The Crystal Structure of III-V Semiconductor Nanowires:

Growth and Characterization

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Abstract

This thesis concerns growth and characterization of gold-particle seeded nanowires of III-V semiconductor materials (III-V NWs). The nanowires were grown using metal-organic vapour phase epitaxy (MOVPE) and characterized by various microscopy techniques. In particular, cross-sectional scanning tunnelling microscopy (XSTM) and cathodoluminescence microscopy (CL) were employed to investigate heterostructured nanowires. In addition, the formation of the crystal structure within the nanowires as an effect of growth conditions was investigated by transmission electron microscopy.

This thesis first presents an extensive description of the crystal structure and phases which have been observed in III-V NWs. It then gives an overview of the main characterization methods that were used in the included papers. Another part that is included concerns epitaxial growth in general and MOVPE in particular. The last part of the thesis is an outlook in which some important questions and possible future directions are presented and discussed.

The basis for this thesis is 9 appended papers: Paper I-II present results from XSTM investigations; papers III-IV and VIII-IX concern investigations of how to control the crystal phases and the density of defects within III-V NWs; paper V present a study of the effect of gold-particle fabrication method and deposition method on MOVPE growth of GaAs NWs; papers VI-VII present measurements of the ambipolar diffusion length in III-V NWs using cathodoluminescence.

Key words: III-V semiconductor materials, nanowires, metal-organic vapour phase epitaxy, MOVPE, scanning tunneling microscopy, XSTM, cathodoluminescence, crystal structure, polytypism

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Division of Solid State Physics
Department of Physics
Lund Institute of Technology
Lund University
vid den tidpunkt då kvinnorna börjar delta i utformandet av världen är denna värld fortfarande en värld som tillhör männen

- Simone de Beauvoir -
Populärvetenskaplig sammanfattning

Idag har de flesta hört talas om nanoteknologi, kanske även att det handlar om något som är väldigt litet – saker som är i storleksordningen nanometer (nm). För att få ett begrepp om hur litet just en nanometer är kan man t.ex. beakta följande två saker:

- Om man delar upp 1 meter av ett snöre i bitar som är 1 nm långa får man 1000 miljoner bitar.
- Atomer har en radie på ungefär 0.1 nm.


När väldigt små volymer av material kombineras kan spännande och användbara effekter uppkomma – detta kallas kvantmekaniska effekter. Genom att variera material för att skapa nanometerstora strukturer (brukar vanligtvis kallas nanostrukturer), kan man skapa användbara komponenter i t.ex. elektroniska apparater. Det finns mycket som talar för att detta kommer att användas mycket i framtiden. Tänk om man i framtiden skulle kunna använda enskilda elektroner eller fotoner som informationsöverförare i en dator? Detta skulle spara både energi och utrymme samt öka kapaciteten och hastigheten i våra vardagliga elektroniska produkter.

Detta arbete har omfattat undersökningar och tillverkning av strukturer som är i storleksordningen nanometer eller mindre – alltså nanostrukturer. En del av arbetet har omfattat undersökning av enstaka atomers positioner relativt varandra i material med hjälp av ett speciellt mikroskop. För att studera något som är så litet får man ta till speciella typer av mikroskop, det går inte att använda sig av ett vanligt optiskt mikroskop. Dess förmåga att förstora räcker helt enkelt inte till. Ett bra optiskt mikroskop kan användas för att åskådliggöra saker som är 200 nm eller större. Om man vill titta på atomerna i ett material får man använda sig av elektroner istället för ljus. Det finns många olika typer av mikroskop som gör det och ett av dessa är
sveptunnelmikroskopet (STM). Detta mikroskop används för att studera framförallt ytan hos ett material. I detta arbete har nanostrukturer klyvts/delats för att kunna studera insidan av nanostrukturerna med hjälp av ett STM.

Principen bakom hur ett STM fungerar kan liknas vid en gammal (vinyl) skivspelare, där en nål läser av ytan på skivan och sedan översätter detta till musik. I ett STM flyttar man en mycket spetsig metallnål över en yta för att läsa av små variationer i ytan. Om spetsen är riktigt spets och avståndet mellan nålen och ytan är mycket litet, typiskt ungefär 1nm, kan man avbilda atomerna i ytan. Man lägger en spänning mellan ytan och nålen och mäter strömmen mellan dem. Eftersom nålen och ytan inte är i kontakt med varandra uppkommer den elektriska strömmen genom något som kallas för tunnling, därav benämningen sveptunnelmikroskop. Detta mikroskop kan användas för att undersöka ytor på atomär nivå, d.v.s. man kan studera hur enskilda atomer är arrangerade i ytan av ett material.


Genom att variera hur man växer trådarna (t.ex. sammansättningen av ångan och temperaturen) kan nanotrådarnas uppbyggnad variera. Detta arbete har handlat mycket om att undersöka och kontrollera hur atomerna arrangeras i trådarna beroende på vilka förutsättningar man använt under växt.

Nanotrådarna är s.k. kristallina, vilket innebär att atomerna är arrangerade periodiskt och man brukar kalla det periodiska arrangemanget för ett materials kristallstruktur. I figur 2 på nästa sida illustreras en kristallstruktur som ofta förekommer i nanotrådarna. Figuren visar också hur kristallstrukturen kan ha samma periodiska arrangemang men ha olika orientering. Atomerna (de färgade bollarna/cirklarna) är lite olika placerade i figur 2a) och b) och dessa två kristaller kallas därför tvilling-kristaller. Om man roterar tvilling A enligt pilen i figuren får man dess tvilling-kristall, tvilling B. Till skillnad från vanliga halvledarkristaller brukar kristallstrukturen i nanotrådarna variera, t.ex. förekommer det ofta att den är roterad på ett sådant sätt att den innehåller tvilling-kristaller (se figur 2c)).

