the impinging atoms will be collected around the whole circumference of the NW. In reality, the impinging flux will reach one facet of the NW and the next facet(s) after some time depending on the speed of rotation.

Although these assumptions are made for simplification, they show in a nice way the $\frac{1}{r}$ dependence of the sidewall diffusion flux towards the top facet.

![Figure 2.10](image)

**Figure 2.10:** Different flux contributions at the NW top facet from the impinging flux originating from the effusion cells and plasma source under an angle $\alpha$. For MBE$^2$, the system mostly used to grow the samples of this thesis, $\alpha = 37.5^\circ$.

### Radial growth

This result of decreasing adatom diffusion towards the top for larger NW radius, is used in the so-called ‘self-limiting radius’ description for GaN NW growth. Sergio Fernández-Garrido *et al.* proposed a model for a self-regulated radius mechanism for self-assembled...
2.5. Growth of GaN nanowires by molecular beam epitaxy

GaN nanowires by MBE, predicting axial or radial growth of the NW\[36].

Since the side facets of GaN nanowires are atomically flat, radial growth should proceed layer-by-layer, with nucleation of a two-dimensional island and further expansion of this island by step-flow. In principle, the islands can homogeneously nucleate at two different places: at the facets, or at the edges between the side surface and the substrate or the top facet. Homogeneous nucleation at the facets is unlikely because it would cause cone-shaped NWs and also because the NW sidewalls are not exposed simultaneously to Ga and N fluxes.

Nucleation at the edge between the side surface and the substrate is also unlikely for dense NW arrays, since this edge is shadowed from the impinging fluxes. Hence, the edge between the top and the side facets is the most plausible nucleation site for radial growth. However, for NW arrays with low densities, also nucleation at the NW bottom part can take place. This can be very beneficial for homogeneous radial growth along the whole NW in order to grow core-shell heterostructures. Therefore, well-separated and uncoalesced NWs are of advantage for these purposes.

Two-dimensional island nucleation requires that the adatom density exceeds a certain critical value. Since the Ga adatom density at the top of the side facet \(n_{side,Ga}\) is related to the Ga adatom density at the top facet \(n_{top,Ga}\) (or shortly \(n_{Ga}\)) by the equality of the chemical potentials, \(\mu_{side,Ga}(n_{side,Ga}) = \mu_{top,Ga}(n_{top,Ga})\), we can conclude that the increase in NW radius occurs because of the Ga adatom concentration at the top facet exceeds a certain threshold when the Ga flux is increased.

So when the NW radius increases during radial growth, the Ga flux from the side surface towards the top facet, \(\phi^{diff}_{Ga}\), continuously decreases. This reduction of diffusing adatoms at top facets lowers \(n_{side,Ga}\) until it eventually becomes lower than the critical value for island nucleation at the NW side facets. At that point, radial growth ceases, and the NW elongates preserving its radius.

It is possible to quantify the (effective flux) conditions for radial growth in a qualitative way, using the understanding of radial growth as just explained. Under the assumptions of no N diffusion\[50] and no GaN decomposition, effectively N-rich growth conditions are required to obtain mainly axial growth instead of radial growth, and thus making the formation of GaN NWs possible. In other words, the impinging N flux must exceed the effective Ga flux:

\[
\phi^{imp}_{N} > \phi^{imp}_{Ga} + \phi^{diff}_{Ga} - \phi^{des}_{Ga}. \tag{2.6}
\]

This result will be very important in order to grow and analyze the axial heterostructures or radial heterostructures. Despite the simplicity of the result, the mathematical derivation makes use of more complex assumptions and ideas\[36].

2.5.3. General conditions for GaN nanowire growth

The general growth conditions for GaN NWs in MBE are using high temperatures between 700°C and 900°C and V/III flux ratios at least larger than one, but often very N-rich. In general, GaN growth on foreign substrates by MBE can either result in three possibilities: (i) a compact layer, (ii) the growth of nanowires, or (iii) no growth at all
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when extreme growth conditions are chosen. For the growth of NWs, they are formed in a hexagonal structure bounded by M-plane side facets and grow axially along the C-direction. The structure and morphology is strongly determined by the growth temperature and the V/III flux ratio and is not so straightforward as the growth in general as discussed until now. The different growth regimes are shown in Fig. 2.11 for a fixed supply of N from the plasma source of $\phi_N = 6$ nm/min\textsuperscript{[47]}. The unit [nm/min] is in this thesis used for fluxes, which is the equivalent growth rate unit for planar layers. The official unit for flux in general, is atoms per area per time, e.g. [atoms/cm$^2$/s]. However [nm/min] is easier and also widespread in daily use for carrying out growth experiments. The Ga and N fluxes are given according to the growth rate of planar GaN layers, and the In flux according to planar InN. So actually, the flux is the nominal flux as deduced from the growth rate of a calibration layer\textsuperscript{[47][51]}.\textsuperscript{[47][51]}

![Growth diagram showing the boundary between compact and nanocolumnar regimes as a function of $\phi_{Ga}$ and growth temperature for a constant value of $\phi_N = 6.0$ nm/min. Taken from Ref.\textsuperscript{[47]}.](image)

**Figure 2.11:** Growth diagram showing the boundary between compact and nanocolumnar regimes as a function of $\phi_{Ga}$ and growth temperature for a constant value of $\phi_N = 6.0$ nm/min. Taken from Ref.\textsuperscript{[47]}.

At very high temperatures, all of the impinging Ga atoms desorb, and no growth occurs since no atoms stay on the substrate. Desorption of Ga is thermally activated, and therefore the required $\phi_{Ga}$ to sustain any growth at all is an exponential function of the temperature. At higher temperatures, decomposition of GaN will also play a role additional to the desorption mechanism, starting from about $830^\circ$. The decomposition of GaN is also temperature dependent and following an exponential function.

In the regime just below this temperature, the remaining Ga atoms are few compared to the N supply, and NWs are formed. This regime is characterized by a larger V/III ratio than 1 (or even very N-rich), since for V/III smaller than 1, radial growth will dominate forming a compact or coalesced layer. Under these conditions in regime (b), axial growth is preferred over radial growth and NW elongation results from differential sticking coefficients, respectively diffusion lengths, on the M- and C-planes. Furthermore Li et. al.\textsuperscript{[52]} calculated the equilibrium crystal shape for wurtzite crystals, like GaN grown at high enough temperature. His results can well explain the experimentally observed NW shape from a thermodynamic point of view in terms of the large anisotropy of surface energies.
When even going lower in temperature, the critical amount of Ga remains on the surface for the growth of a compact layer. This regime is again defined by an exponential function governing the desorption of Ga, but without GaN decomposition playing a role. Therefore, the larger slope between region (b) in Fig. 2.11 and the ‘no growth’ regime results from the extra exponential function from the GaN decomposition and the temperature dependence of the nucleation time.\cite{47, 53}

Furthermore, as mentioned before, GaN can be grown Ga- or N-polar, both having different properties. More in depth research about the GaN NW polarity has been done by e.g. Sergio Fernández-Garrido et al.\cite{19, 54, 55}. Until now it is not fully understood, but in short, it is known that self-assembled NWs grow mostly N-polar instead of Ga-polar. It is assumed that this N-polarity has huge consequences for the optical properties of the NWs. However the highly interest of this topic, we will not further dive into the details of it here and we will take the N-polarity as a fact for now.

In summary, one can say that the self-assembled growth by PAMBE of GaN NWs takes place within a fairly broad range of growth condition: highly N-rich conditions corresponding to effective (taking adatom diffusion and desorption rates into account) V/III ratios larger than 1 and most of the time combined with a high growth temperature in the range of 730°C and 830°C for GaN, which results in N-polar self-assembled NWs.

The self-assembled growth can be described by two successive regimes, namely the nucleation phase and the growth phase. Both thermodynamics as well as a kinetic description are needed to describe the behaviour of NW formation and elongation. In the next section, an overview and description of the GaN nanowire evolution will be given.

### 2.5.4. Evolution of GaN nanowires

So far, we have discussed the theoretical kinetic effects which possibly play a role in NW elongation. And secondly, a general overview has been given under which conditions GaN NWs are formed. Let us now have a deeper look in the evolution of GaN nanowires on Si, starting from the formation of nuclei. We remark that this particular discussion hold for the growth on Si, however, for other substrates the theory is similar but not fully identical.

The evolution of the growth of GaN nanowires can be globally divided into four different stages as sketched in Fig. 2.12a, including a nucleation phase (i), followed by a shape transition (ii) and radial growth (iii), eventually leading to axial growth of the NW (iv).\cite{36}

The nucleation phase is important for the further growth of the NWs and partly governs the structural properties (morphology) of the nanowires, such as the density and smallest radius of the nanowires. Most probable, GaN NW nuclei in the form of spherical cap-shaped 3D islands are formed. The formation of GaN NW nuclei should be distinguished from standard crystal growth (in which an initial nucleus is formed) in the sense that GaN does not nucleate with the NW shape.\cite{19}

Then, more stable spherical cap-shaped 3D islands grow until reaching a certain critical radius of $\sim 5\text{nm}$. After this radius is reached, a shape transition of the nuclei is taking place. This period is characterized by the coarsening of clusters and by one or several shape transitions leading to the self-assembled formation of NW nuclei. At this point in the growth, the flat $\langle 000\overline{1} \rangle$ top facet and $\langle 10\overline{1}0 \rangle$ side facets occur and every NW is
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Figure 2.12: Schematic illustration of the different stages during the spontaneous nucleation and growth of GaN NWs on Si(111). (i) Nucleation stage with the formation of stable spherical cap-shaped 3D islands. (ii) Shape transition to the NW-like morphology. (iii) NW elongation and radial growth until the Ga adatom density at the NW top facet is reduced below the threshold for 2D island nucleation at the NW side facets. (iv) Final stage where GaN NWs elongate preserving their radius. Image taken from Ref. [36].

able to collect a significant amount of Ga from the impinging fluxes and substrate since shadowing effects from neighbouring NWs is not yet operative [56].

As explained before, at this moment, the Ga adatom concentration on the NW top facet will typically exceed the specific threshold value for two-dimensional island formation at the NW side facets, and radial growth will set in. Besides radial growth, the NW will also grow in axial direction. Further nucleation at the edge between the substrate and NW side facets is also possible because that edge is not shadowed yet.

As time evolves, the NW grows in radial and axial direction and shadowing progressively sets in. Additionally, while the NW radius increases, the adatom diffusion towards the top decreases. Thus as the NW radius increases, the Ga adatom density at the top facet continuously decreases until its value is below the threshold for two-dimensional island formation at the side facets. At that point, the radial growth ceases and the NW elongate, preserving their radius if the Ga atoms impinging on the NW sidewalls can reach the NW top facet by sidewall diffusion. If this is not the case, the NW radius can increase during growth, but with a growth rate that is more than one order of magnitude lower than the axial growth rate. This mechanism, the so called self-limiting radius effect [36], will appear to be very important during our growth experiments; especially for core-shell structures it will play a major role.
2.6. Epitaxial GaN growth on Ti film

Before our knowledge about axial and radial growth can be used in order to grow In$_x$Ga$_{1-x}$N heterostructures, the so-called GaN NW base or template is grown. This is a well established growth of GaN NWs grown on Ti which are, in contrast to the growth on e.g. Si, rather thin and uncoalesced, as established and reported in literature by M. Wölz[43]. The optimization and better understanding of longer GaN NWs on Ti was carried out together with D. van Treeck and G. Calabrese at PDI; the main results of the GaN NW template, which are used as a starting point for the In$_x$Ga$_{1-x}$N growth, will be discussed in this section.

2.6.1. Growth of nanowires on metallic substrate: titanium

For the growth of GaN nanowires, several different substrates can be used like Si or growth on an AlN buffer layer. One of the advantages of growing NWs that makes it unique compared to other semiconductor structures, is the absence of a lattice constraint. Growth on substrates other than single crystals could make GaN NWs more cost-effective and better scalable than planar GaN grown epitaxially. From a growth perspective point of view, the choice of a substrate is guided by three criteria[44]:

- withstand the GaN NW growth temperature of around 800°C for at least one hour. The substrate should not degrade or react chemically with GaN.
- be UHV-clean, i.e. not release contaminants into the vacuum growth chamber. Integration of foreign atoms from the substrate into the growing semiconductor could have undesired effects, such as a reduced carrier lifetime.
- possess a flat surface to allow device integration by planarization. (not the main requirement for this thesis.)

As shown by Samsun Electronics, the metal Ti can be used as a substrate for the growth of GaN. Furthermore, metal Ti film has several advantage like it serves as a mirror and as a good ohmic back contact. These advantages are with respect to the fabrication of LED devices. From growth perspective point of view, for the growth of core-shell heterostructures it is required to have a nanowire template with well-separated wires. GaN nanowires grown on Ti appear to have this property as we will see in the next part, which is one of the main reasons to use Ti as a substrate to grow on[44].

The growth and structure of GaN NWs on its own is not changed by a different substrate. The purpose of this section is not the analysis of different substrates to grow on, but to show the established self-assembled GaN NWs growth on Ti in PAMBE as a starting point for the rest of the experiments discussed in this thesis.

2.6.2. Growth and properties of GaN nanowires on Ti

The Ti was sputtered onto C-plane Al$_2$O$_3$, also known as ‘sapphire’, up to a thickness of 1.3 µm. The sputtering was done in a DC magnetron using a blue argon plasma with a voltage $V_{plasma} = 369$ V, current $I_{plasma} = 1.80$ A and Ar flow $f_{Ar} = 30$ sccm.

Before the GaN NWs are nucleated, the Ti is exposed to the N plasma. Ti is known to be very reactive, forming TiN even under N plasma atmosphere at temperatures as
2. The (In,Ga)N material system for nanowires

low as 700°C. Additionally it is most likely that TiO is forming from the oxygen diffusion from the sapphire into the Ti interlayer. The exact mechanisms are still under debate, but the presence of TiN and TiO is at least clear, from i.e. RHEED and XRD results\cite{44}.

The base of the GaN nanowires is in principle grown larger than 600 nm. The GaN nanowire density, coalescence degree, diameter and axial growth rate depend strongly on the substrate temperature and V/III ratio. The nanowire base of a typical sample is grown at 695°C, which is the temperature from the thermocouple $T_{TC}$. The real exact temperature is difficult to measure, but is roughly $\sim 100^{\circ}C$ higher than $T_{TC}$, measured with a pyrometer. The fluxes are $\phi_{Ga} = 5.3$ nm/min and $\phi_{N} = 11.7$ nm/min, yielding a nominal V/III ratio of 2.2, as used in every base GaN NW growth experiment in this work. The axial growth rate can be determined by measuring the lengths of the NWs in SEM images, see App. B. A typical axial growth rate for this so-called ‘template’ was $\sim 10$ nm/min, not taking into account the nucleation time or surface diffusion contributions to the axial growth in the beginning. The maximum N flux is used which could be obtained from the plasma source throughout the growth ‘run’, since the growth rate should be optimized (as fast as possible), but keeping V/III ratios constant.

The NW density on established substrates, e.g. Si, is relatively high in comparison to the GaN nanowire density TiN. For these wires a typical NW density between 10-20 NWs/\mu m² has been found, and the GaN nanowires are in the order of 40-80 nm thick, which is thinner than the wires grown on Si, mostly due to the absence of coalescence.

Fig. 2.13 shows scanning electron micrographs (SEM) of a typical GaN template. The side-view image (a) shows clearly the thin and well-separated NWs with a length above 1 \mu m. The top-view image (b) shows how well-separated the NWs are in comparison to their thickness.

\begin{center}
\begin{tabular}{c}
\textbf{Figure 2.13}: SEM (a) side-view and (b) top-view images of the established GaN template on TiN.
\end{tabular}
\end{center}

Furthermore, as already mentioned before, well-separated NWs reduce the impact and possibility of shadowing effects and enable the growth on the NW sidewalls. This is one of the requirements for the growth of core-shell structures.

Besides small fluctuations in the NW length at a specific point on the sample, e.g. center or edge, fluctuations in the NW length of the NW ensemble appear as a gradient over the
sample due to a temperature gradient during growth. In the center of the substrate, the temperature is typically several degrees higher than at the edge, originating from the fact that heat at the edge of substrate heater also radiates away from the substrate. Secondly, the edge of the substrate lies on a holder where the heat can be conducted away more easily than in the center where the substrate is only exposed to the impinging fluxes.

2.7. Characteristics of (In,Ga)N growth

The growth of In\textsubscript{x}Ga\textsubscript{1-x}N/GaN nanowire heterostructures is a main aspect of this thesis. So far, GaN NW growth is treated and an established GaN NW template is shown as a starting point for the growth of NW heterostructures. Before we continue to the next chapter, we have to discuss the properties and characteristics of growing the ternary alloy In\textsubscript{x}Ga\textsubscript{1-x}N.

Increasing the In content in In\textsubscript{x}Ga\textsubscript{1-x}N QWs leads to a lower bandgap as we have seen before. However, because of the lattice mismatch between In\textsubscript{x}Ga\textsubscript{1-x}N and GaN, the defect density is typically high and increases for higher In content\textsuperscript{[40]}. As discussed before, In\textsubscript{x}Ga\textsubscript{1-x}N QWs in GaN NWs as an alternative to planar layers are investigated because interface strain can relax laterally at the free sidewall surfaces, reducing the defect density.

In the case of growth on bulk substrates, it is known that In\textsubscript{x}Ga\textsubscript{1-x}N deposition on GaN obeys either the Frank-van der Merwe (FM) or the Stranski-Krastanov (SK) growth mode, depending on the In content\textsuperscript{[40]}. For the In\textsubscript{x}Ga\textsubscript{1-x}N growth on GaN NWs, the In content and NW diameter are the key sources for the formation of (two-dimensional) 2D layers or three-dimensional (3D) islands, reducing the elastic energy associated with the In\textsubscript{x}Ga\textsubscript{1-x}N-GaN lattice mismatch.

Growing In\textsubscript{x}Ga\textsubscript{1-x}N is more complex than the growth of GaN NWs, however, some growth conditions remain the same. The condition of N-rich growth should be preserved when growing In\textsubscript{x}Ga\textsubscript{1-x}N axial QWs, as is shown before for the case of GaN NWs. The main difference for In\textsubscript{x}Ga\textsubscript{1-x}N growth is the lower substrate temperature needed, since InN decomposition and significant In desorption occurs at lower temperatures than is the case for GaN\textsuperscript{[23]}.

InN is the least thermally stable amongst the III-nitrides semiconductors, with thermal decomposition of (0001) InN films starting at temperatures as low as 470°C. Therefore, the In\textsubscript{x}Ga\textsubscript{1-x}N growth at temperatures as high as the GaN NW growth would result in no significant In incorporation, since all the In\textsubscript{x}Ga\textsubscript{1-x}N would be decomposed. The temperature at which In\textsubscript{x}Ga\textsubscript{1-x}N is decomposed is of course dependent on the actual In content, and is between that of GaN (830°C) for x = 0 and InN (470°C) for x = 1\textsuperscript{[23]}.