Nanotrådarna som växts och studerats i detta arbete har oftast undersöks med flera olika typer av mikroskop för att titta på både deras yttre form och deras inre kristallstruktur. T.ex. går det att klyva speciellt utformade prover som innehåller växta nanotrådar och på så vis avbilda insidan av nanotrådarna med ett STM. När man klyver prover för att titta på en klyvta kallas det för tvärsnitts-STM och det brukar förkortas XSTM. I figur 2d) visas en bild tagen med STM. Här har atomerna i ett prov som har tvilling-kristaller avbildats. I bilden syns endast en typ av atomer, antingen de röda eller de gula atomerna i modellerna i figur 2. Detta beror på att elektronerna hellre vill vara kring atomerna av det ena slaget i detta material och därför syns just dessa atomer mest i bilden.
Figur 2: Här visas hur atomerna kan vara arrangerade i ett kristallint halvledarmaterial. De gula och röda bollarna/cirklarna motsvarar två olika typer av atomer. Denna struktur benämns zinkblände. a) och b) visar hur två kristaller kan ha samma struktur men vara roterade relativt varandra. I detta fall säger man att de två kristallerna är ”tvillingar” av varandra. c) visar hur kristallstrukturen i nanotrådar ofta ser ut. De består ofta av flera tvilling-kristaller som sitter ihop. I d) visas en bild taget med ett sveptunnelmikroskop (STM). Detta är en del av en yta på ett material som har tvilling-kristaller. De vita linjerna i bilden motsvarar rader av atomer. Tittar man noga ser man att linjerna i själva verket är ljusa prickar och varje prick motsvarar en atom.

De studier som gjorts i detta arbete har ökat kunskapen om hur kristallstrukturen i nanotrådar påverkas av de förutsättningar som applicerats under deras tillväxt. Detta har kunnat användas för att delvis styra vilken kristallstruktur nanotrådarna får. Denna ökade kunskap är av betydelse för
framtida användning av nanotrådar. Nanotrådarnas elektriska- och optiska 
egenskaper beror nämligen bland annat på vilken kristallstruktur de har.
List of Papers

This thesis is based on the following papers, referred to in the text by their roman numerals:

I. *GaAs/AlGaAs Nanowire Heterostructures Studied by Scanning Tunneling Microscopy*


*Nano Letters, 7*(9), 2859 (2007)

This work concerns cross-sectional STM (XSTM) investigations of the interior of axially- and radially heterostructured GaAs/AlGaAs nanowires. Here an AlGaAs segment and shell were grown simultaneously in and on GaAs nanowire cores and the formed interfaces between the two materials were studied. The Al content in the nanowire core was analyzed and a memory effect due to material stored in the seed-particle was observed. It was found that abrupt axial interfaces within the nanowires are possible when switching from GaAs to AlGaAs but that switching from AlGaAs to GaAs is more problematic. Further, in this work it was shown that the growth rates of the AlGaAs on the nanowire sides, under the seed-particle and on the substrate surface are significantly different. In addition, from the result of the AlGaAs shell grown on the twinned nanowire cores an approach to achieve atomically flat side facets onto twinned nanowires by growing shells is suggested.

*I performed parts of the STM preparations and measurements. I contributed to the discussions of the results and in the development of the paper.*
II. *Direct observation of atomic scale surface relaxation in ortho twin structures in GaAs by XSTM*

J. Bolinsson, L. Ouattara, W. A. Hofer, N. Sköld, E. Lundgren, A. Gustafsson and A. Mikkelsen


Here the results of XSTM investigations of the (110) GaAs surface of a structure containing ortho twins are presented. In addition, the experimental results are compared to ab initio density functional theory calculations and STM simulations. Both the experimental and the theoretical results show that the surfaces of different ortho twin crystallites are significantly displaced with respect to each other. This is explained by the difference between the atomic configuration of the ortho twins and the surface relaxation of the atoms in the ordinary (110) GaAs surface.

*I performed parts of the STM preparations and measurements. I did the analysis of the experimental data and most of the analysis of the theoretical data. I was responsible for the development of the paper and wrote the paper.*

III. *Effects of Supersaturation on the Crystal Structure of Gold Seeded III-V Nanowires*


*Crystal Growth & Design, 9*(2), 766 (2009)

In this paper it was investigated how the supersaturation affects the crystal structure of GaP nanowires grown by MOVPE using gold-particles as seeds. We studied the effect of pulsing the source for the group III species (TMG) and the effect of having a background of indium (In) during nanowire growth. A model based on classical nucleation theory was developed and the experimental results were discussed in connection with this model. In this work it was found that the supersaturation affects the probability of forming twins in
zincblende nanowires, a high supersaturation of group III increases this while a lower supersaturation leads to more pure zincblende structure within the nanowires. In addition, it was shown that pulsing the group III source and a background of In leads to lower supersaturation and thus to less twin defects within GaP nanowires.

_I took part in the nanowire growth experiments and I contributed to the discussions of the results and in the development of the paper._

IV. _Control of III-V nanowire crystal structure by growth parameter tuning_

K. A. Dick, P. Caroff, J. Bolinsson, M. E. Messing, J. Johansson, K. Deppert, L. R. Wallenberg and L. Samuelson


In this work, the variation of the crystal structure of gold-seeded nanowires with growth parameters was investigated for several III-V materials (GaAs, InAs, GaP, InP, GaSb and InSb) using MOVPE. The focus was on growth temperature, precursor molar fraction and V/III ratio. The experimental results were presented and discussed in connection to existing reports in the literature concerning the crystal structure of III-V nanowires, including both experimental results and theoretical modeling. In the light of the results presented and discussed here, it is proposed that changes in the crystal structure with growth parameters are related to changes in the stable side facets.

_I performed some of the nanowire growth experiments (I grew the GaAs nanowires). I contributed to the discussions and took part in the writing and development of the paper._

V. _A Comparative Study of the Effect of Gold Seed Particle Preparation Method on Nanowire Growth_

M. E. Messing, K. Hillerich, J. Bolinsson, K. Storm, J. Johansson, K. A. Dick and K. Deppert

_Nano Research, 3_, 506-519 (2010)
In this work the effects of gold-particle fabrication method and deposition method on MOVPE growth of GaAs nanowires were investigated. The most common fabrication and deposition methods were used to prepare substrates with deposited gold-particles and different growth conditions were used to compare the resulting nanowire growth. Aerosol-generated particles, colloidal particles, particles generated by annealing of thin films and electron beam lithography defined particles were compared in this work. It was found that nanowires seeded with these different particles exhibit highly similar growth behavior and crystal structure. The major conclusion was that direct comparisons of nanowire growth studies done in similar systems can be performed, also when the fabrication or deposition method of the gold particles differ.

I contributed actively to the planning of the experimental work, the measurement data analysis, the analysis of the results and to the development of the paper.

VI. Determination of diffusion lengths in nanowires using cathodoluminescence

A. Gustafsson, J. Bolinsson, N. Sköld and L. Samuelson


Here the ambipolar diffusion length in nanowires was investigated by cathodoluminescence imaging. Homogeneous GaAs nanowires, and axial AlGaAs/GaAs and InGaAs/GaAs heterostructured nanowires were studied. In this report it is proposed and shown that the ambipolar diffusion length in nanowires can be determined by CL imaging, using local variations in the emission intensity from single nanowires. It was found that the diffusion length is reduced by surface recombination for uncapped nanowires. Further, it is suggested in this paper that crystal irregularities and composition variations could limit the diffusion length for capped nanowires.

I contributed actively to the planning of the experimental work, in the analysis of the result and in the writing and development of the paper. I planned and performed most nanowire growths.
VII. **Diffusion length measurements in axial and radial heterostructured nanowires using cathodoluminescence**

**J. Bolinsson**, K. Mergenthaler, L. Samuelson and A. Gustafsson

*Journal of Crystal Growth,*

In press, DOI:10.1016/j.jcrysgro.2010.08.054

This work continues the study presented in paper VI, focusing on axial heterostructured nanowires with and without a shell. It is shown that by combining lower- and higher bandgap material axially along the nanowire length, important carrier transport properties of the nanowire core can be found. It is found that in order to reach long diffusion lengths along the nanowire cores, it is necessary to decouple the axial- and radial growth during particle-seeded nanowire growth. It was demonstrated that capping the nanowire core with a radial quantum well is as detrimental for the diffusion along the core as surface states on an uncapped core. Further, it was observed that ternary alloys can have a different composition whether the material is grown axially or radially during particle-seeded nanowire growth. It is suggested that this can be related to the different growth mechanisms involved.

*I planned the experimental work and analyzed the results in collaboration with A. Gustafsson. I was responsible for the development of the paper, wrote main parts of the paper and planned and performed all nanowire growths.*

VIII. **Crystal Phases in III-V Nanowires: From Random Toward Engineered Polytypism**

**P. Caroff, J. Bolinsson** and J. Johansson

*The IEEE Journal of Selected Topics in Quantum Electronics,*

Accepted (DOI: 10.1109/JSTQE.2010.2070790)

In this paper the progress towards the realization of pure crystal structures within III-V nanowires is extensively reviewed. The current theoretical understanding and the experimental achievements of
controlling the crystal phases and defects in III-V nanowires are presented. In addition, possible future directions in studies of controlling the crystal structure are suggested. An important discussion in the paper concerns the possibility of crystal phase engineering in single nanowires for future applications and the efficiency of combining the tuning of several standard growth parameters.

_I contributed actively to the development and in the writing of the paper. I designed and made many of the illustrations that are presented in this paper._

IX. _Wurtzite-Zincblende Superlattices in InAs Nanowires using a Supply Interruption Method_

_J. Bolinsson, P. Caroff, B. Mandl and K. A. Dick_

Manuscript.

In this work growth of gold-seeded InAs NWs by MOVPE was performed using a supply interruption method (SIM). It was found that by using this approach wurtzite segments can be inserted on demand into pure zincblende InAs nanowires. In addition, a very high purity of both phases in the designed wurtzite-zincblende polytypic nanowires was achieved. It is suggested that a similar approach as was explored in this study could also be useful to controllable mix the wurtzite and zincblende crystal phases in other III-V nanowires.

_I contributed actively to the analysis of the experimental results and in the discussions. I was responsible for the development of the manuscript and wrote the main parts._

**Papers not included in the thesis**

The following papers are not included due to overlapping content or content outside the scope of this thesis:
X. *The influence of lysine on InP(001) surface ordering and nanowire growth*

A. Mikkelsen, **J. Eriksson**, E. Lundgren, J. N. Andersen, J. Weissenrieder and W. Seifert

*Nanotechnology*, **16**(10), 2354 (2005)

XI. *Au-free epitaxial growth of InAs nanowires*


*Nano Letters*, **6**(8), 1817 (2006)

XII. *Au wetting and nanoparticle stability on GaAs(111)B*

E. Hilner, A. Mikkelsen, **J. Eriksson**, J. N. Andersen, E. Lundgren, A. Zakharov, H. Yi and P. Kratzer


XIII. *Effects of growth conditions on the crystal structure of gold-seeded GaP nanowires*


XIV. *Diameter Dependence of the Wurtzite-Zinc Blende Transition in InAs Nanowires*


XV. **Low-temperature cathodoluminescence studies of GaAs nanowires in the SEM**
A. Gustafsson, N. Sköld, J. **Bolinsson**, J. Trägårdh and L. Samuelson