Regarding In\textsubscript{x}Ga\textsubscript{1-x}N growth, the fast decomposition and large In desorption in comparison to GaN makes it more difficult to quantify the different flux contributions to the actual growth. The lower bond strength for In-N (1.93 eV) than for Ga-N (2.24), as well as the size difference of In and Ga, results in preferred Ga incorporation over In. Furthermore, this property gives rise to In\textsubscript{x}Ga\textsubscript{1-x}N segregation resulting in an inhomogeneous In composition along the growth direction\textsuperscript{[16,17]}.

If Ga and In are compared, the In diffusion length over the substrate and NW sidewalls is longer than that for Ga, which results in larger In than Ga diffusion. Secondly, the In desorbs more easily than the Ga atoms, having the opposite effect for its diffusion length.
2. The (In,Ga)N material system for nanowires

Considering Ga (ad)atoms at the lower growth temperatures for In$_x$Ga$_{1-x}$N, they desorb less easily than at higher GaN growth temperatures. Also the diffusion length of Ga is temperature dependent and changes during In$_x$Ga$_{1-x}$N growth. The diffusion of Ga adatoms is considered in literature not only to be a function of temperature, but also the presence of In can alter the diffusivity of Ga\(^{[47]}\). In general it is assumed that the diffusivity of Ga is enhanced in the presence of In\(^{[44]}\).

Recent evidence suggests enhanced In incorporation at the N-polar $\langle 000\bar{1} \rangle$ plane in comparison to the Ga-polar $\langle 0001 \rangle$ case. Furthermore, N-polar InN growth allow temperatures $\approx$ 100°C higher than the thermal dissociation limit of In-polar InN surfaces (or Ga-polar for (In,Ga)N)\(^{[23]}\).

As discussed here, a lot of mechanisms have to be taken into account during In$_x$Ga$_{1-x}$N growth. Therefore, the growth of In$_x$Ga$_{1-x}$N heterostructures is not always straightforward and an interplay of optimized growth parameters is needed to gain fully control over the heterostructure and its morphology, strain relaxation and (non-radiative) defect reduction. The In incorporation is also dependent on the V/III ratio and growth temperature\(^{[22]}\)\(^{[23]}\)\(^{[40]}\)\(^{[57]}\). The growth temperature appears to be a very powerful but also critical parameter in order to grow NWs with a good morphology and high incorporation of In in the QWs. When lowering the growth temperature, less metal is desorbed and more In is theoretically incorporated. At the same time, radial growth is setting in at a certain point for decreasing growth temperature, and the required N-rich conditions might not been maintained. In the next part, the expected In incorporation will be discussed.

2.7.1. Theoretical In incorporation during (In,Ga)N N-rich growth

In order to grow (In,Ga)N segments or QWs on top of the GaN template, N-rich growth conditions by MBE should be preserved for axial growth. Then, the In incorporation is not limited by the N supply, but by the decomposition of In and the desorption of In adatoms $\phi_{In}^{des}$, as discussed here above. Therefore, (In,Ga)N is grown at lower temperature ($\sim$ 200°C) than GaN. If all the In atoms which are not incorporated ultimately desorb, the In composition $x$ is given by\(^{[44]}\):

$$x = \frac{\phi_{In}^{imp} - \phi_{In}^{des}}{\phi_{Ga}^{imp} + \phi_{In}^{imp} - \phi_{In}^{des}}.$$  \hspace{1cm} (2.7)

This is under the assumption of N-rich conditions, there will always be more N atoms available for growth than metal atoms. During In$_x$Ga$_{1-x}$N growth, decomposition, reincorporation and desorption occur simultaneously and determine the total loss of In. The temperature dependence of these single processes is hard to determine and therefore the In loss under N-rich conditions has not been quantified and remains unknown.

2.7.2. Theoretical In incorporation during (In,Ga)N metal-rich growth

The incorporation of In for metal-rich growth conditions is different than for N-rich growth. As stated before, atoms from the vapor phase are not directly incorporated into the NW but adsorb first on the substrate surface. When Ga and In adatoms compete for incorporation in the (In,Ga)N shell, the Ga is incorporated preferably because the Ga-N
bond strength is higher than the one of In-N. The maximum amount of In incorporation
at low growth temperatures is hence given by the difference in Ga and N supply. Ad-
ditionally the decomposition of InN, resulting in new In adatoms, and the desorption of
In adatoms also play a role. The decomposition of In$_x$Ga$_{1-x}$N can be described by the
following relation since its an thermally activated process$^{[44][58]}$:

$$\phi_{\text{InN}}^{\text{dec}} = C x \exp \left( -\frac{E_{\text{dec}}}{k_B T} \right),$$  \hspace{1cm} (2.8)

with a constant C and $E_{\text{dec}}$ the activation energy for InN decomposition at a specific
temperature $T$. The literature value of $E_{\text{dec}}$ for InN decomposition from the N-polar C-
plane surface is 1.2 eV$^{[59]}$. Since for core-shell structures we are dealing with In incorpo-
ration efficiencies at different facets, we should distinguish between the In incorporation
at the top facet and NW sidewall.

**In incorporation at the top facet**

The In incorporation at the top facet can be deduced from the planar and axial NW het-
terostructure cases. In the case of metal-rich growth, where $\phi_{\text{Ga}} + \phi_{\text{In}} > \phi_{\text{N}}$, the reduction
of incorporated N due to InN decomposition yields an effective N flux $\phi_{\text{N}}^{\text{eff}} = \phi_{\text{N}} - \phi_{\text{InN}}^{\text{dec}}$.
The composition $x$ depends on the total N left, which is not bound to Ga. Therefore $x$
is given by$^{[44][58]}$:

$$x = \frac{\phi_{\text{N}}^{\text{eff}} - \phi_{\text{Ga}}}{\phi_{\text{N}}^{\text{eff}}} = 1 - \frac{\phi_{\text{Ga}}}{\phi_{\text{N}} - \phi_{\text{InN}}^{\text{dec}}}. \hspace{1cm} (2.9)$$

Therefore, $x$ at the top facet does not depend on the impinging In flux. This approach
was confirmed for planar growth on the N-polar surface and on off-orientations. In our
case, the nitride NWs grow in the N-polar C-direction in MBE.

**2.8. 3D analysis by atom probe tomography**

Slight variations in the chemical composition can significantly alter electronic and op-
tical properties of the (In,Ga)N NW heterostructures. Atom probe tomography (APT)
is an analytical characterization tool of high chemical sensitivity and spatial resolution.
It can characterize the composition in three dimensions with subnanometer resolution
and 1-10 ppm sensitivity. Therefore, this technique can provide very useful and inter-
esting structural and compositional information about the samples$^{[60]}$. This is definitely
complementary and additional information for the growth and characterization of the
(In,Ga)N NW heterostructures grown within the scope of this thesis.

**2.8.1. Principles of atom probe tomography**

In APT, a bias voltage of a few thousands volts is applied between a needle-shaped speci-
men, or tip, and a counter electrode to facilitate electric field-induced evaporation of ions.
A combination of a constant voltage with a pulsed laser induces the evaporation of single
ions, which are subsequently captured by the detector.
2. The (In,Ga)N material system for nanowires

The data of APT consist of X- and Y-positions of hit events on the detector plate, the time of flight of the atoms, the voltage at the time of evaporation and the evaporation sequence. The time-of-flight is converted to a mass-to-charge (m/n) ratio by considering the ion flight path, and a histogram of the observed m/n ratios is the mass spectrum. In this mass spectrum, ranges of mass-to-charge ratio are assigned to identify ions or ion complexes. The 2D position of the hit event is converted to the 3D position of the species identified in the mass spectrum by taking into account the flight path and the time of the hit within the entire sequence of hit events. Under optimal experimental conditions, individual ions field-evaporate uniformly from the topmost surface of the specimen only during laser pulses with an equal probability per pulse, and at a typical detection rate of one ion per 10 laser pulses. Uncorrelated evaporation between the laser pulses produces background noise and should therefore be minimized.

Experimental conditions are adjusted empirically to optimize the quality of data as judged by the following criteria: (i) A mass spectrum should have high signal-to-noise ratio with a minimal number of unidentified peaks. (ii) Hit events should be spatially homogeneous without significant influence from processes that obscure actual positions of ions, such as surface migration and clustering. (iii) Ion count rate variations with run conditions should be similar for the elements of interest and measurement conditions are optimized in order to obtain stoichiometry.

After the measurement itself, first of all, the mass spectrum of a specimen is important and represents the start of the APT analysis. Secondly, one is most often interested in the spatial distribution of various elements. Hence, a reconstruction of the data into a representation of the measured sample is highly interesting for the start of data analysis. With high-quality data and reliable reconstruction parameters, APT can display the distribution of elements with ∼1-10 ppm detection sensitivity and subnanometer spatial resolution, typically 0.2-0.3 nm in lateral direction and 0.1 nm in depth[60][61].

Furthermore, APT can detect all elements with equal efficiency and does not require a priori knowledge of compositions. Various quantitative and statistical methods have been developed to analyze and represent data from reconstructions.
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

Until now, (In,Ga)N/GaN NW heterostructures were grown on Si, possessing a high degree of coalescence and rather thick NWs. Moreover, the QWs do not possess a well-defined structure with sharp interfaces between the QW and QB as expected on beforehand, but a more parachute like In$_x$Ga$_{1-x}$N insertion, possibly surrounded by a shell. The established thin and well-separated GaN NWs shown in the previous chapter offer the possibility to grow In$_x$Ga$_{1-x}$N/GaN multi-quantum-well (MQW) axial heterostructures on top of these wires, aiming for better shaped In$_x$Ga$_{1-x}$N QWs with sharp interfaces and actual disk shape.

The main aim of these axial NW heterostructures on TiN is to use these NWs for a structural and composition studies by atom probe tomography (APT), which has never been reported in literature before. Several groups have shown in literature the fabrication of GaN NWs with repeated axial In$_x$Ga$_{1-x}$N MQWs on Si substrates by PAMBE. Luminescence with peak emission wavelengths from 440 to 640 nm has been reported. The control of the emission wavelength by varying the In concentration as function of the growth temperature has been more extensively investigated by M. Wölz at PDI. His findings for the growth of (In,Ga)N NW heterostructures on Si, will be used in this thesis as a starting point.

In order to achieve the abovementioned goals, the (In,Ga)N/GaN MQW heterostructure NWs are grown at three different temperatures. The fluxes, and thus V/III ratio, are mostly chosen on the basis of experiments carried out prior to this thesis. As preliminary experiments a temperature series of In$_x$Ga$_{1-x}$N segments on the GaN NW template is grown. There are several reasons for growing these In$_x$Ga$_{1-x}$N segments, namely:

(i) Verifying N-rich conditions in order to preserve a good NW morphology.
(ii) Determining the growth rate of (In,Ga)N at different temperatures.
(iii) Getting information about the In content $x$ and compositional fluctuations by photoluminescence.

The knowledge gained during the (In,Ga)N segment experiments is used to grow a temperature series with a 6-fold In$_x$Ga$_{1-x}$N MQW axial heterostructure.

In this chapter, the MBE growth, morphology and optical properties, and finally the compositional information of the MQW region of the axial NW heterostructures by APT will be treated. We will start giving an overview of the intended structures to be grown and the experimental details for MBE growth.
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

3.1. Growth of axial (In,Ga)N segments and heterostructures

Two series of samples are discussed in this chapter of the thesis, which are labeled as A1-A3 for the (In,Ga)N segments series and B1-B3 for the 6-fold MQW heterostructure series. Both temperature series (T-series) contain three samples for lowering temperatures at 570°C, 540°C and 510°C respectively, grown with fluxes of $\phi_N = 11.7$ nm/min, $\phi_{Ga} = 0.8$ nm/min and $\phi_{In} = 12$ nm/min for both series, with a deviating In flux for sample B3, using $\phi_{In} = 8$ nm/min as we will see later.

The samples with an $In_xGa_{1-x}N$ segment on top of the GaN NWs, have a targeted segment length of around 200 nm long. Fig. 3.1a shows the intended structure having an (In,Ga)N segment on top of the GaN NW.

The heterostructure by contrast, is composed of six alternating $In_xGa_{1-x}N$ quantum wells, which forms the so-called ‘active region’ of the sample, having a QW thickness $d_{QW}$, typically targeted around 3.1 nm and GaN barriers with a thickness $d_{\text{barrier}}$, typically ~10nm. These are kept constant within a sample. More QWs gives rise to brighter luminescence of the active region, which is an advantage over just having one QW. The NWs are grown with a cap to minimize non-radiative surface recombination at the NW top. Fig. 3.1b shows the intended NW heterostructure consisting of three main parts: the GaN base (template), then the active region containing a 6-fold quantum well (QW) - quantum barrier (QB) structure followed by the GaN cap.

In the following, the experimental details during $In_xGa_{1-x}N$ growth will be further treated.
Table 3.1: Step-by-step growth recipe for the growth of the GaN template followed by the growth of a N-rich grown (In,Ga)N axial MQW heterostructure.

<table>
<thead>
<tr>
<th>growth step</th>
<th>t (min.)</th>
<th>T (°C)</th>
<th>active sources</th>
<th>fluxes (nm/min)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-ramp and pyrometer check</td>
<td></td>
<td></td>
<td>Ga, N, N</td>
<td>ϕ_{Ga} = 5.3, ϕ_N = 11.7</td>
<td></td>
</tr>
<tr>
<td>GaN base</td>
<td>150</td>
<td>720</td>
<td>Ga, N, N</td>
<td></td>
<td>pyrometer check</td>
</tr>
<tr>
<td>T_{Ga} ramp</td>
<td>1</td>
<td>720</td>
<td>In, Ga, N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% desorption test</td>
<td></td>
<td></td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-ramp</td>
<td>2.08</td>
<td>510-570</td>
<td>In, Ga, N</td>
<td>ϕ_{In} = 12, ϕ_{Ga} = 0.8, ϕ_N = 11.7</td>
<td></td>
</tr>
<tr>
<td>6x QW ((In,Ga)N)</td>
<td></td>
<td></td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5x QB (GaN)</td>
<td>1.08</td>
<td>510-570</td>
<td>Ga, N</td>
<td>ϕ_{Ga} = 4, ϕ_N = 11.7</td>
<td></td>
</tr>
<tr>
<td>cap (GaN)</td>
<td>3.3</td>
<td>510-570</td>
<td>Ga, N</td>
<td>ϕ_{Ga} = 4, ϕ_N = 11.7</td>
<td></td>
</tr>
</tbody>
</table>

3.1.1. Experimental growth details of the (In,Ga)N segment and active region

The experimental details for the (In,Ga)N segment as well as the heterostructure are roughly the same, except for a different final structure which depends on the growth scheme of the various shutters in front of the effusion cells. In order not to repeat here most growth steps for both series, one can assume the same steps to be carried out for the (In,Ga)N segment as for the MQW heterostructure, unless stated otherwise. The latter one will be discussed here into detail.

The established GaN NW template on TiN as discussed in chapter 2, is used as a starting point, followed by the InxGa1-xN growth. The different experimental growth steps carried out in the MBE system are listed, following the compact overview of a typical growth run for a NW heterostructure as found in Table 3.1.

During the growth of the GaN NW base, the In source is brought to the operating temperature for the growth of the active region. When growing InxGa1-xN, the growth temperature should be lowered due to InxGa1-xN decomposition at at GaN growth temperatures. Furthermore, lowering the temperature reduces the desorption of In from the substrate and nanowire. In-situ line-of-sight quadrupole mass spectrometry (QMS) is used for measuring desorption of the metal atoms and therefore gives information about ϕ_{des}^In. The relation between I_{QMS} and ϕ_{des}^metal must be known in order to learn something about the actual amount of desorbed metal. To achieve this calibration, after the growth of the GaN template, the temperature is kept at high temperatures (∼700°C) and all shutters are closed. After waiting some time, in order to distinguish the background signal and ramp the Ga source to the correct and stable temperature for InxGa1-xN growth, the In, Ga and N shutters are opened. At this, still, high growth temperature, all the impinging In desorbs, ϕ_{imp}^{In} = ϕ_{des}^{In} and I_{QMS}^{In} / ϕ_{des}^{In} can be calibrated. This ratio depends drastically on the surface morphology (e.g. M. Wöelz found that it is two times higher for GaN nanowires than for clean silicon [44]) and on the condition of the residual gas analyzer. Therefore, the so-called In "100% desorption test" must be carried out after the growth of the GaN NW template in every individual experiment, which is explained in more detail in Appendix B.1.

After the In desorption test, all shutters are closed again and T_{TC} is ramped down to
the growth temperature of the active region. The growth temperature is monitored by the pyrometer showing \( T_{\text{pyro}} \), but regulated via a thermocouple which is remote from the substrate. The thermal capacity of the sample holder delays the response to temperature changes. For this reason, the rate of change is progressively changed towards the end of the ramp, and some time (several minutes) is incorporated for stabilization. Since from experience, the most reproducible temperature seems to be the thermocouple temperature \( T_{\text{TC}} \), this temperature is interpreted as the growth temperature. This is most probably due to the fact that the pyrometer is not properly calibrated. Additionally, the pyrometer is influenced by different artifacts like coating of the viewports and the tilt of the possible (small) tilt of the sample. Furthermore, for growth on TiN the emissivity of the pyrometer is not exactly known. However for growing on Si, this value is known (70%), and a comparison between the real temperature measured by the pyrometer and the thermocouple reveals a real growth temperature of about 100°C higher than \( T_{\text{TC}} \).

For the growth of the MQW active region, as well as the (In,Ga)N segment, there are two so-called ‘growth approaches’: the low temperature and thus less desorption approach versus the high temperature with higher desorption. What is important for both of the approaches, is the effective V/III ratio at the NW top surface has to be kept in the NW regime: N-rich. Fig. 3.1c shows these two growth approaches. The ‘low temperature’ conditions, in the range of 400-500°C were used in previous experiments at PDI for the growth of In\(_x\)Ga\(_{1-x}\)N-GaN NWs on Si. This is done since InN is decomposing for higher temperatures, and no In would be incorporated at the end. However, if higher growth temperatures are used, > 510°C, and in addition more In is provided by the impinging flux (see again Fig. 3.1c), the net In incorporation can be the same since the ratio between \( \phi_{\text{imp}}^{\text{In}} \), \( \phi_{\text{des}}^{\text{In}} \) and \( \phi_{\text{dec}}^{\text{In}} \) stays the same. It is hoped for and expected that, growing at high temperature has more advantages over growing at lower temperature:

(i) Better crystal quality with lower density of (non-radiative) defects and thus brighter luminescence.

(ii) More homogeneous In composition.

Therefore the so-called ‘high temperature approach’ is the used ‘Ansatz’ for growing the active region and cap of the (In,Ga)N/GaN heterostructures.

Just regarding the heterostructure, as a last step, a GaN cap was grown, where the same \( \phi_{\text{Ga}}^{\text{imp}} \) is used as in the QB. For the samples in this thesis, the GaN cap was typically grown to 30 nm.

The specific growth time for every part, is determined from the (In,Ga)N and GaN growth rates at a specific temperature. These growth rates at their turn are determined by the growth of In\(_x\)Ga\(_{1-x}\)N segments. For the growth of the GaN QB and GaN cap, the Ga flux is therefore adjusted in such a way that the growth rate of the QW and the QB (and cap) is the same.

3.2. Morphology of (In,Ga)N segments and MQW heterostructures

In the following section, first the morphology of this segment series as well as the determination of growth rates will be discussed. Secondly, the (In,Ga)N heterostructures and microstructures of the In\(_x\)Ga\(_{1-x}\)N QW insertions is treated.
3.2.1. (In,Ga)N segments

In Fig. 3.2a, side-view NW ensemble SEM images of the segment T-series are shown (series A). From the SEM images, a change in the morphology of the NW top part can be observed when lowering the growth temperature. Looking to sample A1, grown at highest temperature, the morphology of the upper part of the NW remains well-defined with sharp edges after (In,Ga)N growth. This means, no broadening of the NW diameter sets in or any other irregularities. The absence of broadening is an indication that the N-rich growth conditions are preserved, as discussed in section 2.5.2.

For lowering the growth temperature, samples A2 and A3, broadening of the NW top can be observed and results in the formation of mushroom-like parts on top. This phenomenon is expected for metal-rich conditions at the NW top facet. For sample A3, the effect of broadening is even more pronounced than in sample A2, since less metal is desorbing and decomposing, resulting in locally more In and Ga at the top facet.

For sample A2, we have to look a bit closer in order to understand what actually has happened. Not all the NWs are widened at the top, but only roughly half of the wires. This means that on average, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment is grown under stoichiometric conditions at the top, i.e. some NWs slightly N-rich and other NWs slightly metal-rich.

Secondly, it can be seen that the thin wires are widening at the top, whereas thick NWs are not. This shows nicely the theory covered in section 2.5.2, that for thin wires the metal diffusion flux towards the top, $\phi_{\text{diff}}^{\text{metal}}$, is higher than for thick wires, resulting in metal-rich conditions and thus broadening.

The observation of NW broadening is important for following growths of the MQW heterostructure. If we want to grow the same temperature series and at the same time prevent NW broadening, apparently we have to change the V/III ratio in order not to become metal-rich at the NW top. Effectively this means, lowering the metal-flux, which is done by lowering $\phi_{\text{imp}}^{\text{In}}$ as we will see in the next section.

Another remark for the growth of (In,Ga)N segments, is the presence of the so-called ‘parasitic growth’ at the NW bottom, as can be seen a bit better when zoomed in on the NW ensemble of e.g. sample A1, as shown in Fig. 3.2b. Here, parasitic growth means the formation of small NWs in between the GaN template and broadening of the NW bottom part.

If we only zoom in on the parasitic NWs withing the black box, Fig. 3.2c, it is quite clear that these parasitic NWs are broadening. The white lines are used as a guide to the eye for this broadening towards the top. As mentioned, the diameter of the top part of the desired long NWs is not increasing and according to the theory of self-limiting radius, locally effective N-rich conditions are preserved. However, the parasitic NWs increase in diameter and therefore we can conclude that the diffusion fluxes at the substrate surface contributing to the parasitic NW growth, are larger than the net diffusion fluxes at the NW sidewall near the top, resulting in locally metal-rich conditions.

The growth rate of the (In,Ga)N segment can be determined from the high-resolution transmission electron micrograph (HRTEM) in Fig. 3.2d. The yellow box indicates the (In,Ga)N on top of the NW, both in Fig. 3.2b and d. The (In,Ga)N growth rate at this temperature can be deduced by dividing the $\text{In}_x\text{Ga}_{1-x}\text{N}$ length by the growth time. On average, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment length is 120 nm for a growth of 2 h. For this purpose, four different NWs are measured by TEM. This results in a typical axial growth rate of 1 nm/min. However, this value changes a bit for changing growth temperature and fluxes,
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

Figure 3.2: (a) Side-view SEM image of the NW ensemble $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment temperature series. (b) Zoom-in of the SEM image of sample A1, the yellow dotted box indicating the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment at the NW top part. The black dotted box indicates a part of the parasitic growth. (c) A zoom-in on the parasitic NWs at the bottom, as indicated in the black dotted box. The white lines are a guide-to-the-eye showing the broadening of the parasitic NW. (d) HRTEM image of the NW top of sample A1, as indicated before in the yellow box, showing the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment, measured by J. Bartolome.
3.2. Morphology of (In,Ga)N segments and MQW heterostructures

but also varies from sample to sample due to fluctuations in e.g. the NW diameter of the GaN template. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth rate is typically between 1 and 2.5 nm/min.

3.2.2. (In,Ga)N heterostructures

Fig. 3.3a and b show the side-view SEM images of the grown temperature series of the (In,Ga)N/GaN MQW heterostructure (series B) as well as a top-view SEM image of sample B2, respectively. First of all, the three samples contain well-separated and thin NWs. The NWs of sample B1, B2 and B3 show a well-defined morphology comparable to that of the GaN template as shown in section 2.6. Such a well-defined morphology means here rather thin and uncoalesced NWs with sharp edges. Furthermore, after the growth of the active region including the $\text{In}_x\text{Ga}_{1-x}\text{N}$ QWs, the NW top part seems to have preserved its radius for all three samples and no significant broadening took place as seen for the (In,Ga)N segment samples A2 and A3 for lowering the growth temperature.

![Figure 3.3a](image1.png)

![Figure 3.3b](image2.png)

![Figure 3.3c](image3.png)

**Figure 3.3:** (a) Side-view SEM images of the NW ensemble (In,Ga)N MQW heterostructure for the temperature series. (b) Top-view image showing a typical NW density and the parasitic NW growth in between the long NWs of sample B2. (c) Growth parameters for the different samples.

Here it has to be noted that growth parameters for the $\text{In}_x\text{Ga}_{1-x}\text{N}$ part, the QWs, are slightly changed in comparison to the (In,Ga)N segment samples, as indicated in Fig. 3.3c. For sample B1 and B2, the same growth parameters are used as for its corresponding (In,Ga)N segment sample A1 and A2. However, for the growth of sample B3 a lower
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

In flux is used of $\varphi_{\text{In}}^{\text{imp}} = 8$ nm/min instead of 12 nm/min, since in the (In,Ga)N segment sample A3 a huge broadening was observed as shown before. Apparently for sample B3, lowering the In flux resulted in less metal near the NW top and no broadening due to metal-rich growth conditions. The NWs in these samples are significantly shorter than in the other two samples, which is most probably due to a slightly too high growth temperature during the growth of the GaN NW template.

Parasitic growth happens to show up in the formation of small NWs in between the long wires or coalesced and attached to the NW foot part, as seen for the (In,Ga)N segments. Fig. 3.3b shows a top-view SEM image of sample B2, having a typical NW density and parasitic growth in between for all the samples. The white dot-like circles correspond to the long NWs, the darker grey parts in between are related to the small parasitic NW in between and attached to the bottom part of the long NWs. As can be observed, the largest part of the sample is covered by the parasitic NWs, whereas the coverage of the long NW ensemble is lower.

The structure and morphology of the parasitic growth seems not to change for different temperatures. However, if we compare it to the parasitic growth at the (In,Ga)N segment samples, it appears different. First of all it contains a different structures, segment versus MQW heterostructure. Secondly, the parasitic wires are shorter for series B, since the growth time of the active region of the heterostructure was shorter than for the segment.

We will see later that both parts, the top part of the NW and the parasitic NWs, formed during the growth of the active region, contain the same heterostructure.

3.2.3. Microstructure of In$_x$Ga$_{1-x}$N disks

We have seen that the well-defined overall morphology of the NWs is maintained after growing the In$_x$Ga$_{1-x}$N/GaN heterostructure. Now it is time to investigate the presence and microstructure of our 6 axial quantum wells in the active region. In order to do this, HRTEM images are needed.

As mentioned in the beginning of this chapter as a motivation, until now, (In,Ga)N NW heterostructures were grown on Si, possessing a high degree of coalescence and rather thick NWs. Moreover, the active region does not possess a nice MQW structure with sharp transitions between the QW and QB, but a more truncated cone shaped In$_x$Ga$_{1-x}$N insertion, possibly surrounded by a shell\cite{40}\cite{44}. This case is shown in a TEM image of Fig. 3.4a, where the In$_x$Ga$_{1-x}$N quantum disks possess an In content of approximately 30\%, which one can keep in mind as a reference point. Now we will compare the active region of NWs grown on Si with our NWs grown on TiN and discuss its properties.

In Fig. 3.4, a HRTEM image of the In$_x$Ga$_{1-x}$N/GaN active region of sample A2 is shown, at the top part of the NW (b) and in a parasitic NW at the bottom (c).

In Fig. 3.4b, the In$_x$Ga$_{1-x}$N QWs appear brighter than the GaN contrast with a darker edge. In general, the image shows the good morphology of the active region in comparison to the one grown on Si. The In$_x$Ga$_{1-x}$N QWs are nicely shaped, which means straight edges between the QW and QB. Furthermore, the QWs seem to possess a shape more towards an ideal heterostructure as shown in Fig. 3.1b without bending or a shape like the truncated triangles for the growth on Si, but a clear disk-like insertion.

Interestingly, we observe that the quantum discs are not reaching the NW sidewall
3.2. Morphology of (In,Ga)N segments and MQW heterostructures

**Figure 3.4**: TEM images of the In$_x$Ga$_{1-x}$N/GaN MQW NW samples. (a) The ‘old’ NW heterostructures grown on Si. The ‘new’ NW heterostructures grown on TiN. (b) Heterostructure at the top part of the NW and (c) in the parasitic growth resp. Data was acquired by C. N. Huang in the PhD thesis of M. Wöelz (a) and J. Bartolome (b,c).
but are embedded in a GaN shell. This kind of structure can be grown bottom-up if In is preferably incorporated in the center of the NW. This has been considered by F. Glas\cite{40} by comparing the sum of the elastic energies and surface energies for the case of In$_x$Ga$_{1-x}$N island growth to the case of In$_x$Ga$_{1-x}$N covering the whole NW top facet. From this point of view, the formation of an In$_x$Ga$_{1-x}$N cylinder in the center of the top facet is favourable, provided the lattice mismatch and the base diameter are high enough. This structure has been claimed experimentally for bottom-up grown (In,Ga)N nanowire heterostructures based on HRTEM images\cite{40}. Another way to obtain this structure is to radially overgrow a structure where the In$_x$Ga$_{1-x}$N insertion reached to the NW sidewall with GaN. However, not observed for these samples as expected, since the highly N-rich conditions are preserved as demonstrated by the absence of radial growth.

Regarding the parasitic growth, a HRTEM image of one of these small nanowires is shown in Fig. 3.4c. It possesses also the In$_x$Ga$_{1-x}$N heterostructure, resulting in two active regions in the samples. The volume of the In$_x$Ga$_{1-x}$N QWs in these parasitic NWs is possibly bigger than in the active region at the NW top, due to the slightly larger diameter of the parasitic NWs. Furthermore, unsharp edges and e.g. In fluctuations more likely to appear here, since effects like shadowing by the long NWs play a bigger role. Generally, it is less obvious and clear which fluxes to which extend are contributing to the growth of the parasitic NWs. Ideally, the parasitic growth should not take place in order address the origin and brightness of luminescence from the active region more easily.

The In concentration in the In$_x$Ga$_{1-x}$N QW can be calculated by strain analysis from HRTEM images. These calculations are based on the measurement of four different wires to get information about compositional fluctuations. In general, several types of compositional fluctuations are conceivable in the In$_x$Ga$_{1-x}$N quantum well:

- The In concentration may fluctuate within the QW.
- The average In concentration might differ from one QW to another within one NW. Recent microscopy studies on similar structures have indicated the the In content may increase progressively as the active region grows, due to a widening of the crystal lattice.
- The In composition might differ from one NW to the next if, for example, the diffusion lengths of In and Ga on the NW sidewalls are unequal and different NW diameters give rise to different ratios of the diffusion fluxes towards the top facet.

In our samples, the composition $x$ differs from one QW to another, between 15 - 30 %. However, a real trend could not be observed from QW to QW, because of the complex strain state. Also In fluctuation within one QW are not possible to address, and a far more difficult study by TEM should be carried out in order to investigate this. The average In content in sample B2 was determined to be 21%.

HRTEM images also provide information about the presence of cubic inclusion, most likely grown at lower temperatures during (In,Ga)N growth or stacking faults (SFs). It is observed that no cubic inclusions are present in the active region of the NW top part or in the parasitic NWs. However, SFs are several times observed in the In$_x$Ga$_{1-x}$N QWs at the NW top. These SFs are stretching over the whole NW diameter until the sidewalls. Stacking faults are also observed in the parasitic NWs.
In the next part, the luminescence properties of these NWs will be discussed. The information about the presence of cubic inclusion, SFs and In$_x$Ga$_{1-x}$N QWs will be very useful in order to understand the results.

3.3. Luminescence of the (In,Ga)N active region

For opto-electronic device fabrication, the NWs preferably exhibit intense emission with a wavelength that can be controlled via the In content. To investigate the luminescence properties on the NWs, the samples are first investigated by ensemble NW room-temperature photoluminescence (RT-PL) measurements.

For the investigated NW ensembles, the density is equal to $\approx 18.5 \, \text{NWs/}\mu\text{m}^2$, slightly fluctuating for varying samples. The laser spot has a diameter of about 1 $\mu\text{m}$, resulting in an area of 0.79 $\mu\text{m}^2$. So, roughly we can say that about $18.5 \cdot 0.79 \approx 15$ NWs are measured. In order to support statements about the luminescence properties of our wires, the sample must be probed and measured several times on different spots to improve statistics. Another, maybe more important reason for probing the sample on different spots, is the inhomogeneity of the samples due to temperature and impinging flux fluctuations or intrinsic wafer problems.

Besides RT-PL measurements, also low-temperature cathodoluminescence (LT-CL) maps with a higher spatial resolution are measured in order to allocate the different peaks in the emission spectra to a specific part of the NW. In principle, the emission of the NW ensemble can originate from three different part of the NW, namely (i) the active region at the top of the NW, (ii) the (base of the) GaN NW itself and (iii) the active region grown as parasitic nanowires at the bottom. For these LT-CL experiments, the wires are dispersed in distilled water and put on a Si grid. A single wire is probed with an electron beam used for excitation of the charge carriers, and the detector is set to the corresponding wavelength. With this, spectrally resolved maps can be obtained as function of the NW length. In these spectral maps the NW distance is shown, measured from bottom to the top, with the corresponding emission wavelength; this will be more clear when discussing the results.

In the next part, the emission properties of the (In,Ga)N segments will be discussed, followed by the axial MQW heterostructure. Since spectroscopy is not the main part of this thesis, and the discussion of the luminescence properties of our (In,Ga)N-GaN NW heterostructures is rather complex, it will only be discussed to a certain extent.

3.3.1. (In,Ga)N segments

The results of ensemble room-temperature PL measurements for the In$_x$Ga$_{1-x}$N segments are shown in Fig. 3.5. In general three different PL bands are visible. The first band, labeled as band I, represents the free exciton transition in the strain-free GaN NW emitting at 3.413 eV at RT and common to all samples. Furthermore, two broad bands are visible, the second one roughly between 2.9 and 3.1 eV, labeled as band II and a third band between 2.0 and 2.7 eV labeled as band III. The intensity of band II and III is lower than that of the GaN related emission, most likely because the volume of the GaN base is larger than that of the (In,Ga)N segment on top or than of the parasitic growth at the bottom. Besides a change in intensity, a clear change or trend in the peak position of band II and III as function of the growth temperature is not visible.
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

In Fig. 3.6 single wire LT-CL results are shown, representative for all measurements. 

In Fig. 3.6a and b show monochromatic CL maps with a superimposed SEM image of several single wires emitting in the range of band II and III respectively. In general, the slightly thicker part of the NW can be regarded as the bottom of the NW caused by the parasitic growth. Fig. 3.6c and d show a LT-CL spectral map of two different single NWs of sample A1 and A3 respectively, with the corresponding SEM image of the NW and direction of measurement. Also here the thicker bottom part of the NW corresponds to the parasitic growth.

The GaN peak can be observed along the whole NW template length. Furthermore, energy band II is visible in the parasitic growth in Fig. 3.6a and c and in the part just below the (In,Ga)N segment on top of the NW in Fig. 3.6a and d. Band III appears in the (In,Ga)N segment on top of the NW and in the segment of the parasitic growth.

As can be seen, bands II and III are quite broad. This, or more specific, the full width at half maximum (FWHM) gives an indication about compositional fluctuations in single NWs as well as NW to NW fluctuations. Regarding the former, the In concentration $x$ will be spatially inhomogeneous resulting in a broader peak, or in other words, several overlapping peaks at different energies leading to a broad energy band. However, we have to keep in mind here that in general, ternary alloys like $\text{In}_x\text{Ga}_{1-x}\text{N}$ have an intrinsic broader PL peak than e.g. GaN.

The emission observed in RT-PL spectra corresponds to the emission observed in the LT-CL maps. Band II around 3.0 eV possibly results from $\text{In}_x\text{Ga}_{1-x}\text{N}$ with a low In concentration, or more likely, cubic material or stacking faults (SF) in GaN or $\text{In}_x\text{Ga}_{1-x}\text{N}$. At room-temperature, stacking faults are only observed if their density is high enough.

Unfortunately, for the present samples the formation of cubic inclusions could not be checked by RHEED during growth, since the RHEED system was not operational. However, SFs are observed in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment by TEM. A stacking fault, as well as cubic inclusions, can emit in a broad range as shown by Lühnemann et. al.\cite{64} depending

![Figure 3.5: Ensemble room-temperature PL spectra of $\text{In}_x\text{Ga}_{1-x}\text{N}$ segments grown at three different temperatures. Data acquired by C. Pfüller.](image-url)
3.3. Luminescence of the (In,Ga)N active region

Figure 3.6: Single NW low-temperature CL measurements of the In$_x$Ga$_{1-x}$N segment NWs. Monochromatic CL maps with a superimposed SEM image showing the spatial location of (a) band II and (b) band III for several single NWs. LT-CL spectral map of a single NW showing the NW distance and the corresponding emission for sample A1 (c) and sample A3 (d). Data acquired by C. Pfüller.
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

on the cubic thickness. Since In$_x$Ga$_{1-x}$N is grown at fairly low temperatures, the
formation of lower quality material is enhanced, i.e. the formation of cubic inclusions and
SFs\cite{57,64,65}. Furthermore, in Fig. 3.6c, the band II emission is quite localized (sharper
peaks), which indicates cubic inclusions in the parasitic growth.