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1. Introduction

This thesis deals with growth and characterization of gold-particle seeded nanowires (NWs) of III-V semiconductor materials. The “nano” in NWs indicates that their size is in the nanometer-range and “wires” that their shape is rod-like. Generally NWs have a large length-to-diameter ratio with diameters that are usually in the order of nanometers (nm) and lengths in the order of micrometers (μm). A bright future for applications of III-V NWs\(^1\) is foreseen by many and the expectations for these as important components in the devices of tomorrow are high. Reducing the size of materials down to the nm-scale, make it possible to explore and employ effects of quantum mechanics and to continue the down-scaling of important devices, such as the transistor [2-4]. Promising results using NWs in prototype applications have already been reported from several laboratories around the world [5-7]. The use of NWs in, for example, optical applications such as light emitting diodes [8], photodetectors [6] and photovoltaic/solar cells [9] has been demonstrated. In the coming years we can expect increasing efforts directed towards the next step: taking the NWs from the research environment towards real applications in products suitable for large-scale industrial fabrication [5]. The large extent and diversity of the research activities surrounding NWs shows that many people also find them fascinating as subjects for fundamental research within material science. This research is indeed necessary in order to control the NWs down to the atomic scale, and to increase the understanding of how features on

\(^1\) For the sake of simplicity, I will from this point and forward use “III-V NWs” as a shortening for nanowires of III-V semiconductor materials.
the atomic scale affect properties such as thermal and electrical conductivity, and optical and mechanical properties.

The aim of my work during the past few years has been to contribute to the field of III-V NWs with insights into the atomic arrangement within the NWs, to increase control in the formation of the crystal phases during epitaxial growth from seed-particles, and to increase the understanding of the optical properties of the NWs.

1.1 The outline of this thesis

My idea when writing this thesis has been to write the kind of thesis I myself would have enjoyed reading when starting my PhD studies. The subjects that are covered reflect my contribution to the appended papers, but also partly what has fascinated me. The crystal structure of the NWs, which is covered in chapter 2, I find particularly fascinating. Furthermore, I have found that this subject is not always discussed with the proper care that it deserves in the literature on NWs. My aim with chapter 2 is therefore to extensively describe the different crystal phases that have been observed in III-V NWs and what, for example, twins are and why these are not to be regarded as the same as stacking faults.

Chapter 3 gives an overview of the main characterization methods which were used in the appended papers. I performed a significant number of STM studies on embedded NWs during the first years of my PhD. This method is therefore discussed in more detail than the others.

The NWs studied in this work were epitaxially grown by metal-organic vapour phase epitaxy (MOVPE). Chapter 4 gives an overview of epitaxial growth, introducing some important concepts. MOVPE is then discussed in more detail, including for example how the set-up of an MOVPE reactor can look and how heterostructured III-V NWs are grown by MOVPE using gold seed-particles. Growth of NWs by MOVPE has also been a significant part of my PhD studies.

Chapter 5 is an outlook in which I discuss some important questions still left open and give my ideas of what could be done next.
There is also an Appendix included in the thesis. This contains parts that have been important for the work but which are too specific to be included in the main body of the thesis. For example, here it is described how XSTM investigations of NWs have been carried out, both how the samples are cleaved in practice and how to proceed in order to find the NWs using this method.
2. The crystal structure of III-V nanowires

III-V semiconductor (s-c) bulk materials are usually arranged according to the zincblende (ZB) crystal structure. In some cases, however, its closely related hexagonal counterpart the wurtzite structure (WZ) is found [10-12]. The WZ structure is especially found when nitrogen is the group V component. In contrast to their bulk counterparts, III-V NWs are often polytypic (i.e. different crystal phases are present in a single NW) [13]. NWs with crystal structures ranging from pure WZ to pure ZB, with all intermediate phase-compositions such as faulted WZ, mixed WZ/ZB, randomly and periodically twinned ZB NWs, have been reported (see papers IV and VIII and references within). In a few reports, other polytypes besides WZ and ZB have also been observed. I will return to these polytypes later on, in section 2.1.

The atomic arrangements of the ZB phase and the WZ phase are illustrated in Fig. 2.1a) and b), respectively. A common and useful way of describing the similarities and the differences of the atomic arrangements of the ZB and WZ crystal structures is to refer to their stacking sequences in the <111> and <0001> direction respectively. The <111> and <0001> represent the same direction but in the cubic and hexagonal lattice respectively. The ZB stacking is described as: …ABCABC… (I) or …AaBbCcAaBbCc… (II), and for WZ it is described as: …ABAB… (I) or …AaBbAaBb…. (II). Each capital letter using notation (I) represent a pair of layers (a bilayer) of vertically stacked group III and group V atoms at three slightly different positions, see Fig. 2.1. In some cases it is useful or even necessary to use type (II) notation, in which each letter represents a single layer of atoms. Here, capital letters and small letters each represent one layer of either the group III or the group V atoms.
Figure 2.1: In a) the atomic structure for the ZB crystal phase is shown and in b) for the WZ crystal phase. Both models are slightly rotated from the <110> viewing direction. Two different types of notation for the stacking sequence, one for the single layers (AaBb…) and one for the double atomic layers (AB…) are included and the different colours denote the two types of atoms (group III and V).

This notation can be used to make a complete description also in the most complicated cases of planar defects and misplacements. For example, it is used when the crystal structure is a mixture of WZ and ZB, has ZB-stacked layers of different twin orientations (see section 2.1), or contains faultily placed layers within the WZ and ZB phases.

The crystal structures of III-V s-c materials are held together by covalent tetrahedral bonds between the atoms. However, the bonds also have some degree of ionicity due to the difference in electronegativity between the atom species [14]. The small energy difference between the two crystal phases of WZ and ZB is the underlying cause for polytypism in semiconductor materials, and the ionicity significantly affects whether the material is more
stable in the WZ or the ZB crystal phase [12, 15]. The higher the ionicity of the material, the more stable is the WZ phase and the lower it is, the more stable is the ZB phase. This is because the ionicity creates a force (Coulomb interaction) that strives towards bringing atoms together; thereby a shorter distance between the atoms is favoured in materials of higher ionicity. There is a difference in the distance between the third nearest-neighbours for the WZ and the ZB crystal phases. For WZ this distance is shorter, which can explain the relationship between ionicity and the stability of the WZ phase. In addition, there is a repelling chemical force that strives towards increasing the same distance (i.e. the steric hindrance), which thus acts to stabilize the ZB phase. Materials with purely covalent bonds, including the elemental semiconductors Si and Ge, are almost always found to be arranged according to the diamond structure which can be regarded as ZB-like stacking involving only one type of atoms.

III-V NWs are usually grown in a <111> direction (see section 4.4) and therefore only a slight change in the order in which the layers are stacked during growth is needed to switch between forming the ZB and WZ phases within the NWs. In papers IV and VIII extensive reviews of the crystal structures found in III-V NWs are presented. These papers review both various observations of crystal phases that have been reported, and the current status in how to control and theoretically model their formation in particle-seeded NW growth.

2.1 Twins, stacking faults and polytypes

Twins are common crystal defects in ZB-arranged III-V s-c materials [16], especially in NWs (see paper VIII and references within). When different parts of a crystal are oriented with respect to one another according to some symmetry rule this is called twinning [17]. The ortho twin, also commonly called rotational twin, is the most commonly-reported type of crystal defect found in III-V NWs. The difference in the atomic arrangement for the transformation of rotational twinning can be illustrated by considering a segment with a ZB crystal structure and then rotating this 60° around a <111> axis, see Fig. 2.2a) and the dashed arrow. When performing this rotation, the stacking sequence changes from … ABCABC … to … CBACBA … This is one example in which it is necessary to specify the complete stacking of layers
Figure 2.2: a) Illustrates two rotational twins and b) two mirror twins. Note that there is a change of the top layer of the atoms in the later case. If the yellow atoms corresponds to group V, mirror twinning gives that the top surface is changed from a \{111\}B into a \{111\}A surface here. This is of significant importance for the bonding configuration between the two twin types (see Fig. 2.3).

using notation II, otherwise it may appear as the structure of two rotational twins are mirror images of each others. The stacking sequences for the two rotational twins “TWIN A” and “TWIN B” in Fig. 2.2 should be described as … AaBbCcAa … and … CcBbAaCc … Mirroring the structure so it instead becomes: … aAcCbBaA …, results in mirror (or para) twins. “TWIN B” and “TWIN C” in Fig. 2.2 are examples of such twins. In this figure it can be seen that by a 180°-rotation perpendicular to the \langle 111 \rangle axis of “TWIN B” (see the
Figure 2.3: a) Here two rotational twinned crystallites, as for example the TWIN A and TWIN B in Fig. 2.2, are joined. The plane in between the two twins is usually called a twin plane (bilayer A). For mirror twins, the bonding configuration across the twin plane would be in between the same atom species. b) This is a periodically twinned crystal structure with the twin planes indicated by the orange rectangles. This is a special case of twinning, where the twinned segments are all equally long and thus this structure corresponds to a type of homostructured superlattice, a twin-plane superlattice.

dashed arrow), one gets its mirror twin, “TWIN C”. Further, in NWs it has been found that rotational twins are frequently present while mirror twins have, to the best of my knowledge, not been reported so far.

The plane that separates two twinned crystal segments is called the twin plane (see the orange bilayer A in Fig. 2.3a)). In the case of mirror twins, this type of plane is called the mirror plane. An important difference between mirror and rotational twinning is the bonding between the atoms across the twin boundary. Between rotational twins, this bonding is between
different types of atoms (i.e. between anions and cations), while for mirror twins the bonding is between atoms of the same species (i.e. either cation-cation or anion-anion bonding). Further, in the literature concerning the crystal structure of NWs a twin plane is sometimes also referred to as a *stacking fault* (SF). Strictly speaking, however, this is not correct. Although twin defects can certainly be considered as faults in the ZB stacking sequence, the term SF implies that there is a local interruption in the regular stacking sequence that continues in the same manner after the SF [18]. Usually a SF refers to a single additional layer (extrinsic SF) or a single missing layer (intrinsic SF) in an otherwise perfect crystal surrounding. However, this is not the case for twinning of the ZB crystal structure as the stacking sequence is different before and after the twin plane. A twin plane results in a change of the orientation of the ZB crystal structure, as seen from Fig. 2.3. Thus, the term SF should not be used interchangeably with twin plane or in connection with twinning in ZB in general. From this point forward, only rotational twinning and twins are discussed and for the sake of convenience this is the type of twinning/twin that is referred to when neither rotational/ortho or mirror/para is explicitly stated.

An interesting structural modification of the pure ZB phase that has been found in NWs is periodic twinning [19, 20]. The atomic model in Fig. 2.3c) shows such a crystal structure. Here the twins occur in a very regular way and not as a local variation in an otherwise ordinary matrix of ZB-type stacking. This could even be considered as a polytype in itself. Indeed, the illustrated structure could be referred to as the 10H polytype (see for example table 1 in ref. [21]). A periodically twinned structure, having \( n \) number of atomic layers of each twin type would then correspond to an \( nH \) polytype. Using Ramsdell notation for polytypes [22], WZ and ZB should be labelled as 2H and 3C, respectively. WZ/2H is the polytype with the shortest period, only the orientation of two bilayers are needed to specify the stacking sequence, while three bilayers are needed for the ZB/3C, four for the 4H and so on (see the table in Fig. 2.4). As mentioned earlier, there are a few reports of other polytypes besides WZ and ZB that have been found in III-V NWs. The 4H [23, 24] and the 6H [25] polytypes, illustrated in Fig. 2.4a) and b) respectively, have recently been observed.
Figure 2.4: a) and b) are atomic models of the crystal structure of the polytypes 4H and 6H, respectively. The table summarizes the different polytypes, with corresponding stacking sequences, that have been reported so far for III-V NWs.