Band III appears in the NW top region where the segment is grown and also in the
parasitic growth. Cubic inclusions are less likely to explain this peak because of the low
energy, but not fully excluded. However, the In$_x$Ga$_{1-x}$N segment with an In content
roughly between 20 - 30% can explain this peak very well. The width of this peak could
originate from NW to NW fluctuations as well as compositional fluctuations. The band
split in Fig. 3.6c might originate from different kinds of defects in the In$_x$Ga$_{1-x}$N. The
(In,Ga)N segment having two parts of different In content could also explain these two
emission bands.

Another important aspect is the brightness of the different parts of the NW. In general,
as also seen in most of the LT-CL measurements, the parasitic growth is much brighter
than the (In,Ga)N segments on top of the NW.

3.3.2. (In,Ga)N MQW heterostructure

The (In,Ga)N segments and QWs are grown under same conditions and the In$_x$Ga$_{1-x}$N
QWs should therefore contain, roughly, the same In concentration. So, if no other effects
such as the QCSE would play a role, the peak position of the emission from the segment
and MQW should correspond.

![Figure 3.7: Ensemble room-temperature PL spectra of the In$_x$Ga$_{1-x}$N MQW heterostructure
grown at three different temperatures.](image)

Fig. 3.7 shows the RT-PL results of the In$_x$Ga$_{1-x}$N heterostructure temperature series.
Here, again several PL bands can be observed, however, occurring at different energies
for each of the samples. Band I, corresponding to the free exciton emission in the GaN
3.3. Luminescence of the (In,Ga)N active region

NWs, is observed in all the three samples. Secondly, band II between 2.7 and 3.2 is observed in sample B1 and B2. A third band III between 2.1 and 2.6 eV is observed only for sample B2. A fourth, less clearly visible band IV is present again for sample B2. Regarding sample B3, the band around 2.9 eV is in between band II and band IV. A clear trend in emission wavelength as function of growth temperature as observed by M. Wölz et al.\textsuperscript{[57]} is not observed in these RT-PL spectra. Furthermore we see that the GaN emission is the most intense, showing that in our samples, possible emission from the NW active region is always less intense than the GaN NW template.

![Single NW low-temperature CL spectral maps of the (In,Ga)N MQW heterostructures](image)

**Figure 3.8**: Single NW low-temperature CL spectral maps of the (In,Ga)N MQW heterostructures (a) B1, (b) B2 and (c) B3. (d) The NW distance shows the spatial origin of the luminescence. Data acquired by C. Pfüller.

Also for this temperature series, single wire LT-CL measurements are carried for which typical results are shown in Fig. 3.8a - c for sample B1 - B3 respectively. For these three samples, typically 4 to 6 wires are measured by LT-CL; the shown spectral maps represent very well the observed emission in all of the wires.

The GaN peak should be observed for all the three samples at 3.471 eV (357.2 nm) at low temperature (7 K)\textsuperscript{[66]}, representing the donor-bound exciton $D^0X$. In Fig. 3.8a-c, this
emission is a bit shifted due to a calibration problem. However, we can be sure that the emission band labeled as I is originating from the D_{0X} exciton in GaN. For sample B1, band II originates mostly from the active region on top of the NW, whereas in B2 and B3 it appears at the NW bottom. Band III is only observed in sample B2 and since the emission is broad and extends over (almost) the whole NW length, it is likely to be yellow luminescence in GaN\cite{66}. Band IV can be observed in sample B2 and B3, so for lower growth temperatures. It appears relatively bright at the top of the NW in the active region. In sample B2, this band perfectly corresponds to band IV as seen in RT-PL and is clearly from the MQW region on the NW top. For sample B3, the bright emission at the top corresponds well to the band in the RT-PL spectrum which appears between band II and band IV.

Regarding the emission between 2.9 and 3.2 eV, a likely explanation are cubic inclusions and SFs. From HRTEM images, SF are observed within the In_{x}Ga_{1-x}N QW, intersecting the entire NW. Such a SF can act as a quantum well within the In_{x}Ga_{1-x}N QW, leading to stronger localization effects\cite{67}. The absence of clear emission well below the GaN band in sample B1 indicates that the growth temperature was too high to incorporate In in the QWs and the emission at the NW top can be better explained by cubic GaN or SFs. For sample B2 and B3, band II can be explained the best as well with cubic GaN. In_{x}Ga_{1-x}N with a low In concentration in the QW is also possible in principle. However, then it is not likely to address the other peaks to In_{x}Ga_{1-x}N having a higher In concentration and therefore cubic inclusions is the most plausible explanation for band II.

The In_{x}Ga_{1-x}N is probably responsible for the emission of band IV, coming from the active region of the NW top.

To confirm the last result, a NW RT-CL measurement on the cross-section of a NW ensemble is carried out and is shown in Fig. 3.9. The different parts, GaN base (A), parasitic growth region (B) and MQW region (C) are highlighted in Fig. 3.9a and the corresponding spectra are shown in Fig. 3.9b. This confirms our last conclusion: the MQW in the parasitic growth emits mainly at the 3.0 and 2.3 eV bands, whereas the In_{x}Ga_{1-x}N active region at the top of the NW mostly emits at the 2.7 eV band as seen in the different spectra, but not as bright as expected. Furthermore, probable yellow luminescence of GaN in region A can also be observed around 2.3 eV, but is by far not as bright as the other parts in our nanowires.

In the single wire LT-CL maps a clear trend is not visible in the peak position of the In_{x}Ga_{1-x}N emission from the active region at the NW top. Furthermore, as seen in general, and as well as found for the (In,Ga)N segments, the parasitic growth is brighter than the active region at the NW top. In these wires, it seems to be very difficult to control the In concentration in the QWs by the growth temperature.

In order to learn something about e.g. compositional fluctuations and atomic distribution of In and Ga in the active region of the NW, measurements with atom probe tomography are carried out. The results of these measurements give us information about the structural properties of the In_{x}Ga_{1-x}N-GaN NW heterostructures in order to also better understand the growth and optical properties of the nanowires.
3.4. 3D structural analysis by atom probe tomography

The axial (In,Ga)N/GaN NW heterostructures with six QWs at the top are measured by atom probe tomography (APT) to obtain 3D structural information. In order to get a high sensitivity and low background noise when measuring different elements, for every new measurement an optimum between the applied voltage and the assisting laser-power has to be found. It is well reported in literature that different elements like Ga, In and O in axial NW heterostructures can be successfully measured\cite{61,68}. However, measuring N seems to be difficult and is not well reported in literature. In this thesis the experimental details of APT will not be discussed in detail, but we will analyze the results in order to gain a better understanding of the growth of axial (In,Ga)N NW heterostructures. Nevertheless, we remark that not the whole NW can be measured, but only a smaller volume as shown by the brighter and small cylinder in Fig. 3.10a. The diameter of this cylinder does not cover the entire NW. In general, about 60% of the NW diameter can be analyzed. Secondly, the exact alignment of the NW appears to be very difficult and the NW might be measured in a slightly tilted way, as exaggeratedly shown in Fig. 3.10b. Furthermore, little bending of the NW during the measurement can cause problems of the same character.

In Fig. 3.11a, a 3D APT result is shown for the MQW sample B2. It shows the different elements in the NW base, the active region containing the QWs and the top part of the NW with the cap. The Ga is shown in yellow, the N in red and the In in blue. In order to have a clearer image, the Ga and N atoms are displayed a bit smaller than the In atoms. The image shows the widening of the QWs, i.e. increasing QW width, from the first to the sixth QW as indicated in the figure. However this APT result on its own cannot conclude a widening of the QWs towards the NW top, it is consistent with the observations in HRTEM images as shown in section 3.2.3. Therefore, this observation is not an artifact of the measurement.

In Fig. 3.11b, the Ga, N, In and O concentrations as function of the NW length (in
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![Diagram showing the axial heterostructure with 60% of the NW diameter measured.]

Figure 3.10: (a) The brighter cylinder shows the part of the NW which is measured by atom probe tomography. Roughly 60% of NW diameter can be measured up to a maximum of ∼200 nm. (b) In APT experiments, the measured volume is often not aligned to the center of the NW. Problems due to bending of the NW can lead to a tilt of the measured volume with respect to the NW.

axial direction) are shown. The concentrations are given as percentage of all the measured atoms. For example, the In concentration is equal to In/(In + Ga + N + O). The numbering of the QWs are taken in order of growth. However, the APT measurement itself starts from the other way, starting with the GaN cap as located on the left at NW distance = 0. At the top part of the NW, roughly concerning the first 10 to 20 nm of the measured volume, the measured Ga and N are not stoichiometric, or i.e. are not found in equal concentrations as would be expected. Surprisingly, in this part, the In concentration is significantly above the noise level. Both observations can be explained by the fact that during the beginning of the measurement the correct parameters (e.g. laser power, applied voltage) have to be found. This results in a changing detection rate until stoichiometric conditions are found for the measurement of the GaN cap. As the measurement, and thus NW distance evolves, the Ga and N concentration in the cap, QB and NW base are roughly equal and constant. When In is measured within the QWs, the Ga signal drops since Ga is replaced by In in the In$_x$Ga$_{1-x}$N QWs.

Besides the Ga, N and In concentration, the O concentration is also shown in Fig. 3.11b. The part in the black dotted box shows the In and O concentration of the first QW and is enlarged on the right side. The presence of O above the noise level is found close to the first QW. As reported in literature, it is likely that the oxygen present in the growth chamber will be incorporated when the shutters are closed and the fluxes are interrupted. This is the case just before the growth of the first QW, when the growth is interrupted to lower the In$_x$Ga$_{1-x}$N growth temperature.

If we zoom in on the region of the MQWs and in particularly the In concentration, we
3.4. 3D structural analysis by atom probe tomography

Figure 3.11: (a) APT measurement of an (In,Ga)N MQW NW heterostructure, showing the element composition of the active region. (b) Graph of the Ga, N, In and O concentration in axial direction of the NW. (c) Zoom-in on the In content in the MQW region, with the average In content per QW indicated as well as the determined QW thickness. Data acquired by A. Rodil Doblado and S. Kölling.
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can determine the thickness of the QWs (in axial direction) as shown in Fig. 3.11c. The QW thickness varies from 3.45 nm to 3.6 nm, with an exception for the third QW having a thickness of 2.45 nm. Comparing these values with the QW thicknesses obtained by HRTEM analysis, we see that both techniques are in good agreement. For the APT analysis, the chosen region of interest (ROI) can result in bigger or smaller lateral fluctuations in QW thickness and it appears to be a critical parameter, also since the QWs do not extend over the full NW diameter.

Furthermore, the In concentration can be determined and is given here as the In content \( x \) as used in the same way as in the rest of the thesis, namely: \( x = \frac{\text{In}}{\text{In} + \text{Ga}} \), which differs from the concentration in Fig. 3.11b. The average In concentration for each single QW is shown in Fig. 3.11c. Taking into account all six QWs, this results in an average In content in the QWs of about 17%. This value is in the range of the values obtained by the HRTEM measurements (15 - 30%). A discrepancy can result from the way of defining the GaN/In\(_x\)Ga\(_{1-x}\)N QW interface in the data shown in Fig. 3.11c. In this figure, the start of the QW is defined at half height of the first increase in In signal above the noise level. In comparing values obtained by APT and HRTEM images, we also have to take into account the statistics of both techniques. For this specific sample (B2), four NWs are analyzed by HRTEM, whereas only one by APT.

Topview images of the QWs are shown in Fig. 3.12a - c, for QW 3, 5 and 6, respectively. The images have a circular field-of-view as sketched in Fig. 3.12d where the red circle indicates the analyzed part of the wire in lateral directions. This region is not aligned to the NW center, which leads to circular shaped edges of the QW in the top-view images. However, a part of the images clearly show the hexagonal QW shape, which has never been shown in literature for In\(_x\)Ga\(_{1-x}\)N/GaN NW heterostructures. Although not the full In\(_x\)Ga\(_{1-x}\)N insertion is covered in these top-view images, it can be assumed that the whole QW possesses this hexagonal structure. What cannot be excluded, is a rotation of the hexagonal structure of the QW relative to the hexagonal GaN. Therefore, analyzing a volume of the NW which covers the whole NW diameter would be a next step.

Concerning a single QW in Fig. 3.12, fluctuations of the In content in lateral directions can be observed. A preference for In to be incorporated at e.g. the center or towards the edge of the QW, is not clearly visible. Indium might be preferred to be incorporated towards the edge of the QW due to strain related effects. However, from a single wire measurement this is difficult to conclude.

Summarizing, we have seen that the QW thickness as well as the average In concentration of the QWs are comparable with values obtained from HRTEM analysis. Furthermore, the APT results are consistent with the HRTEM images which showed that the QWs are not reaching the NW sidewall. Only a part of the total NW volume can be analyzed; a possible solution to detect a cylinder with the diameter of the NW, overgrowth of the NW with a thick enough shell would be needed. It has also been shown that the QWs possess a hexagonal structure, as expected, but never observed in literature for (In,Ga)N-GaN NW heterostructures. It cannot be excluded yet that the hexagonal structure of the (In,Ga)N disc is rotated relative to the GaN, which would however be unlikely. More wires have to be investigated in order to increase the statistics and draw any conclusions about In fluctuations in lateral directions and possible preferences for the In to be incorporated in the center or more towards the edge of the quantum disc.
3.4. 3D structural analysis by atom probe tomography

Figure 3.12: Top-view images showing the hexagonal shape of three different In$_x$Ga$_{1-x}$N quantum discs for QW 3 (a), QW 5 (b) and QW 6 (c). A sketch of a top-view image of the quantum disks (d). Only a part of the disc is imaged as shown in the red circle which shows the part of the wire which is measured in lateral direction. Data acquired by A. Rodil Doblado.
3. Growth and characterization of (In,Ga)N/GaN axial heterostructures

3.5. Conclusion and outlook

In general, the purpose of the growth of these (In,Ga)N/GaN axial NW heterostructures was to investigate these wires by atom probe tomography and fulfill a better understanding of the fundamental physics concerning the synthesis of axial (In,Ga)N heterostructures embedded in GaN NWs. The structural and compositional information gained by APT could be compared with other techniques like HRTEM.

We were able to grow axial (In,Ga)N heterostructures in thin and well-separated GaN NWs at three different temperatures. The GaN NWs were formed in a self-assembled way on the metal TiN. After the (In,Ga)N/GaN growth of the multi-quantum wells (MQWs), the active region, the well-defined NW morphology of the GaN NW template was preserved for all the three different temperatures. However, during (In,Ga)N growth, parasitic growth of smaller NWs at the bottom and in between the longer NWs showed up. Important growth parameters are the growth temperature and V/III ratio, especially at the NW top facet. We have seen that if the local V/III ratio at the top facet is smaller than one, which means metal-rich conditions, NW widening at the top facet will set in. The local V/III ratio results from an interplay between the applied fluxes and the growth temperature, since metal diffusion, desorption and material decomposition are temperature dependent quantities. We managed to obtain a constant NW diameter during the growth of the active region, which indicated a preservation of N-rich growth conditions.

Furthermore, we have seen the formation of well-defined (In,Ga)N QWs with sharp edges and disk-like morphology within the GaN NW. The microstructure of these (In,Ga)N insertions having such a “nice” morphology has never been reported in literature so far. A remarkable result was the observation of the QWs not reaching across the whole NW diameter. Moreover, the QW width appeared to increase, whereas the QW thickness would decrease for the different QWs as seen from the first to the last grown QW. By strain analysis of HRTEM images, the average In content in the QWs was determined to be between 15 - 30% for the sample grown at 540°C. Fluctuations between successive QWs as well as in the QW could not be observed by this technique, whereas NW to NW fluctuations have been seen for the four NWs which were measured.

The luminescence properties of these NW heterostructures were investigated by NW ensemble RT-PL and single wire LT-PL experiments. From the spectra, we could conclude that the emission from the active region was less bright than from the parasitic growth at the bottom of the NW ensemble. Furthermore, it seemed that the emission wavelength was not well controllable by the growth temperature.

The structural and compositional analysis by APT showed also the presence of well-defined (In,Ga)N QWs within the GaN NW. It also showed that the QWs are not fully reaching towards the NW sidewalls, which is consistent with the HRTEM results. Here we have to remark that not the whole NW in lateral direction could be measured, as well as, although very little, bending of the NW played a role here. For future experiments, the NW heterostructures could be overgrown by a thick enough shell (e.g. GaN shell) in order to enable the measurement of the whole region of interest. Besides these structural properties, the average In content in the six QWs could be determined to be around 17%, which is in the range of the values obtained by HRTEM. However, the discrepancy between both techniques can be caused by NW to NW fluctuations, since this is the APT result of only one NW. Also oxygen was found in the NW at places where the growth was interrupted or ended. This is a common observation in MBE growth. The 3D infor-
3.5. Conclusion and outlook

Information gained by APT could also give information about the actual shape of the QWs. Top-view images of the (In,Ga)N insertions showed the hexagonal shape of the QWs as expected for hexagonal GaN NWs, but never observed in literature before. For the future, more NWs could be measured to increase statistics and possibly gain more well funded information about In fluctuations from QW to QW and within one QW.
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

The (In,Ga)N core-shell structure might overcome some problems encountered in the axial heterostructures due to several conceptual differences, like e.g. the growth on non-polar $M$-plane sidewalls. Also a larger active region could be obtained in comparison to axial or planar heterostructures and consequently increases the light output intensity $[41]$.

In$_x$Ga$_{1-x}$N shell growth on GaN NW $M$-plane sidewalls on thin and well-separated self-assembled NWs on metal both grown by MBE, has not been presented in literature so far. Furthermore, as seen in the previous chapter of this thesis, the axial (In,Ga)N heterostructures are not as bright in the active region as wanted and expected before. From an experimental point of view, it is a next step towards high quality nanowire LEDs if one could grow by MBE an In$_x$Ga$_{1-x}$N shell containing a significant amount of In. Until now people have realized PAMBE grown (In,Ga)N shells obtained on selective area grown (SAG) GaN microwires with MOVPE, using a top-down principle. Most (In,Ga)N-GaN core-shell columnar heterostructures have micron-size diameter and height, rather than nanoscale dimensions as is the case in this thesis. The In contents in the shell could be varied by changing the growth temperature and V/III ratio, where the In/Ga ratio had little effect within the range considered in those works. The In content varied from several percent $\sim$ 4% up to $\sim$ 12 %.$[9][42]$. Two difficulties regarding the growth of (In,Ga)N on the sidewalls have to be overcome. First, finding the proper growth conditions for radial growth along the whole NW, i.e. growth on the $M$-plane sidewalls instead of the $C$-plane top-facet. The material incorporation on the latter plane is preferred. Secondly, when sidewall growth conditions are found, In should be incorporated. It appears that In is preferably incorporated on the $C$-plane in comparison to the $M$-plane.