When two or more polytypes are mixed within a single NW, an important (and fundamental) question arises: How many layers of the correct stacking sequence of a certain polytype are needed to define a part of the crystal as a segment of that specific polytype? From the literature about twinning in III-V NWs, the opinions seem to differ. For example, following the definition of a WZ-type stacking sequence, part of the crystal in Fig. 2.3a) can be viewed as a tiny WZ segment of only 3 bilayers (CAC). At the same time, the lower part of the structure is perfectly ZB-stacked up to the A bilayer and the upper part is...
also perfectly ZB-stacked from A. One bilayer in the twinned crystallite in Fig. 2.3a), A, could be considered to be in a completely WZ-like or hexagonal surrounding. It is therefore natural that some refer to this as a tiny WZ segment. However, the two adjacent bilayers are on the other hand in a ZB-like surrounding. Therefore it cannot be assumed that all of the atoms in A have a complete WZ-like bonding configuration, especially not considering the electronic configuration of the shared electrons. Therefore it can be argued that it is appropriate to make a clear distinction between twin interfaces and the WZ crystal phase and only use the term WZ when the stacking sequence follows the WZ-type for at least 4 bilayers.

Similarly, for faults or interruptions in a WZ stacking sequence of the type: ABABC\_BABA, the term ZB phase is inappropriate to describe the small part of the structure that follows this type of stacking. Here it is a single bilayer that is “misplaced” and thus this follows more the definition of (extrinsic) SFs mentioned above. However, when a structure follows a ZB-type stacking for at least 4 bilayers in a row this should be considered as an example where the crystal is partly of this phase. The above definitions of the smallest unit of the WZ and ZB phases (4 bilayers) are the same as the ones used in the appended papers, with the exception of paper I.

2.2 The influence of polytypism and crystal irregularities on the properties of the nanowires

The electronic band structure of a material depends not only on the atom species present but also on their periodic arrangement. Whether the crystal structure is of the WZ or ZB phase can therefore have a noticeable effect on the optical and electronic properties of the NWs. In the case of mixed structures in single NWs, the energy bandgaps vary throughout the NWs and this can result in a rather complex potential for the electrons and holes, especially considering the band alignment at the interface between different crystal phases. For example, some of the III-V s-c materials may have so called type II band alignment (see Fig. 2.5) between the ZB and WZ phases [26-29]. SFs and twin planes break the symmetry of the crystal and can act as scattering centers for electrons and holes [30, 31]. The presence of these crystal irregularities may therefore have a significant influence in for example the electron transport through the NWs. In addition, rotational twins in an
Figure 2.5: Here type I (a) and type II (b) band alignment between two materials (A and B) are shown. For type I, the valence- and conduction band edges are symmetrically aligned, but for type II they are not. Here the valence- and conduction band edges of the higher-bandgap material (material A) are higher than the valence- and conduction band edges of the lower-bandgap material (material B). A third type exists, type III, in which the valence band edge of the higher-bandgap material exceeds the conduction bandedge of the lower-bandgap material.

otherwise pure ZB NWs may have a stronger scattering effect than SFs. The wave functions of the electrons and holes for the differently oriented ZB twins have been suggested to be highly symmetry-mismatched and to result in significant scattering of electrons at the interface or twin plane [30, 32]. An intriguing possibility is a transition from an indirect to a direct (or vice versa) bandgap in a material depending on whether it is arranged in the WZ or the ZB phase, as suggested in the work by De and Pryor [33]. This effect would of course be important for NW optical properties.

The band structures of the WZ phase for most III-V materials are not completely known and there are some discrepancies in the reported values [26, 27, 33, 34]. Due to the small volume of the NWs, even a very low density of SFs or insertions of other polytypes can complicate the interpretation of measurements of their optical and electronic properties. NWs
composed of purely one polytype (not found in bulk) may be required for the bandgaps of polytypes to be determined with complete certainty.

Although there is no clear answer, I would like to end this chapter by highlighting a very important fundamental question in this context: *How many layers must be stacked according to one specific polytype (or a crystal phase in general) before it becomes reasonable to assume that this volume of material has identical, or close to identical, energy band structure as when the stacking sequence continues infinitively?* (That is, how many layers does it take for a bulk-like approximation of energy band structure to be valid?)
3. Characterization of nanowires

This chapter presents an overview of the main tools that have been used to characterize the NWs that were investigated in the appended papers. These tools can, and indeed have, themselves each comprise a subject for a PhD thesis. It takes sophisticated and rather complex equipment and methods to explore materials on the nm-scale or smaller.

The section about Scanning Tunnelling Microscopy (STM) is more in depth, which reflects that part of my PhD time was devoted to STM investigations solely. Besides STM, I have also carried out part of the Scanning Electron Microscopy (SEM) characterization of the NWs involved in several of the appended papers. Cathodoluminescence microscopy (CL) and spectroscopy as well as Transmission Electron Microscopy (TEM) measurements have been used to characterize the NWs in several of the appended papers. However, these measurements have not been carried out by me but by one or several of the other co-authors of the respective paper.