The main goal of the experiments carried out in this part of the thesis is to grow a clearly observable (In,Ga)N shell around the GaN NWs, preserving a good morphology. Additionally In should be incorporated during growth on the sidewalls, and not only on the top facet of the nanowires which was the case in the axial heterostructures. If In is incorporated in the shell one could continue growing heterostructures which can lead eventually to the fabrication of an (In,Ga)N core-shell heterostructure LED. The focus of the next sections will be on showing shell growth preserving a good morphology. Secondly the In incorporation and sidewall luminescence will be discussed in the subsequent sections.

4.1. Growth of (In,Ga)N shells

To grow an (In,Ga)N shell around the GaN core, radial overgrowth of the GaN template is needed. Different specific models for radial growth are proposed by S. Fernandez-Garrido et al.$[36]$ and V. G. Dubrovs'kiĭ et al.$[69]$, i.e. radial growth by sidewall nucleation,
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

radial growth by the step flow with many step or radial growth by the step flow with just one step anytime, one more likely to occur than the other. For more details I would like to refer the reader to the corresponding articles.

Radial growth occurs during metal-rich growth, and at low enough growth temperatures as well during N-rich growth. However, the growth rate on the top facet is strongly preferred over sidewall growth under N-rich conditions. For metal-rich growth conditions, broadening of the NW top facet and also radial growth along the whole NW length is more pronounced.

For the (In,Ga)N shell overgrowth on GaN NWs, two different key points for material incorporation at the sidewalls are of importance. First of all, one can try to suppress the favourable incorporation on the C-plane top facet over sidewall M-plane incorporation. It is not clear if this can be achieved by a change of growth conditions. Secondly, it might be possible to suppress the diffusion along the NW sidewalls and hence less incorporation at the top facet, but at the sidewall.

Since radial growth, and more specific, widening at the NW top is preferred during metal-rich conditions, this will be used as a first ‘Ansatz’ for the growth of core-shell heterostructures. However, N-rich growth conditions will also be pursued in order to investigate the window of growth conditions for (In,Ga)N shell growth.

The In incorporation depends on several flux contributions as discussed in chapter 2.7. In order to control these contributions by the growth temperature, and hence the In incorporation, a temperature series for (In,Ga)N shells is grown under metal-rich conditions. This temperature series is noted in Appendix A as ‘series C’ containing three samples grown at 490°C, 460°C and 400°C, labeled as C1, C2 and C3 respectively. In order to compare the morphology and luminescence properties, a dummy sample is grown for sample C2, labeled as C2. A so-called dummy sample means a sample with the same growth conditions as the initial one, but the In shutter stays closed during the (In)GaN growth. The total applied metal flux ($\phi_{In} + \phi_{Ga}$) will remain the same for this sample, which means $\phi_{Ga}$ has to be increased by the amount of $\phi_{In}$, i.e. the V/III ratio was the same for sample C2 and C2. The N-rich grown samples are labeled as D1 and E1, grown at the same temperature as sample C1 (490°C) and C2 (460°C), respectively. Sample D1 is grown under strong N-rich conditions (nominal V/III = 4.08), whereas E1 under slightly N-rich conditions (nominal V/III = 1.1). An overview of the growth parameters of these samples is also shown in Fig. 4.1.

4.1.1. Experimental growth details

The (In,Ga)N shells were grown by molecular beam epitaxy on a GaN NW template as shown in section 2.6. In contrast to GaN NW growth, the growth temperature of (In,Ga)N is reduced by $\sim$200°C to enable the growth of (In,Ga)N. Furthermore the rotation speed should be increased in such a way that one rotation corresponds to the growth of one (In,Ga)N mono-layer (ML). Of course, in principle every integer of rotations per ML can be taken in order to prevent compositional fluctuation in lateral direction due to a different exposure time to the fluxes for different sides of the NW.
4.1. Growth of (In,Ga)N shells

Metal-rich growth conditions

In Tab. 4.1, a typical growth recipe of series C is shown for the growth of a GaN template followed by a metal-rich grown (In,Ga)N shell.

Every growth starts with the in chapter 2 discussed growth of the GaN template. After this growth part at ‘high’ temperature, the 100% In desorption test is done in order to achieve information about In desorption and deposition on the substrate as discussed in section 3.1.1. To achieve this calibration, the temperature is kept high (695°C) after the growth of the GaN base, in the same way as discussed for the growth of the axial heterostructures. Since one of the main questions in these core-shell experiments is if In is present or not, this test is of main importance for continuing growth experiments.

After the In desorption test, the metal fluxes are interrupted and $T_{TC}$ is ramped down to the (In,Ga)N growth temperature of 490, 460 or 400°C. The thermal capacity of the sample holder assembly delays the response to temperature changes. Therefore, the rate of change is progressively decreased towards the end of the ramp, and an additional 5 min (or more) is allowed for stabilization.

The In$_x$Ga$_{1-x}$N shell is grown with $\phi_{In} = 4$ nm/min, $\phi_{Ga} = 4.5$ nm/min and $\phi_{N} = 6.5$ nm/min, giving a V/III ratio of 0.76. The shell is targeted to have a thickness $> \sim 10$ nm in order to prove with certainty a shell presence by SEM images. From preliminary experiments, the growth rate at the sidewalls was estimated around 0.3 nm/min, lower than on the top facet. Therefore, the (In,Ga)N was grown for 30 min, most likely resulting in a shell thickness of at least 10 nm. This growth rate is determined by measuring the diameter increase dividing by the growth time as we will see in one of the next sections.

N-rich growth conditions

In order to explore the growth parameter space as mentioned in the introduction of this chapter, (In,Ga)N shells are also grown under N-rich conditions and further investigated.

Figure 4.1: The (a) V/III ratio and (b) In/Ga ratio versus growth temperature are shown for the different samples. Sample C1 - C3 and C2 are grown under metal-rich conditions. Samples D1 and E1 are grown under N-rich conditions.
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

Table 4.1: Step-by-step growth recipe for the growth of the GaN template followed by the growth of a metal-rich grown (In,Ga)N shell.

<table>
<thead>
<tr>
<th>growth step</th>
<th>t (min.)</th>
<th>T (°C)</th>
<th>active sources</th>
<th>fluxes (nm/min)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-ramp and</td>
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<td></td>
<td></td>
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<tr>
<td>pyrometer check</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>GaN base</td>
<td>75</td>
<td>695</td>
<td>Ga, N</td>
<td>$\phi_{Ga} = 6.6$, $\phi_{N} = 14.7$</td>
<td></td>
</tr>
<tr>
<td>$T_{Ga}$ ramp</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>100% desorption</td>
<td>1</td>
<td>695</td>
<td>In, Ga, N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>test</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>T-ramp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(In,Ga)N shell</td>
<td>30</td>
<td>400-490</td>
<td>In, Ga, N</td>
<td>$\phi_{In} = 4$, $\phi_{Ga} = 4.5$, $\phi_{N} = 6.5$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Step-by-step growth recipe for the growth of the GaN template followed by the growth of a N-rich grown (In,Ga)N shell.

<table>
<thead>
<tr>
<th>growth step</th>
<th>t (min.)</th>
<th>T (°C)</th>
<th>active sources</th>
<th>fluxes (nm/min)</th>
<th>comments</th>
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<td>T-ramp and</td>
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<td>pyrometer check</td>
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<tr>
<td>GaN base</td>
<td>75</td>
<td>695</td>
<td>Ga, N</td>
<td>$\phi_{Ga} = 6.6$, $\phi_{N} = 14.7$</td>
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<tr>
<td>$T_{Ga}$ ramp</td>
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<tr>
<td>100% desorption</td>
<td>1</td>
<td>695</td>
<td>In, Ga, N</td>
<td></td>
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</tr>
<tr>
<td>test</td>
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</tr>
<tr>
<td>T-ramp</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shell ((In,Ga)N)</td>
<td>180</td>
<td>490</td>
<td>In, Ga, N</td>
<td>$\phi_{In} = 2.4$, $\phi_{Ga} = 1.2$, $\phi_{N} = 14.7$</td>
<td></td>
</tr>
</tbody>
</table>

In principle the growth recipe is the same as for the metal-rich grown samples of series C, except for two key changes:

- $\phi_{metal} = \phi_{In} + \phi_{Ga} < \phi_{N}$, otherwise it wouldn’t be ‘N-rich’ growth.
- The growth time is increased drastically in order to grow a shell of at least the same thickness.

A typical growth recipe for this kind of (In,Ga)N shell growth can be found in Table 4.2. The main difference between the two N-rich grown samples is the V/III ratio. Sample D1 is grown highly N-rich, with a nominal V/III ratio of 4.1, whereas E1 is grown under slight N-rich conditions having a V/III ratio of 1.1.

This growth recipe looks very similar to the one for the In$_x$Ga$_{1-x}$N segments treated in chapter 3. Nevertheless, the growth approach is different. The segments were grown using the ‘high temperature approach’ and high In flux, whereas now, the (In,Ga)N shell is grown at lower temperatures with low In flux similar to a ‘low temperature approach’ in order to e.g. suppress the diffusion along the sidewalls.
4.2. Morphology analysis of GaN/(In,Ga)N core-shell NWs

In Fig. 4.2, SEM images are shown of the main samples important for understanding (In,Ga)N sidewall growth. It can be seen as a kind of growth map, an overview of the most significant growth experiments carried out as part of this work to reveal (In,Ga)N sidewall growth on self-assembled well separated thin GaN NWs by MBE. Cross-section SEM images are obtained to analyze the morphology for different growth approaches, metal-rich vs N-rich. The growth temperature, and to a lesser extend the V/III ratio, is used to control (In,Ga)N sidewall growth. As introduced before, the samples are divided in a metal-rich grown temperature series, labeled as C1, C2 and C3, shown in the upper row of the figure. The second row shows the metal-rich grown dummy sample C2 and the N-rich grown samples D1 and E1, at two different temperatures and V/III ratios. In the lower row, the GaN template is shown again as a reference for comparing the morphology.

In the following part the influence of these parameters on the morphology will be discussed. Since radial shell growth is demanded, the metal-rich growth approach will be taken as a starting point in the jungle of different growth parameters and their combinations.

From Fig. 4.2 it is immediately clear that changing the temperature or V/III ratio has a large influence on the final morphology after (In,Ga)N growth.

Regarding the metal-rich temperature series, we see a clear change in the NW top morphology with decreasing temperature. For sample C1, NW broadening at the top did not occur so clearly. When the growth temperature is lowered, for sample C2 and C3, widening of the NW top facet during (In,Ga)N growth clearly appears and some kind of mushrooms appear on top of the NW. This feature is more pronounced for decreasing growth temperatures.

The NW diameter of this series can be compared with the NW diameter of the GaN template, and apparently from this first rough comparison, it seems that shell growth appeared for all the samples of series C grown under metal-rich conditions. A quantitative analysis of radial growth will be discussed later on, which will confirm the presence of a shell.

So, when lowering the temperature, radial growth at the top becomes more dominant resulting in more pronounced and larger mushrooms on top. This indicates a larger effective metal-flux $\phi_{\text{metal,eff}}$ at the top facet for lowering growth temperature. In general, decreasing $T_{\text{TC}}$ means less diffusion of In and Ga, but also less In desorption (negligible Ga desorption in this temperature regime). In principle the effective metal flux at the top facet is given by, taking into account the temperature regime:

$$\phi_{\text{metal,eff}} = \phi_{\text{Ga}}^{\text{imp}} + \phi_{\text{Ga}}^{\text{diff}}(T) + \phi_{\text{In}}^{\text{imp}} + \phi_{\text{In}}^{\text{diff}}(T) - \phi_{\text{In}}^{\text{des}}(T),$$

with $\phi^{\text{imp}}$, $\phi^{\text{diff}}$ and $\phi^{\text{des}}$ the impinging, diffusion and desorption fluxes of Ga and In respectively. The decomposition of In$_x$Ga$_{1-x}$N is taken into account within $\phi_{\text{In}}^{\text{imp}}$ and $\phi_{\text{In}}^{\text{des}}(T)$, since the In resulting from the (In,Ga)N decomposition can either be desorbed or reincorporated again, and is difficult to distinguish.

Thus, decreasing the temperature increases the $\phi_{\text{metal,eff}}$ at the top facet, which indicates that due to lowering the growth temperature, the reduction of In and Ga diffusion towards the top was less strong than the smaller amount of In desorption. This indicates
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

**Figure 4.2**: Scanning electron micrographs of (In,Ga)N core-shell NWs grown under different conditions. Sample C1 - C3 are grown under metal-rich conditions, belonging to temperature series C. The ‘dummy’ sample (C2) is grown under the same conditions as C2, but the In is replaced by Ga. Sample D1 and E1 are grown under N-rich conditions, both at different temperature and V/III ratio.
4.2. Morphology analysis of GaN/(In,Ga)N core-shell NWs

a stronger temperature dependence of metal desorption than diffusion. Or in slightly other words, decreasing the temperature under metal-rich conditions means more metal staying on the substrate contributing to the NW growth by diffusing to the NW top. What also should be mentioned here is that the presence of In can increase the Ga diffusivity as reported in literature. If for lower growth temperature, more In remains on the sample, this can also improve the Ga diffusivity towards the top resulting in faster broadening of the top facet, opposing the effect of a lower Ga diffusivity at lower temperature.

The dummy sample, C2, is also grown under metal-rich conditions and the same nominal V/III ratio and growth temperature as C2. It also shows widening of the top facet, indicating locally metal-rich conditions in this region. Here, shell growth apparently succeeded as well when we compare it to the GaN NW template image. The mushrooms on top of the wire are not as pronounced and clear as in sample C2, where In was present. If the widening at the top is considered as an indication for the magnitude of $\phi_{\text{metal,eff}}$, one can clearly see from the SEM images in Fig. 4.2 that the effective amount of metal reaching the top facet of the dummy sample (C2) was smaller than the normal sample (C2) where (In,Ga)N is grown, so: $\phi_{\text{metal,eff}}^{C2} < \phi_{\text{metal,eff}}^{C2}$. Several explanations can be given, with the most probable:

- The In diffusion length is larger than for Ga resulting in $\phi_{\text{diff}}^{\text{In}} > \phi_{\text{diff}}^{\text{Ga}}$, and just more In will reach the top facet to be incorporated.

- The Ga diffusion length is enhanced in the presence of In and more Ga will reach the top facet to be incorporated.

Most likely, both effects play a role and they are consistent with calculations about the amount of material incorporated at the top part or sidewall of the NW. We calculated the grown volume on top of the NW $V_{\text{top}}$ and on the sidewalls $V_{\text{side}}$ by measuring the dimensions of the different parts of the NW with the software imageJ. With this software, SEM images can be loaded and dimensions of the NWs can be measured with high accuracy. The ratio of the volume of the grown material on top and at the sidewalls of the NW ($V_{\text{top}} / V_{\text{side}}$) for sample C2 and C2 are 1.11 and 0.46, respectively. This shows that for the dummy sample much less material is incorporated at the NW top, due to the effects described here above. Ultimately, it remains difficult to relate the Ga diffusion length qualitatively to the presence of In.

Looking to the N-rich grown samples D1 and E1, we see no real formation of these mushrooms on top of the wires. Secondly, also here a shell growth has probably been worked out, since the wires seems thicker than the ones of the GaN NW template. However, also a difference in the NW sidewalls can be seen; the NW sidewalls of D1 seem to be a bit more bumpy than those of E1. This can be due to the difference in growth temperature, however not very likely since this effect is not seen for the metal-rich grown samples. More probably this is because of the difference in V/III ratio, where sample D1 is grown very N-rich, or the difference in (In,Ga)N growth time. The (In,Ga)N part in D1 is grown for 180 min, whereas 45 min for sample E1. One can imagine when growing for a longer time, it is possible to become less smooth sidewalls.

So from a morphology point of view, apart from the parasitic growth, these N-rich grown shells are nicely shaped, having more or less straight sidewalls and no strange
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

morphology on top. The overall morphology comes close to the one which can be used for further processing of e.g. an LED.

![Bird-view SEM image of (a) sample C1 and (b) sample D1, showing the well-separated NWs with different final morphology and parasitic growth at the bottom of the NW ensemble.](image)

Furthermore, it is clear that the so-called ‘parasitic’ growth is present in all the samples for both growth conditions. Fig. 4.3 shows a bird-view image of samples C1 and D1 grown at the same temperature but with a radically different V/III ratio. Its final morphology depends strongly on the V/III ratio as expected before: under metal-rich conditions a parasitic layer is formed as expected, since layer growth is established for V/III < 1 conditions. In contrast, the parasitic growth for N-rich conditions is from the same nature as during the growth of the axial (In,Ga)N heterostructures and new smaller NWs are nucleated and formed during (In,Ga)N growth.

Under locally stronger metal-rich conditions (smaller V/III ratios) near the parasitic growth, the layer becomes more dense due to the metal excess and preferred radial growth. The opposite is true when going towards stochiometric conditions or V/III ratios larger than one. The presence of parasitic growth makes the analysis of volume measurements of the deposited material, interpretation of QMS signal and luminescence measurements again more complicated.

To discuss a little deeper the widening of the NW top facet during metal-rich growth, we zoom in on the NW top part of sample C2 and C3, as shown in Fig. 4.4a and b respectively. For both samples it seems that semi-polar planes are formed during (In,Ga)N growth. This is observed only for the samples grown at lower temperatures < 490°C, which might be related to the formation of cubic GaN. The formation of a NW top morphology having a 3-fold symmetry suggests the formation of zinc-blende material[5]. We have seen in several SEM images that these semi-polar facets tend to appear to a greater extent.
4.2. Morphology analysis of GaN/(In,Ga)N core-shell NWs

Figure 4.4: SEM images of the top part of the NW formed during In$_x$Ga$_{1-x}$N growth of sample C2 (a) and C3 (b).

for lower growth temperature.

The second unexpected result, on first hand, is the absence of continuous radial growth of the top facet. Since for these samples, the nominal, i.e. impinging, metal flux is always larger than the N flux, constant metal-rich conditions are expected. However, this is not observed, and especially well observable in NW 2 as indicated in Fig. 4.4b, where no semi-polar facets appear and the NW diameter is self-limited by growing in axial direction from a certain moment, indicated with the white dashed line. For the NWs which contain semi-polar facets, it is less clear what is going on there.

However, let’s concentrate on the wires like NW 2. When (In,Ga)N growth starts, the metal concentration at the top facet is larger than the N concentration and radial growth sets in. This continues until a certain point, the white dashed line. Let’s assume for the discussion that the radius became so large that diffusion from the sidewalls to the NW top becomes negligible from this white line on. To become N-rich conditions, the desorption of In (and maybe Ga, although not likely at this temperature) plus the decomposition of (In,Ga)N is larger than the impinging metal fluxes reducing the effective metal flux at the top. This could explain the local N-rich conditions for these NWs. The desorption of In from the sidewalls is also reported in literature where it is found that In desorbs more easily from the $M$-plane than the $C$-plane. An additional effect can be that at a certain moment the side facets of the NW top are not reached by the impinging flux anymore and less metal reaches this part by diffusion.