3.1 Scanning Tunnelling Microscopy

The Scanning Tunnelling Microscope (STM) is a powerful tool, the strength of which lies in the high resolution it can provide under the right conditions. The Nobel Prize committee awarded half the 1986 prize in Physics to its inventors, Gerd Binnig and Heinrich Rohrer (the other half of the prize was given to the inventor of the electron microscope, Ernst Ruska) [35]. Today,
about 25 years later, the STM is keeping a strong position in the limelight as a sophisticated surface science tool and is used in the front line of research in many research laboratories. Using a special growth scheme to embed NW structures and by cleaving the samples it is also possible to explore the interior of NWs on the atomic scale by revealing a cross-section of the grown structure (see section 3.1.3 and Appendix A1). In papers I and II investigations utilizing this type of STM measurements are presented.

Performing STM measurements is time-consuming and demands a lot of hard work, patience and skill. However, the reward is breathtaking, being able to have insights into the atomic and electronic structure of interesting samples. The first published STM image with atomic resolution was published in 1983, showing the $7	imes7$ reconstruction of the Si (111) surface [36].

### 3.1.1 The basic principles of STM

The basic principle of performing STM measurements is to probe the topography and electronic structure of a sample surface with a sharp tip. The main limiting factor is that both the tip and the investigated surface need to be conductive, as the microscope records the topography and electronic structure of the surface by measuring a small electrical current between the two. Usually the tip is made from a metal material; Tungsten (W) and Platinum-Iridium (Pt-Ir) are the most used materials for STM tips. A common method of fabricating STM tips is by electrochemical etching of W wires, which was also how the STM tips were prepared in this work. For details of this method see, for example, the work by Ekvall et al [37].

Placed in close proximity to each other (5-10Å), quantum mechanical tunnelling of electrons can take place between two conductive materials (see Fig. 3.1a)). The number of electrons that tunnel depends strongly on the width of the potential barrier they penetrate, i.e. the tip-sample distance. The same number of electrons will tunnel from the tip to the sample as from the sample to the tip through the barrier, and therefore no net current will flow in between. By applying a bias voltage between the tip and the sample, there will be a net current of electrons moving across the separating barrier (see Fig. 3.1b)).
Figure 3.1: The electrons can tunnel through the separating barrier (grey area) when this is narrow. This is illustrated by an overlap between the "tails" of the electron wave functions of the tip ($\phi_t$) and the sample ($\phi_s$). a) When no bias voltage between the tip and sample is applied, there will be no net current. In b) a bias voltage, $V$, is applied and a net current will be induced between the tip and sample. The red areas corresponds to occupied electron states of the tip and sample and the electrons that contribute to the tunnelling current are tunnelling from occupied states of the tip into unoccupied states in the sample. ($E_{F,s}, E_{F,t}, E_{vac}$ are, respectively, the Fermi level of the sample and tip, and the energy level of an free electron in vacuum. $W_s$ and $W_t$ are the corresponding work functions.)
The magnitude of this tunnelling current can be approximated as [38]:

\[ I_{tun.} = C \cdot \rho_{sample} \cdot \rho_{tip} \cdot e^{-s \cdot \Theta^2} \]

This equation describes how the tunnel current \( I_{tun.} \) is related to the tip-sample separation \( s \), the electron density of the tip \( \rho_{tip} \) and the electron density of the sample surface \( \rho_{sample} \). The parameter \( \Theta \) is related to the separating potential barrier, and to the first approximation to its height and width, and \( C \) is a constant. This equation describes the basics of the theory behind STM measurements well. The key to the whole microscope, and what makes it possible to achieve atomic resolution, is the exponential dependence of the magnitude of the current on the tip-sample distance.

*Constant current imaging* is the most common mode of operation for STM measurements and the type of STM imaging that was employed in this work. During this mode, the tip is moved in small steps laterally (usually referred to as the \( xy \)-plane) over a sample surface while the tunnelling current is kept constant. A feedback regulator adjusts the vertical position (\( z \)-position) of the tip to maintain a set-point tunnelling current, which is set by the STM operator. The STM is operated by the user through a computer, using a software interface to communicate with an electronic control unit (see Fig. 3.2).

The control unit sets the commands from the STM user into action by adjusting signals that are transferred to different parts of the STM. The fine lateral and vertical movement of the tip in an STM measurement is done by a scanner, in which properties of piezo-electrical materials are utilized to make the necessary sub-Ångström movements. The \( xy \)-positions and the \( z \) variations of the tip are recorded during constant current measurements. When the conditions of the sample surface and the STM tip during a measurement are good; the vertical adjustment (\( z \)-position) for different lateral positions can be interpreted as a contour map of constant density of states (DOS) of the sample surface.
Figure 3.2: This shows the basics of the design and operation of an STM. In the large arrows it is indicated which parameters that are inputs set by the STM operator and the outputs which usually are monitored during an STM measurement.

A less common mode of operation than constant current imaging, is constant height imaging. Here the feedback loop does not adjust the vertical position of the tip. Instead variations in the tunnelling current are measured at different lateral positions above the sample surface. That is, the $xy$-positions and the $I_{\text{tun}}$ are recorded at the same time as the vertical position of the tip is kept constant. During constant height imaging, there is a strict restriction of extremely flat sample surfaces. In constant current imaging, however, the surfaces do not necessarily have to be as flat because of the vertical adjustments of the tip during scanning. Too large geometric features of the surface can of course necessitate larger vertical adjustments than are possible.
Figure 3.3: Here some common features that can appear in an STM image when scanning over a step-edge are illustrated. a) An ideally sharp tip records the step-edge well. A somewhat blunt tip records the same step-edge less abruptly, as seen in b). When there are different parts of the tip in almost equal proximity to the sample surface, as for the “double-tip”-shape in c), the imaging part of the tip can change during scanning. In this case the recorded image may show multiple features of single features on the sample surface.

within the range of the scanner which is in use. Further, detailed information of the electronic structure give rise to small variations in the vertical position of the tip in comparison to the variations from geometric features and may therefore be “lost” when the surface is not atomically flat. In this case, the image will mostly be a topographic map of the sample surface in which geometric features have been probed and the detailed electronic structure is not observable. Almost atomically flat sample surfaces are a requirement if an STM study involves atomic-scaled features or properties. In the end, it is the STM operator that has to interpret the z-variations of the scanned area to rule out what is linked to effects from geometrical features and what is linked to effects of variations in the DOS.