So, when comparing metal- and N-rich growth conditions, we see a clear difference in the NW top morphology, constituted during the last growth step. Under metal-rich conditions, increasingly present for lowering growth temperature, a broadening of the NW radius occurs as theoretically expected. This feature does not appear for N-rich growth conditions. Although radial growth for sample C1 is also not that clear as in C2 and C3, and comparing C1 and D1 could indicate having more or less the same growth conditions, we see a clear difference in widening of the NW top when comparing C2 and E1, grown at the same temperature. Additionally, the parasitic growth of sample C1 and D1 are not of the same nature which shows the (radically) different growth conditions.

So far we have seen a change in the morphology for (In,Ga)N grown at different tem-
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...peratures, due to the changing diffusion, desorption and decomposition rates of the metal adatoms as function of temperature. Furthermore, we can conclude that the growth of these ‘mushrooms’ on top of the GaN NW is not something to be very useful in order to produce an LED or other opto-electronic device.

Furthermore, shell growth can be observed for every sample compared to the GaN NW template. To a more or less extend, disregarding the NW top, all the samples contain a homogeneous shell grown along the whole NW length with rather smooth NW sidewalls.

4.2.1. Quantitative analysis of shell growth

In the next part, we will quantify the radial growth to draw better conclusions about which growth conditions are suited the best for the growth of a thick and homogeneous (In,Ga)N shell. The most practical way is to compare the NW diameter before \((d_{\text{NW, before}})\) and after \((d_{\text{NW, after}})\) the (In,Ga)N shell growth resulting in the structure initially expected as shown in Fig. 4.5a, which also shows a SEM image, 4.5b, of the GaN template used as a basis for shell growth.

![Figure 4.5](image.png)

**Figure 4.5**: (a) Intended NW structure and increasing diameter before and after (In,Ga)N shell growth; a clear increase in diameter proves shell growth, which can be measured by SEM imaging. (b) SEM image of an ensemble GaN NW template with typical NW properties having a diameter of \(~40\) nm and length of \(~800\) nm.

The cross-sectional SEM images are loaded with the free software ImageJ (ref. xxx) after which geometrical properties of the NW ensemble can be measured with high accuracy. The GaN template as used for (In,Ga)N core-shell growth experiments resulted in NWs with a diameter of \(40 \pm 16\) nm and a NW length of \(800 \pm 73\) nm after 75 min of growth, having a NW density of \(~1\cdot10^9\) NW/\(\mu m^2\). Here, 60 NWs of the GaN template are measured from cross-sectional SEM images in order to improve the statistics. About 15 to 25 NWs are measured for all the other samples, after (In,Ga)N growth.

Regarding the measurement of shell thickness and NW length after (In,Ga)N growth, one has also take into account the fluctuations in reproducing the GaN NW template. Not every template has the same NW density, thickness and length. This would result in values for shell thickness and sidewall growth rates with a larger standard deviation. Considering the NW density, this value doesn’t change more than roughly two times the
value given for the template, and in that regard, is reproducible. However, we have never
grown a multiple templates at the same conditions to check and quantify the standard
deviation in the NW morphological parameters. Therefore, this effect is difficult to take
into account.

As shown in Fig. 4.5, to prove shell growth the increase in radius \( \left( d_f - d_t \right) \) dividing by the
growth time \( t_{growth} \) gives the NW sidewall growth rate:

\[
R_{side} = \frac{d_{final} - d_{template}}{2t_{growth}},
\]

(4.2)

with \( d_{template} \) equal to \(~40\ nm. The shell thickness as well as sidewall growth rate \( R_{sidewall} \)
for the metal-rich temperature series and N-rich grown shells can be calculated, for which
the measured diameter is taken in the middle of the NW to determine the shell thickness
and not near or at the top facet for the mushrooms. The results are shown in Fig. 4.6a
and b.

Fig. 4.6a shows an increase in shell thickness for lowering \( T_{TC} \) in series C, however
the trend is not very strong. However, the shell thickness for the dummy sample \( C2 \) is
clearly larger than for sample \( C2 \). And also the N-rich grown samples show some larger
variations, but no trend since they don’t belong to a growth series.

The increase in shell thickness from C1 to C3 can be partly explained by In and Ga
adatoms possessing a lower diffusion length at lower temperature. Therefore the amount
of metal adatoms which will reach the top facet is lower and more metal can be incorpo-
rated at the sidewall. In addition, less In is desorbing from the sidewalls for lower growth
temperature and thus more In is available to be incorporated.

For the dummy sample, we assume the GaN NW template was comparable to all the
others, so the wires of \( C2 \) were not initially thicker. Here, the lower Ga diffusion flux
in comparison with In towards the top, and higher In desorption rate than for Ga, can
explain the thicker wires.

The comparison of the N-rich grown samples with the metal-rich grown ones is not
totally fair, since the growth time was adjusted for these samples. Where for all the sam-
ple of series C the (In,Ga)N is grown for 30 min, shell growth for D1 took 180 min and
45 min for E1. In order to really compare the samples we will have a look to the growth
rate at the NW sidewalls, which takes into account the longer growth time.

An important point in calculating \( R_{sidewall} \) is the possibility of shadowing: a NW can
be shadowed by its neighbors for the impinging flux. Secondly the mushroom growth on
top of the NW can also shadow the part of the NW (directly) below it, mainly present for
the samples of C2 and C3. Therefore, the actual growth rate shown for series C could be
larger than shown in Fig. 4.6b, since if shadowing has set in at a certain moment, radial
growth is prevented and the actual radial growth time for the sidewall is shorter. Since it
is not as straightforward to calculate the moment when shadowing sets in and its actual
influence, it is very difficult to take this into account for the growth rate.

So we can carefully say that, although the shell thickness between samples can vary
a lot, the sidewall growth-rate \( R_{side} \) which takes into account different growth times is
in our samples comparable for N-rich and metal-rich growth at a specific temperature,
see samples C1 and D1 and also C2 and E1. However, since the N flux for series C and
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Sample D1 was not equal, the general growth rate is already different for these samples and a fully legitimate comparison between N-rich and metal-rich conditions is difficult to make.

![Graph of (a) the (In,Ga)N shell thickness as function of the growth temperature. The decrease of shell thickness for higher \( T_{TC} \) can be attributed to the higher desorption fluxes and diffusion of atoms towards the NW top facet. (b) Graph of the NW sidewall growth rate for different growth temperatures. Interestingly, the growth rate appears to be in the same range for metal- as well as N-rich conditions.]

**Figure 4.6:** Graph of (a) the (In,Ga)N shell thickness as function of the growth temperature. The decrease of shell thickness for higher \( T_{TC} \) can be attributed to the higher desorption fluxes and diffusion of atoms towards the NW top facet. (b) Graph of the NW sidewall growth rate for different growth temperatures. Interestingly, the growth rate appears to be in the same range for metal- as well as N-rich conditions.

4.2.2. Shadowing of NW sidewalls

It is seems to be useful to know the importance of shadowing for the self-assembled growth of GaN NWs on TiN. Fluctuations in the NW density and nearest neighbour distance play a role here, because the NWs are not (pre)patterned on a grid (i.e. SAG). To investigate if shadowing of neighboring NWs actually takes place, some assumptions and simplifications have to be made. In principle, shadowing can be expressed in two different ways, which in essence complement each other in describing shadowing:

(i) The length of the part of the NW which is shadowed from a (nearest) neighbor NW, \( L_{\text{shadowed}} \).

(ii) The percentage of total growth time in which the NW is shadowed, considering the sample’s rotation during growth.

Fig. 4.7a shows the part, \( L_{\text{shadowed}} \), of the NW which is shadowed from the impinging flux reaching the sample under an angle \( \alpha \), which is related to the first part of describing shadowing. This value depends further on the average NW length \( l \), average distance between NWs \( \rho \), the NW diameter \( d \) and the angle of impinging fluxes \( \alpha \) as also sketched in Fig. 4.7a.

Considering the geometry, one can write \( L_{\text{shadowed}} \) as:

\[
L_{\text{shadowed}} = l - y = l - \frac{\rho - 2r}{\tan(\alpha)} = l - \frac{\rho - d}{\tan(\alpha)}. \quad (4.3)
\]
4.2. Morphology analysis of GaN/(In,Ga)N core-shell NWs

Since the NWs grown in the scope of this work are self-assembled, the distance between the NWs vary a lot and calculations have to be based on average values. The fact that we use the average distance between NWs, gives the opportunity to model our NW grid as shown in Fig. 4.7b, with a hexagonal closed packed structure, having a smallest equal distance to every nearest neighbour. From this, the average distance between NWs, \( \rho \), can be calculated and is equal to [69]:

\[
\rho = \frac{1}{\sqrt{\pi n}},
\]

with \( n \) the NW average number density.

For the growth of core-shell heterostructures it is highly unwanted to have shadowing. For smaller values of \( \alpha \) the shadowing effect becomes less pronounced (smaller \( L_{\text{shadowed}} \)), which shows a basic but important argument for a good design of the MBE system for growing core-shell structures. Secondly, it shows that shadowing from neighboring NWs sets only in after the NW has reached a length equal to \( y \), indicated in Fig. 4.7a. Additionally to shadowing from the nearest neighbours, also the second, third, and so on, nearest neighbours can play a role in theory. Since this is effects appears to be small for our wires due to the low NW density, this will not be considered.

With Eq. 4.4 the nearest neighbour distance \( \rho \) is determined to be \( \sim 180 \) nm for the GaN template, with a NW density \( n = 1.0 \cdot 10^9 \text{ NW/cm}^2 \), determined from a top-view

\[ L_{\text{shadowed}} \]

\[ \rho \]

\[ d = 2r \]

\[ \gamma \]

\[ l \]

\[ y \]

\[ \alpha \]

\[ \Phi_{\text{imp}} \]

\[ \rho_L \]

\[ \Phi_{\text{imp}} \]

\[ \text{cells and plasma source} \]

\[ \text{a)} \]

\[ \text{b)} \]

**Figure 4.7**: Sketch of a NW shadowed by a nearest neighbour NW, including geometrical parameters to calculate the effect of shaddowing (a). Idealized model of the NW grid for smallest equal distance to every nearest neighbour, resulting in a hexagonal grid (b).
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

SEM image as shown in Fig. 4.8a on an area of \(12.6 \cdot 10^6\) \(\text{nm}^2\). Subsequently, \(L_{\text{shadowed}} \approx 600\) nm. On first hand this value seems to be large since most of the NW sidewall is shadowed for the impinging flux which reduces radial growth along the whole NW length. However, one has to remember the rotation of the sample during growth and the model used for the NW grid in Fig. 4.7b: the NW is not shadowed 100% of the time exposed to the impinging flux.

Lets have a look for the case of the red NW in the middle, as shown in Fig. 4.7b. When rotating the sample, this NW sees sometimes one of the blue nearest neighbour NWs in its ‘field of view’, namely 6 times during one ration over a length equal to the diameter of the wires. Therefore, for one ration the shadowing percentage \(S_{sh}\) is equal to:

\[
S_{sh} = \frac{6d}{2\pi \rho} \cdot 100\%.
\]  

(4.5)

For \(d = 40\) nm and \(\rho = 180\) nm, the NW is shadowed for \(~20\%\) of the time.

Summarizing, we can specify how much shadowing, in theory for our (idealized hexagonal grid) GaN template, takes place: the lowest 600 nm of the NW suffer from shadowing for about 20% of the time. Shadowing of the NW sidewalls for the impinging fluxes takes place for our well-separated GaN NWs on TiN, but for only one fifth of the total growth time. It is also not a problem for the upper 200 nm of the wire and core-shell experiments don’t seem to be too much influenced by the effect of shadowing.

![Figure 4.8](image.png)

**Figure 4.8**: (a) Top-view SEM image of the GaN template ensemble. The NW number density can be calculated from this image. (b) The part of the NW length which is shadowed \(L_{\text{shadowed}}\) as function of the NW number density for two different NW diameters.

Besides this quantitative description of shadowing, we will have a deeper look to the NW morphology of samples C2 and C3 shown in Fig. 4.4a and b concerning shadowing. In specific, we can have a closer look to the broadening of the NW part just below the
4.2. Morphology analysis of GaN/(In,Ga)N core-shell NWs

mushroom.

First of all, in both samples, we see a difference of the final NW diameter just below the mushroom in comparison with the rest of the NW towards the bottom. For C3, the thinner part of about 44 nm wide is very likely a shadowing effect resulting from the fast radial growth of the top part. When the In and Ga shutters are opened, the nominal metal flux is high enough, to start immediate radial besides axial growth. So, the part just below the top of the NW is shadowed and no impinging atoms can reach this part from almost the first moment. Consequently, the only atoms which can be incorporated are the diffusion adatoms from the part of the NW sidewall which is not shadowed by the mushroom. Therefore radial growth is much less pronounced at the NW part just below the mushroom top part. With only an increase of about 4 nm in diameter compared to the GaN NW template, it implies that sidewall diffusion is very limited at this low temperature (400°).

So far the diffusion of adatoms is treated only qualitatively. For planning and carrying out growth experiments however, it is good to know some ‘house or reference numbers’ for specific flux contributions, especially the diffusion fluxes, since these play a major role in forming the final morphology of the GaN-(In,Ga)N NW core-shell heterostructure. Therefore, in the next part I will try to give a quantitative relation and magnitude for the diffusion of Ga.

4.2.3. Calculation of contributing diffusion fluxes

To quantify the Ga diffusion it is needed to make assumptions and distinguish between different growth conditions. The two main growth conditions I want to distinguish and discuss are:

(i) N-rich GaN growth of the template (at ∼700°)

(ii) N-rich In$_x$Ga$_{1-x}$N growth of a shell, with a segment on top of the GaN template (at lower temperature)

Under N-rich growth conditions and the assumption of only axial growth, in case 1 the NW axial growth rate $R$ is given by the net Ga flux at the top, $R = \phi_{\text{Ga}}^{\text{eff}}$, which can not exceed $\phi_N$. The growth rate can be determined by the length $l$ grown during a time $t$. Here we don’t take into account the nucleation phase which is shorter than the growth phase, and takes for the growth of the template roughly 20 minutes, but never explicitly measured for these samples and thus not precise when using this time in the calculations. Secondly, the NW growth rate is assumed to be constant, which is also not necessarily the case since in the beginning of the NW elongation substrate diffusion contributes also to the axial growth giving a larger growth rate.

In case 2 for growing In$_x$Ga$_{1-x}$N, the axial growth rate $R$ is equal to the total effective metal flux

$$R = \phi_{\text{In}}^{\text{eff}} + \phi_{\text{Ga}}^{\text{eff}} = x\phi_{\text{metal}}^{\text{eff}} + (1 - x)\phi_{\text{metal}}^{\text{eff}}, \quad (4.6)$$

with $x$ the In concentration, and thus $(1 - x)R = \phi_{\text{Ga}}^{\text{eff}}$. 

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The total effective Ga flux at the top facet $\Phi_{Ga}^{eff}$ is given by:

$$\Phi_{Ga}^{eff} = \Phi_{Ga}^{imp, top} + \Phi_{Ga}^{diff} - \Phi_{Ga}^{des}.$$  (4.7)

Here, the decomposition of GaN and (In,Ga)N is again taken together in all the other fluxes, since it is difficult to quantify these fluxes separately. For case 1, Ga desorption is in principle not equal to zero and we cannot exclude this flux. For case 2 at lower temperatures during (In,Ga)N growth, the Ga desorption is zero at these low temperatures. However, In desorption and In$_x$Ga$_{1-x}$N decomposition should be taken into account. Therefore, we will calculate a value for the Ga diffusion length dependent on $\Phi_{Ga}^{des}$, which includes the desorption and decomposition fluxes of Ga.

Taking this into account and writing the impinging Ga at the top facet as $\Phi_{Ga}^{imp, top} = \Phi_{Ga}^{imp} \cos(\alpha)$, the Ga diffusion flux arriving at the NW top facet is given by:

$$\Phi_{Ga}^{diff} = \left[(1-x)R\right] - \left[\Phi_{Ga}^{imp} \cos(\alpha)\right] + \Phi_{Ga}^{des}.$$  (4.8)

The diffusion flux can be written as the in Chapter 2 mentioned relation, eq. 2.10. From this, a relation for the Ga diffusion length $\lambda_{Ga}$ can be deduced. After filling in and rewriting a bit eq. 4.8 and eq. 2.10 we get:

$$\lambda_{Ga} = \left[(1-x)\frac{l}{t} - \Phi_{Ga}^{imp} \cos(\alpha) + \Phi_{Ga}^{des}\right] \frac{r}{2\Phi_{Ga}^{imp} \sin(\alpha)}.$$  (4.9)

In case 1, for the GaN template growth, $l = 800$ nm, $t = 75$ min, $x = 0$, $\Phi_{Ga}^{imp} = 6.6$ nm/min, $\alpha = 30^\circ$ and $r = 20$ nm. These NW properties give a diffusion length of Ga for the NW template growth at $\sim700^\circ$, equal to:

$$\lambda_{Ga} = (A1 + B1 \cdot \Phi_{Ga}^{des}),$$  (4.10)

with $A1 = 38$ nm and $B1 = 3$ min.

And for case 2, using properties of sample D1 with $l = 460$ nm, $t = 180$ min, $x = 0.3$, $\Phi_{Ga}^{imp} = 1.2$ nm/min, $\alpha = 30^\circ$ and $r = 44$ nm equal to the mean radius during (In,Ga)N growth, results in $\lambda_{Ga}$ at $\sim490^\circ$, equal to:

$$\lambda_{Ga} = (A2 + B2 \cdot \Phi_{Ga}^{des}),$$  (4.11)

with $A2 = 68$ nm and $B2 = 37$ min.

If we assume zero Ga desorption, both diffusion lengths are in the range of values found in literature.[69] (few tens of nanometers) for the growth of GaN NWs on Si. How-
however, $\phi_{Ga}^{des}$ not exactly equal zero, which would result in a larger value for $\lambda_{Ga}$ in both cases.

A smaller $\lambda_{Ga}$ for case 2 than in case 1 would make sense since this value is calculated for (In,Ga)N growth conditions at lower temperature, which means less energetic adatoms resulting in a lower diffusion length. Furthermore, the assumption of $x = 0.3$ can be wrong for this sample, however this is what was measured by low-temperature cathodoluminescence (LT-CL) as we will see later. Another parameter which is in general different for GaN NWs on Si is the radius $r$, which is smaller for our samples and would increase the diffusion flux of Ga.

The larger $\lambda_{Ga}$ at lower temperatures could be explained by the earlier mentioned increase of $\lambda_{Ga}$ in the presence of In. Since for case 2, In was present which would increase the Ga diffusivity as already more often presented in literature.

Summarizing, we see that under assumptions for the growth rate, the Ga diffusion length can be calculated relatively easily. This results in values in the range of the literature value for $\lambda_{Ga}$ on GaN NWs on Si. Its shows the significant role of diffusion in explaining the NW morphology. Furthermore, we see that the diffusivity at lower temperatures is increased, which can be explained by the presence of In enhancing the Ga diffusion length. This enhancement of Ga diffusion due to the presence of In can be one of the reasons why growing GaN/(In,Ga)N core-shell NWs under metal-rich conditions and preserving a good morphology at the top is difficult, since lowering the growth temperature and trying to suppress the metal sidewall diffusion towards the top is not achieved in the range of our growth conditions of series C.

4.3. In incorporation at the sidewalls

So far, the morphology of the (In,Ga)N core-shell NWs on TiN was the major topic of discussion and we have seen that shell growth on the NW sidewalls is possible. However, this is not the only important feature of these NWs in order to investigate the possibilities for producing real LED (In,Ga)N core-shell heterostructures. Besides a good NW morphology, it should be able to tune the emission wavelength of the NWs by controlling the In incorporation and additionally a bright emission is desired. Therefore it is of great interest to investigate the In incorporation at the NW sidewalls. As stated earlier in the introduction, the In incorporation at the top facet is not the most difficult part of these heterostructures, but getting a significant amount of In at the sidewalls appears to be more challenging.

In the next sections we will see if it is possible to grow a real In$_x$Ga$_{1-x}$N shell or QW heterostructure with $x > 0$. Therefore we try to prove the presence of In in the shell, with several techniques such as QMS, room-temperature photoluminescence (PL) and low-temperature cathodoluminescence (CL). Let us first shortly discuss the In incorporation at the non-polar NW sidewalls.

**Expectation of In incorporation at the NW sidewall**

In contrast to the In incorporation at the top facet, the In incorporation at the NW $M$-plane sidewalls is less straightforward. When searching in literature, the bunch of work, theoretical as well as experimental, is based on In incorporation at the Ga-polar (0001) or N-polar (0001) C-plane.
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However, there is a handful of scientific papers about In incorporation at (non-)polar and semi-polar facets. Northrup and Neugebauer showed already in 1999\cite{21} that In incorporation at semi-polar surfaces is energetically more favorable than at polar or non-polar GaN surfaces. The difference is a consequence of the different binding sites available for In on the different surfaces. For instance, on $\langle 0001 \rangle$ surfaces, In bonds to three N atoms, whereas on $\langle 10\overline{1}1 \rangle$ surfaces only to one or two N atoms, which costs in the end less total binding energy. The N-polar GaN NWs, grown and investigated within this thesis, in general consists of a polar (C-plane) and non-polar (M-plane).

Comparing the In incorporation between the polar and non-polar planes, it is known from experimental point of view that In incorporation at the non-polar sidewalls is more difficult than on the polar top facet\cite{9}.

In short, we can expected from literature studies and experimental growth experience, that the In incorporation at the non-polar NW sidewalls is more difficult than on the polar NW top facet.

4.3.1. In-situ metal desorption by QMS

The in-situ use of the QMS system gives information about In and Ga desorption and material decomposition, and thus indirectly also about In incorporation somewhere on the sample. However, the QMS signal should be treated carefully. Especially regarding In incorporation in the NW, statements can only be made with a certain probability, since the NW coverage $\Phi$ on TiN is low compared to GaN NW densities on silicon. Because the NWs are well separated, a lot of free space is present in between the wires. The metals desorbing in this free space from the substrate in between the NWs, are also measured by the QMS and contribute to the signal with a large amount of desorbing atoms. We will see that the use of the QMS is still a useful indication for the presence of In on the sample.

Fig. 4.9 shows the Ga (red) and In (blue) desorption in arbitrary units of the metal-rich grown NWs of series C (C1 - C3), the dummy sample $\tilde{C}2$ and N-rich grown samples D1 and E1.

The In background level is indicated by a dashed black line. The background level differs for Ga and In, which is related to the noise level.

As already mentioned in chapter 3, the metal desorption strongly depends on the NW density as well as the morphology. Since the NW density of the template can slightly differ (within a factor of 2), the In background level can be higher or lower. For all the sample except D1, the scale on the y-axis is the same since for these samples the same N flux from the plasma is used, which mainly determines the high pressure in the growth chamber during growth. For sample D1 a more than double as large N flux is used and the background level is increased.

In general, the level of metal desorption abruptly increases when the shutter is opened, labeled as time $t = 0$ min. The QMS level, scales with the impinging flux and, maybe even more important to realize, inversely with the metal incorporated in the NW ensemble. So if less metal is desorbing and the signal goes down, more material is incorporated on the sample. This property we will use next to tell if In is desorbing from or incorporating at the sample.
4.3. In incorporation at the sidewalls

Figure 4.9: Metal desorption (in arb. u.) for metal-rich samples C1 - C3, dummy sample \( \tilde{C}2 \) and N-rich samples D1 and E1, measured by quadropole mass spectroscopy (QMS) during the growth of the (In,Ga)N shell. The In background level is indicated by a dashed black line.
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First of all we see a clear change for samples C1 to C3 from the metal-rich temperature series. For higher growth temperature (C1) at $t = 0$, no In is desorbed. Then, the In desorption increases with time, which indicates that more and more impinging In is desorbing again. This behaviour is not expected since normally at $t = 0$ the In signal will be at its maximum of the growth. A speculative explanation could be that at this higher temperature, there is something going on with the impinging In (at $t = 0$) and the substrate due to thermally activated reactions with the TiN. Another explanation could be that In is incorporated very well in the beginning and less later on. However, deeper investigations of this sample regarding possible reactions of In and the TiN have not been carried out and the increasing QMS signal remains not fully understood.

Secondly, for decreasing temperature, C2 and C3, the In signal goes down after a specific time with comparable slopes. At intermediate temperature, this drop in QMS signal starts later than for the lowest temperature, after roughly 15 and 3 min respectively.

If we assume In is not incorporated more effectively when time evolves, this drop in QMS signal can be well explained by a broadening of the NW top facet, as shown in literature by S. Fernandez-Garrido et al.\[36\]. For sample C2 and C3 the NW broadening is caused by metal-rich conditions at the top facet as shown and discussed in the previous part, which matches with the decreasing In signal.

This argument is confirmed by the fast broadening of the NW, which indicates that more metal can be incorporated on the larger top facet and radial growth occurs due locally metal-rich conditions at the C-plane. Since the Ga desorption remains negligible at this temperature, the decreasing In desorption is likely an indication for significant broadening of the NW.

For the dummy sample (C2) the metal desorption is as expected: the In shutter is not opened and remains at the background level and no In is present in this sample. In contrast, the Ga desorption is increasing a little when the shutter is opened.

So far, the metal, and in specific the In desorption has shown a clear trend. For low enough growth temperatures under metal rich conditions, In is incorporated at the sample.

For the N-rich conditions we also observe a decrease in the In desorption with time, but only until a certain amount of time. Under these very N-rich conditions it is almost impossible to be metal rich at the top facet. Therefore broadening according to the self-regulated radius mechanism is unlikely here. However, the metal desorption shows a decrease in the first ~20 min which would imply at first sight, under the assumption of constant In incorporation, a NW broadening during the first part and then preserving radius. As stated, the growth conditions were very N-rich (V/III = 4.1) and diffusion fluxes must exceed ‘astronomical’ values so to say to be metal-rich at the top facet. Therefore it is more likely that the decreasing signal is due to the parasitic growth in between the NW template. When these small parasitic NWs nucleate, they will grow in axial and in radial direction. Since with the QMS we mostly measure the parasitic growth, the drop in In signal for D1 and E1 is most likely due to the radial growth of the parasitic wires.

In conclusion, we have strong indications for the presence of In on all the samples, except the dummy sample and C1. For sample C1 it is not so clear since the behaviour of the QMS signal is not well understood. A qualitative comparison between the metal-rich and N-rich grown samples is difficult, since the growth time is radically different.
However, if we compare C2 and C3, it can be assumed that for lower temperatures (C3) more In is deposited on the sample, because of the earlier drop in In signal and lower signal in metal desorption.

Since metal desorption measurements are very difficult to interpret, we cannot say quantitatively how much and where the In is incorporated and have to use other experimental techniques. The next step to identify In incorporation in the NW is performing and analyzing ensemble room-temperature PL experiments, which will be discussed next, followed by single wire LT-CL experiments.

4.3.2. Luminescence properties

To verify the presence of In and at the same time how much and where in the NW it is incorporated, ensemble RT-PL measurements as well single wire LT-CL experiments are performed. The measurements are carried out with the same setup as discussed in chapter 3. The complex morphology of our core-shell NWs makes the allocation of luminescence very different when probing an ensemble of NWs during e.g. the ensemble RT-PL experiments. Additionally, the parasitic growth makes it even harder to conclude about the spatial origin of the emission. In can be incorporated relatively easily at the top facet of the NW or in the parasitic material (NW or layer, depending on growth conditions). A third possibility, and our goal, is In incorporation at the NW sidewall. For an overview, Figs. 4.10a and b show a typical SEM sideview image of the NW ensemble for (a) metal-rich and (b) N-rich (In,Ga)N shell growth, with the main three different locations in a NW ensemble that can possibly be luminescent at longer wavelengths. On the right of these SEM images, such a typical final NW structure is sketched and the three different locations where In can be incorporated are marked, namely (i) in the (In,Ga)N segment at the NW top (facet), (ii) in the grown shell and (iii) shows the parasitic growth. The differences for metal- versus N-rich growth is visible in the parasitic growth and the morphology at the top.

Regarding possible emission from In$_x$Ga$_{1-x}$N, the top segment, shell and parasitic growth can be luminescent. The corresponding luminescence band would depend on the In content $x$, shifting to lower energies for higher In concentration. As mentioned before, for the incorporation of In, reduced growth temperatures are required. This reduced growth temperature may increase the density of point defects in the crystal and can facilitate the nucleation of zinc-blende (ZB) inclusions\cite{65}. Therefore, the emission in the three different parts can also be due to other reasons as we have seen in chapter 3, like the formation of cubic inclusions, SFs and also yellow luminescence as sometimes observed in GaN nanowires. As a start, the ensemble RT-PL results will be discussed in the next part.

Ensemble room-temperature PL

Fig. 4.11a - c shows the ensemble RT-PL results for the different (In,Ga)N core-shell structures. In Fig. 4.11a the samples of series C are shown. Mainly three different energy bands can be observed, labeled as I, II and III in the figure. A clear trend of the peak position of these bands as function of the growth temperature is not observed.

As already discussed in Chapter 3, the emission around 3.413 eV (band I) represents the free exciton transition in the GaN NW at RT and is seen in all the three samples. The intensity of this peak is probably correlated with the morphology at the NW top, and thus indirectly with the temperature. The GaN peak intensity for sample C2 and C3 is
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

Figure 4.10: SEM image of the (a) metal-rich and (b) N-rich grown sample with a sketch of the general NW morphology. The boxes indicate the possible different locations at the NW which can be luminescent at longer wavelengths. The scale bar represents 500 nm.

lower than for sample C1. The radial growth induced by metal-rich conditions result in a layer-like morphology at the nanowire tip, which, most likely, inhibits excitations of the GaN core.

In order to discuss bands II and III, we first have a look to Fig. 4.11b, where the dummy sample C2 containing no In is compared with sample C2, both grown at the same temperature. Since cubic inclusions or SFs are likely to be formed during the (In,Ga)N growth at low temperature, it is plausible that emission from these zinc-blende (ZB) inclusions appears next to the GaN emission at longer wavelengths, resulting in a rather broad band I emission in the C2 spectrum. Regarding band III, this one is present for the dummy sample but much less pronounced as for sample C2. This band in the dummy sample cannot originate from any In$_x$Ga$_{1-x}$N luminescence, since the In shutter remained close during growth. Secondly, it is quite unlikely to find cubic inclusions or SFs emitting at this low energy. Therefore, the most likely explanation for band III in the dummy sample is yellow luminescence at 2.2 eV as frequently observed for GaN layers, but less frequently in NWs.

Back to series C shown in Fig. 4.11a, we can now address band II and band III to In$_x$Ga$_{1-x}$N emission since these were not present (band II), or not as pronounced (band III) in the dummy sample. If band II would be only from c-GaN, it should also appear more or less to the same extent in C2 since the growth temperature was the same as for C2. This is not the case, and band II should be somehow correlated with In$_x$Ga$_{1-x}$N. Since two bands appear, the In$_x$Ga$_{1-x}$N has to contain different amounts of In. The In incorporation is expected to be different in the segment on top, the NW sidewall and in the...
parasitic growth, which would fit to the presence of more than one peak below the GaN. In addition, it is also possible that band II reveals the emission of cubic inclusions or a high density of SFs somewhere in the In$_x$Ga$_{1-x}$N, as indicated for the axial heterostructures in Chapter 3. For now, the exact origin and allocation of the different bands remains uncertain and LT-CL mapping is needed to draw more conclusions.

The ensemble RT-PL results for the N-rich grown (In,Ga)N shells are shown in Fig. 4.11c. We see again roughly the same three bands appearing as for the metal-rich grown shells in Fig. 4.11a. Also here, a clear trend as function of temperature is not observed, but we should remind the reader that sample D1 and E1 were grown for (very) different V/III ratios and a direct comparison is not possible. The intensity of the GaN peak in D1 is lower than in E1, again most likely due to a larger (In,Ga)N segment at the top for sample D1.

Band I in sample D1 and E1 can be attributed again to the emission of the GaN core. The broader appearance of the GaN peak in sample D1 will also be discussed in one of the next paragraphs. The other bands, II and III, can be explained in the same way as the spectra of series C. Band II and III can be both due to In$_x$Ga$_{1-x}$N having a different In concentration, which is likely when comparing the (In,Ga)N of the top segment and the shell. Furthermore, band II can also be explained by cubic inclusions at the NW top, in the parasitic growth at the bottom or in the shell, formed during (In,Ga)N growth.

Before we continue with the results of single wire LT-CL measurements as we did in Chapter 3 for the axial heterostructures, we have to address another important feature of the GaN/(In,Ga)N core-shell NWs.

### GaN core peak shift

When an In$_x$Ga$_{1-x}$N shell is grown around the GaN core, the core will be strained due to the lattice mismatch between GaN and In$_x$Ga$_{1-x}$N. The magnitude of the strain depends on the In content $x$ and the shell thickness, as well as the core diameter. The emission of the GaN core would be redshifted, since the lattice parameter of the core will adapt to the (In,Ga)N lattice and thus experiences a tensile strain. The opposite statement applied to the shell: the (In,Ga)N peak is blueshifted due to the GaN core. However, we will speak only about the shift of the GaN peak since for GaN emission the peak position at low- and room-temperature is exactly known in contrast to the In$_x$Ga$_{1-x}$N emission, for which the In content is not exactly known and peaks appear much broader.

In Fig. 4.12, O. Marquardt, a colleague from PDI, calculated the expected redshift of the GaN core. The shift for an In content of 5 and 10% in the shell is shown. In general, the shift is in the order of several nm increasing with shell thickness and In content $x$. Such a GaN core peak shift can now be investigated in the the spectra of Fig. 4.11 for the metal- as well as the N-rich grown (In,Ga)N shells.

The high energy part of the RT-PL spectra is shown in Fig. 4.13a and b for the metal-rich and N-rich grown shells, respectively. The presence or absence of a GaN peak shift can be deduced from these figures. At room temperature (300 K) conditions, the free exciton emission of the strain-free GaN NW has emits at 3.413 eV as indicated by the dashed line in both figures.

Regarding the samples C1 - C3 in Fig. 4.13a, we see for all three samples the GaN peak appearing at the same energy at the dashed line, for an unstrained GaN core. One could argue for sample C2 having a shell thickness of $\sim$15 nm, that the peak is slightly shifted, but definitely less than 1 nm towards the red. According to the calculations shown in
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

**Figure 4.11:** Ensemble room-temperature PL spectra of (a) the metal-rich samples, (b) a comparison of sample C2 with the dummy sample, and (c) the N-rich samples.
4.3. In incorporation at the sidewalls

**Figure 4.12:** Theoretically expected GaN core peak shift due to the strain in case of an $\text{In}_x\text{Ga}_{1-x}\text{N}$ shell for different shell thickness and In content $x$. Calculated by O. Marquardt.

**Figure 4.13:** High-energy part of the ensemble room-temperature PL spectra of (a) the metal-rich temperature series and (b) the N-rich grown samples.
4. Growth and characterization of GaN/(In,Ga)N core-shell heterostructures

Fig. 4.12, a peak shift of less than one 1 nm for this shell thickness would indicate an In concentration of less than roughly half a percent; which is definitely not any evidence for any In incorporation in the shell.

For sample C3, it might look on first hand that the broader GaN emission is shifted relative to the dashed line. This would imply a strained GaN core and an indication for In incorporation in the shell. However, it is also possible that this band shows the superimposed emission of two other bands; one band from the GaN and the other from cubic inclusions, SFs or (In,Ga)N with a low In content. In order to verify a possible strained GaN core, we will investigate single wire LT-CL spectra in the next part. From these ensemble RT-PL spectra for the metal-rich grown (In,Ga)N shells, we have to conclude that most likely no In is incorporated in the shell.

When looking to the N-rich grown samples as shown in Fig. 4.13b, we see something different than for series C. The GaN peak is not shifted for sample E1, whereas for sample D1 a broader band can be observed. This broader band, most likely a superposition of two smaller bands labeled as 1 and 2, is similar to the GaN emission of sample C3. Band 1 might be redshifted several nm. The shell in sample D1 has a thickness of almost 50 nm. Band 1 might be redshifted 4 - 5 nm, which would imply an In content of ~2% according to the calculations shown in Fig. 4.12. Band 2 could then be attributed to the (In,Ga)N shell. In order verify this, single wire LT-CL spectra will be analyzed.

So far, this is the most plausible indication for the growth of a shell containing In. Since there is no indication for a shell containing In in samples C1, C2 and E1, only single wire LT-CL results of sample C3 and D1 are basically of further interest. However, the morphology of sample C3 is far from optimal for further investigations and we did not perform any LT-CL measurements on this sample. Whereas for sample C2 and D1 single LT-CL experiments are carried out in order to map and attribute the different energy bands in the RT-PL spectra and verify a redshifted GaN core emission.

**Single NW low-temperature cathodeluminescence**

The results of a typical single wire low-temperature CL measurement are shown in Fig. 4.14a and b, for sample C2 and D1, respectively. In general, four single wires are measured for each sample and the LT-CL map as shown here represents the typical result. The NW distance shows the location of excitation with the electron beam, from bottom towards the top, which gives spatial information about the emission; i.e. from which part of the NW the emission is coming from.

The measurement of sample C2 shows mainly three bands. The first, labeled as 1, is the GaN NW core emission along the whole length of the NW template. Theoretically, this emission should be at 3.471 eV, the D⁰X bound exciton energy. Secondly, band 2 comes from the (In,Ga)N segment at the NW top and matches with band II from the RT-PL measurement. As discussed already there, it can be InₓGa₁₋ₓN emission. However, if we look to band 3, this also originates from the (In,Ga)N segment at the top. It is not very likely to have two such well defined bands from the same region coming from InₓGa₁₋ₓN. Therefore, it appears to be more reasonable if we address the band with lowest energy to the InₓGa₁₋ₓN band 3 and thus band 2 to cubic inclusions or SFs formed during InₓGa₁₋ₓN growth within the segment. Addressing the peaks the other way around is not plausible, since, as already mentioned earlier, cubic inclusions are unlikely to emit at those low energies. In addition, no emission besides that from an unstrained GaN core is found along.
4.3. In incorporation at the sidewalls

Figure 4.14: Single wire low-temperature CL measurements of two different NWs grown under (a) metal-rich conditions, sample C2 and (b) N-rich conditions, sample D1. The NW distance shows the spatial position of the luminescence origin in axial direction as indicated in the sketch on the right. Different peaks are labeled from 1 - (3)5. Data acquired by C. Pfüller.
the whole NW length. This shows again the absence of $\text{In}_x\text{Ga}_{1-x}\text{N}$ emission along the whole NW length where the shell is grown, which indicates again that no In has been incorporated in the shell for this sample.

A typical single wire LT-CL measurement of sample D1 is shown in Fig. 4.14b. The GaN emission appears again along the whole length of the NW core, labeled as 1. The emission around 2.8 eV is labeled as 2 and 3 and corresponds to band II in the RT-PL spectra. This is also the case for band 4 and 5, which corresponds to band III seen in RT-PL. The same arguments can be given as discussed for sample C2. However, for this sample we expect $\text{In}_x\text{Ga}_{1-x}\text{N}$ emission along the whole NW length according to the GaN core peak shift as observed before. Unfortunately, this is not the case and for instance band 2 and 3 don’t show up along the whole NW length but only in the (In,Ga)N segment at the top and parasitic growth, respectively. Therefore, we have to conclude the same as for sample C2, that the emission from band II in the RT-PL spectra and band 2 and 3 in the LT-CL map is coming from cubic inclusions or a high density of SFs in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment on top and in the parasitic growth. Band 4 and 5, corresponding to band III before, is most likely emission from the $\text{In}_x\text{Ga}_{1-x}\text{N}$ segment on top and the parasitic growth.

The $\text{In}_x\text{Ga}_{1-x}\text{N}$ emission from the shell as indicated in Fig. 4.13b, is possibly also measured by LT-CL, however, this emission might be not distinguishable from the GaN emission in the map as shown in Fig. 4.14b. Therefore we need to have a look at the single spectra at a specific height of the NW, where only a shell is present and thus not at the top or bottom of the NW.

To check the possibility of a luminescence band originating in a shell with low In concentration appearing just next to the peak of the GaN core, the high-energy part (smaller wavelengths) spectra around the GaN peak at a NW distance around $(0.5 \pm 0.05) \, \mu \text{m}$ and $(0.8 \pm 0.05) \, \mu \text{m}$ are shown in Fig. 4.15a - d, for two different wires. The spectra at this ‘NW distance’, or actually NW height, is chosen because there only a shell should be present and we are definitely not in the region with the (In,Ga)N segment on top or the parasitic growth.

The first peak in all the four spectra can be attributed to the GaN NW core. The expected wavelength for this transition is 3.471 eV or equivalent, 357.2 nm. As discussed before, this peak should be shifted due to its strained state. Typically, the spectra show a peak at 3.470 eV, which is no significant peak shift. This indicates that no In has been incorporated in the shell. The second peak, at higher wavelengths, can be attributed to $\text{In}_x\text{Ga}_{1-x}\text{N}$ at the top of the NW or in the parasitic NWs with a very low In concentration. It is also likely that the emission originates from cubic inclusions or SFs.

Summarizing, we can say that In incorporates very well at the C-plane of the nanowires, at the top as well as in the parasitic growth at the bottom. The incorporation of In in the shell is apparently impossible for the shells grown under the conditions used in this thesis.
4.3. In incorporation at the sidewalls

Figure 4.15: High-energy part of two LT-CL single wire spectra at two different positions (a),(c) and (b),(d) for two different wires (a),(b) and (c),(d). Data acquired by C. Pfüller.
4.4. Conclusion and outlook

The main aim for the growth of GaN/(In,Ga)N core-shell NW heterostructures was to overcome the problems of poor luminescence properties of the axial heterostructures. Therefore, we started to attempt the MBE growth of an (In,Ga)N shell on the established self-assembled GaN NW template on TiN. The incorporation of In in the M-plane sidewalls along the whole NW length is expected to be a challenging task. Also because the MBE growth of (In,Ga)N shells on bottom-up MBE grown rather thin and well-separated GaN NWs with a diameter in the (sub-)nanometer range had not been reported in literature so far.

In order to grow core-shell structures, radial growth along the whole NW length should occur. For GaN NWs, bounded by M-plane sidewalls and a C-plane top facet, the incorporation of Ga and In atoms is in general preferred at the top facet. To grow radially along the whole length of the NW, material should be incorporated at the sidewalls. Different growth conditions have been tried in order to increase the material incorporation at the M-plane sidewalls. It became clear quite fast that this is not so easy or even impossible. Therefore, the main attempt became the suppression of Ga and In diffusion. For the growth of (In,Ga)N, the growth temperature has to be decreased well below the growth temperature of GaN. At these temperatures, radial growth of the NW top facet occurs to a much larger extend under metal-rich conditions. For these reasons, a temperature series under nominally metal-rich conditions was grown. However, N-rich grown shells were investigated as well.

We have seen a change in the NW top morphology after (In,Ga)N growth for most of the metal-rich grown (In,Ga)N shells. Due to locally metal-rich conditions near the top facet, widening of the NW top set in and ‘mushroom’-like morphologies were formed at the top. When lowering the growth temperature under metal-rich conditions, this widening of the NW top part got more pronounced indicating stronger metal-rich conditions, which in turn resulted from less In desorption at lower temperature. For these metal-rich grown samples it could never be obtained to preserve a well-defined NW morphology without any layer-like growth on top. For the eventual usage of these NWs as building blocks in opto-electronic devices, this layer-like morphology on top of the NW is unwanted. For the N-rich grown (In,Ga)N shells the NW morphology was preserved quite well and no broadening of the NW top facet took place.

For the metal-rich as well as the N-rich grown (In,Ga)N shells, an extensive morphology analysis on the basis of, mainly side-view, SEM images has been carried out. From these investigations, it became clear that a shell was grown for all the samples, but with a different thickness. For the metal-rich temperature series, the thickness was correlated with the growth temperature. For lower growth temperature, the shell thickness, or equivalent to say for this series, the growth rate at the NW sidewall increased. The shells grown under N-rich conditions showed a sidewall growth rate in the same range as for metal-rich conditions. However, a good comparison could not be made due to the difference in applied N flux.

For the growth of core-shell structures, atoms from the impinging fluxes should be able to reach the NW sidewalls. Therefore, the NW sidewall should not be shadowed by nearest-neighbours NWs. Since the array of self-assembled GaN NWs is distributed randomly, we modeled our NW grid with a hexagonal closed-packed structure, resulting in a specific nearest neighbour distance depending on the NW density. A typical NW density in our samples is $1 \times 10^9$ NW/cm$^2$. From this value and the typical NW length
and diameters of our wires, being 800 and 40 nm, respectively, it could be calculated that the lower 600 nm of each NW is shadowed by its nearest neighbours for 20% of the time taking into account the rotation during growth. Thus, shadowing is expected not to be a strong factor limiting shell growth.

Besides the possible effect of shadowing playing a role in the understanding of the final NW morphology, diffusion of In and Ga plays an important role as well. We calculated the Ga diffusion length on the NW sidewall, for atoms which can reach the NW top facet. This diffusion length depends on several parameters, like the growth temperature, NW radius and presence of In. We have to remark here that several assumptions had to be made in these calculations and in addition, the unknown desorption of Ga and decomposition of (In,Ga)N could not be taken into account quantitatively. The Ga diffusion length is calculated for two different growth conditions, first the GaN NW template growth under N-rich conditions at high temperature. Secondly, for the N-rich (In,Ga)N growth at lower temperature. The calculated Ga diffusion length for the latter case is larger, which is on first hand unexpected due to a lower growth temperature. However, during the growth of an (In,Ga)N shell, the presence of In is assumed to be responsible for the strong enhancement of the Ga diffusivity.

The main goal was to incorporate In in the shell. In order to check the presence of In in the shell, first of all metal desorption profiles obtained from in-situ QMS measurements are analyzed. In general, these results showed for the metal-rich grown (In,Ga)N shells, a decreased In desorption for lower growth temperatures. This implied an increased In incorporation on the substrate, but without any spatial information about the location of In incorporation. For the N-rich grown shells a drop in In desorption was also observed at higher temperature, indicating In incorporation at the substrate. In addition, NW ensemble RT-PL as well als single wire LT-CL experiments were carried out. From these investigations, we can say that In incorporates very well at the C-plane of the nanowires, at the top as well as in the parasitic growth at the bottom. If In is incorporated in the shell, it would be expected that the peak of the luminescence of the GaN core is redshifted, in case it is strained by the overgrowth of an (In,Ga)N shell. Unfortunately, mainly based on the luminescence properties of the GaN core and the absence of a clear peak shift in NW ensemble RT-PL results as well as in the single wire LT-CL spectra, we could not conclude that the shell contains In in any of our samples.

For future experiments, other growth conditions might be pursued in order to incorporate In on the sidewalls. It is worth trying to grow an (In,Ga)N shell under N-rich condition at lower temperatures than conducted in this thesis.
5. Conclusion

Semiconductor nanowires are promising candidates for future applications in opto-electronic devices and therefore have been the focus of intensive research over the last years. The topic of this thesis was the growth by molecular beam epitaxy of (In,Ga)N heterostructures in self-assembled GaN nanowires on TiN. Significant progress has been made in this field in the last years, but mainly based on (In,Ga)N/GaN NW ensembles on silicon. However, even for the established growth on Si, most of the fundamental physics of these structures is still poorly understood and the development of such NW technologies is still in its early stage. In this thesis two studies are carried out, concerning the growth of axial and radial (In,Ga)N heterostructures on thin and well-separated GaN NWs. The first atom-probe-tomography (APT) results on such NW heterostructures is a key novelty of this thesis as well. In general, the aim was to obtain a better understanding of the fundamental processes going on during growth and investigate the structural and optical properties of the NW heterostructures.

The first study presented in Chapter 3 concerns the growth of axial (In,Ga)N/GaN NW heterostructures in order to carry out structural and compositional analysis by atom probe tomography (APT). For this purpose a temperature series for the axial (In,Ga)N NW heterostructures was grown. During growth, the important parameters defining the final NW morphology and composition, are the growth temperature and V/III flux ratio. Axial growth is preferred under V/III ratios larger than one, i.e. N-rich growth conditions. In contrast, under nominally or locally metal-rich conditions, radial growth of the NW can set in. We were able to grow axial (In,Ga)N NW heterostructures in thin and well-separated GaN NWs at three different temperatures. After the growth of the active region of the NW which is formed by six (In,Ga)N quantum wells (QWs), the well-defined overall NW morphology of the GaN NW template was preserved. However, parasitic growth of smaller NWs at the bottom and in between the longer NWs showed up. For further investigations by APT as well as investigations of fundamental growth phenomena in strained NW heterostructures, this well-defined morphology of thin and uncoalesced NWs is of high importance and thus a great achievement.

We have also shown the formation of well-defined (In,Ga)N QWs with sharp interfaces and disc-like structure. It was seen in HRTEM images that the QWs are not intersecting the whole NW diameter. Moreover, their aspect ratio (length over width) became smaller for successive QWs, which might be related to strain effects due to the lattice mismatch of GaN and (In,Ga)N. HRTEM analysis on four different NWs showed an In content in the QWs between 15 and 30 %. The average In content in the QWs was determined to be 21% for the sample grown at 540°.

Regarding the luminescence properties of the active region, we investigated our samples by NW ensemble RT-PL measurements and single wire LT-CL experiments. In general, the spectra showed that the emission from the QWs in the active region was less bright than emission from the parasitic growth at the bottom of the NWs. Moreover, the emission wavelength could not be controlled very well by the growth temperature.

The structural and compositional analysis by APT showed also the presence of well-
defined (In,Ga)N QWs within the GaN NW. These data showed the six QWs not inter-
secting the whole NW diameter, which is consistent with the HRTEM data. Moreover,
the APT results showed a trend in QW width, which is increasing from the first to the
last grown QW. This is again in agreement with the trend observed in HRTEM images.
Moreover, for the first time the hexagonal structure of the (In,Ga)N insertion is observed.
The average In content of the six QWs was determined to be around 17%, which is within
the range of values obtained by strain analysis of HRTEM images. The discrepancy can
result from NW to NW fluctuations, since this value is based on the APT result of only
one NW, whereas for HRTEM four different wires are measured.

The second study contains the growth and characterization of Ga/(In,Ga)N core-shell
heterostructures. The main goal of this part was the growth of an (In,Ga)N shell in order
to improve luminescence intensity and control the emission energy of the NW ensembles.
In order to investigate a broad range of growth conditions, a temperature series for the
GaN/(In,GaN) core-shell NWs was grown under nominally metal-rich conditions. In
addition, growth under nominally N-rich conditions was pursued. To grow core-shell
structures, radial growth along the whole NW length should occur. However, for GaN
NWs the incorporation of atoms at the C-plane top facet is preferred over incorporation
of atoms at the M-plane sidewall. Growth conditions were chosen to increase the In
incorporation at the NW sidewalls. Moreover, the attempt of the temperature series was
to suppress sidewall diffusion towards the top and increase radial growth.

The NW morphology after (In,Ga)N shell growth under metal-rich conditions appeared
to be not very promising due to the formation of a layer-like structure with widening di-
ameter at the tip of the NWs. This structure was observed to a greater extend for stronger
metal-rich growth conditions as resulting from lower substrate temperatures. In contrast,
the morphology of the NWs after (In,Ga)N growth under N-rich conditions remained as
attempted, showing a well-defined NW morphology without a widening diameter of
the NW top. Analysis of SEM images of the NW morphology showed the presence of a
clear shell around the GaN core for all NW ensembles, grown under metal-rich as well as
under N-rich conditions.

The growth of core-shell structures requires well-separated wires which are not shad-
owned by their (nearest-)neighbours. The effect of shadowing from nearest neighbours
has been calculated. Taking into account the sample’s rotation during growth, it was
determined that the lowest 600 nm of the NW is shadowed for about 20% of the time.
Since in general a shell was grown along the whole NW length, we can conclude that this
amount of shadowing does not hamper shell growth.

Besides growing a shell around the GaN core, the goal was to incorporate In in the
shell. First of all the presence of In on the substrate was investigated by metal desorption
profiles from line-of-sight quadrupole spectrometry (QMS) measurements. These results
implied an In incorporation on most of the samples, with increasing In incorporation
at the substrate for lower growth temperature. In order to check the presence of In in
the shell, NW ensemble RT-PL as well as single wire LT-CL experiments were carried
out. From these investigations, we can say that In incorporates very well at the C-plane
of the nanowires, at the top as well as in the parasitic growth at the bottom. The peak
of the luminescence of the GaN should be redshifted in the order of several nm when
the GaN core is strained due to (In,Ga)N overgrowth. Unfortunately, mainly based on
the luminescence properties of the GaN core and the absence of a clear peak shift in NW
ensemble RT-PL results as well as in the single wire LT-CL spectra, we could not conclude
that the shell contains In in any of our samples.

For future experiments, it might be interesting to try to incorporate In in the shell by the growth of an (In,Ga)N shell under N-rich conditions at lower growth temperatures.
A. Sample list

Overview of grown samples.
B. Line-of-sight quadrupole mass spectrometry, QMS

The operational principle of a quadrupole mass spectrometer is explained in an article by J.H. Batey\cite{70}. In this Appendix, we will shortly discuss the most important aspects of the QMS. In brief, residual gas atoms are ionized at the entry to the mass spectrometer. The charged particles then travel in z-direction through an electric field with equipotential lines in the x,y-plane as shown in Fig. B.1a. The electrodes as arranged in Fig. B.1b, create this field by using a combination of direct and alternating voltages. (The smaller details in this figure are not of importance.)

Defined by the applied voltage and geometry of the quadrupole, the particles are deflected from its original path which are generally divergent, but stable for a certain mass. Batey illustrated this with the figure as shown in Fig. B.1c. Ions with a mass of 27 u have an unstable trajectory in the x-direction. Ion of 28 u have a stable one and can pass the filter, whereas heavier ions (> 28 u) have an unstable trajectory in the y-direction. The resulting ion current is a measure for the partial pressure of an atomic species in the growth chamber. The desorption of In and Ga atoms from the sample can thus be determined from the partial pressures of the Ga69 and In115 isotopes. The QMS used in our system possesses a continuous dynode electron multiplier to detect the ion current, which allows to measure partial pressures down to $10^{-12}$ torr.
B. Line-of-sight quadrupole mass spectrometry, QMS

Figure B.1: Operation principles of the line-of-sight quadrupole mass spectrometry (QMS) measurement. Image taken from Ref. [70]

(a) Quadrupole field.  
(b) Quadrupole analyzer.  
(c) Ion trajectories.

**B.1. 100% metal desorption test**

Before lowering the growth temperature in order to grow In$_x$Ga$_{1-x}$N, a 100% metal desorption is carried out, just after the growth of every GaN template. Fig. B.2 shows the metal desorption measured by QMS directly after the growth of the NW template.

The figure can be divided in three parts, which show the metal desorption test (A), the time for lowering the growth temperature (B) and the start of In$_x$Ga$_{1-x}$N growth. During period A, the shutters of the In, Ga and N sources are opened for one minute at the temperature of the GaN template growth. At this temperature all (100% of) the In should desorb, and the QMS level depends on several factors, dependent on the unique conditions during every single growth experiment, i.e. growth chamber pressure, temperature and NW ensemble morphology.

During period B the growth temperature is lowered for the In$_x$Ga$_{1-x}$N growth and the shutters are closed. In this time, the metal desorption level is again at the background level for zero fluxes.

With the opening of the In, Ga and N shutters at the beginning of period C, the QMS level rises and the In$_x$Ga$_{1-x}$N growth is started. By comparing the two In desorption levels of A and C, one can say something about if and how much In is incorporated at the substrate and/or NWs. In the case shown in Fig. B.2, all the In is desorped again since the metal desorption level stays the same as measured in the 100% metal desorption level.
B.1. 100% metal desorption test

Figure B.2: Metal desorption (in arb. u.) measured by quadropole mass spectroscopy (QMS) during the 100% desorption test followed by lowering the growth temperature for (In,Ga)N growth and the (In,Ga)N growth itself.


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