The tip is not always as ideally sharp and spherically uniform as needed to probe small geometric features or electronic properties of a surface. It is not unusual to find features in the STM images, which are caused by a blunt or in other way deformed tip rather than by features of the surface. As illustrated in Fig. 3.3, the sharpness of the tip can affect how geometric features on the surface appear in a measurement. Fig. 3.3a) illustrate a sharp and
uniformed tip-shape and schematically the appearance of a corresponding line scan over a sharp step-edge on the surface. Using an ideal tip, the step-edge is also imaged as sharp and gives a true representation of the surface step. In Fig. 3.3b), the tip is not ideally sharp and the corresponding line scan of the step-edge is less sharp. A so-called double tip is illustrated in Fig. 3.3c).

This shows how height differences, such as step-edges or other geometric or electronic features, can appear double or more complex depending on the shape of the tip. For this kind of "multiple" tip, the part at the closest proximity to the surface may vary for different measuring points or lines in a recorded image. When the imaging part of the tip is changing during a measurement it can be difficult to analyze the images, and to interpret the results can be a difficult and time-consuming part of the STM investigations. Ideally, the tip should be uniform, sharp and stable when performing STM. Regardless of looking at nm-sized structures or a more detailed electronic structure of flat surfaces, the influence of the tip itself on the result needs to be considered.

STM measurements can be performed both in normal atmosphere and in closed ultra high vacuum (UHV) systems. In most STM studies, however, UHV conditions are employed and this thesis has solely involved STM investigations performed under UHV conditions. In a UHV system, the base pressure is around $10^{-9}$ mbar or lower. Measuring under UHV condition is first of all done to slow down and limit the contamination of the sample surface (see also section 3.1.3). However, it also helps isolating the STM from acoustic noise. Ideally, there should not be any vibrations present in an STM measurement because of the small and important tip-sample separation. Even really small vibrations may cause variations in the tip-sample distance and thus affect the measurements seriously. Therefore, the main problem in the original design of the microscope was in fact to find a solution to how to isolate the microscope from external vibrations. To reduce building vibration, the whole UHV system (containing the STM) can be isolated from the main building by placing it on its own concrete boulder on the ground floor. It also helps if the system is situated on a table which has some kind of damping mechanism. By suspending the STM stage using springs, mechanical vibrations are prevented from proceeding from the vacuum chamber itself (or other equipment inside the system) to the microscope.
3.1.2 Voltage dependence in STM imaging

The tunnelling current in STM measurements can flow either from the tip to the sample or vice versa, depending on how the bias voltage is applied between the sample and the tip. If the electric potential of the sample is set higher than the tip (positive sample bias voltage), the current will flow from the sample into the tip. In this situation the electrons will tunnel from the tip to the sample (see Fig. 3.1b)). For negative sample bias, the direction of the tunnelling current and of the tunnelling electrons will be the opposite. By performing measurements at different bias voltages, the density of both unoccupied and occupied states of a sample surface can be investigated and analyzed for different energies. The same surface can appear very different depending on the bias voltage polarity and also for different voltages within the same polarity. For example, when imaging GaAs (110) one can by the choice of bias voltage polarity, distinguish between imaging either Ga or As atoms. It is known that the GaAs crystal has slightly ionic bonds. In STM measurements, this results in imaging the Ga atoms for a positive sample-bias (unoccupied states) and the As atoms for a negative sample-bias (occupied states) (see also Appendix A2).

It is also possible to perform current spectroscopy measurements (IV-characteristics) by STM, this is called Scanning Tunnelling Spectroscopy (STS). During these measurements the feedback loop is turned off for a short period of time, and the tunnelling current is measured while the applied bias voltage is changed. If this is done at every xy-position during constant current imaging it is called Constant Current Imaging Spectroscopy (CITS). The appended papers do not concern such measurements and this will therefore not be discussed further here.

3.1.3 Cross-sectional STM of nanowire structures

When a sample is cleaved in vacuum and the revealed surface is probed by an STM; it is called cross-sectional STM or XSTM. In Appendix A1.2 the procedure which was used to cleave samples in this work is briefly described. By using XSTM it is possible to probe layers and interfaces in buried or embedded structures by revealing a cross-sectional plane of for example superlattices, embedded quantum dots and NWs [39, 40]. In papers I and II XSTM investigations of embedded NW structures are presented. An important
advantage with XSTM is the possibility of achieving clean surfaces for STM investigations. Creating the surface inside the protected environment of a vacuum system by cleaving, limits the contamination of the surface. In particular, the vacuum limits the rate of oxidation of the surfaces, which for many surfaces can be very severe and significantly reduce their conductivity. There are other methods of limiting or for removing for example oxides (or other contaminations) before introducing a sample surface into a UHV system. However, these methods often require preparation in terms of different etching processes.

When creating a surface by cleavage, it will start to be exposed to particles and molecules immediately. How fast a monolayer of adsorbates will form onto the surface depends on the pressure, temperature and the probability of the surrounding molecules and atoms to become adsorbed on the surface. Assuming that everything that impinge on the surface will stick, room temperature and UHV conditions; a monolayer will form within 3 hours [41]. However, not everything will stick to all surfaces when impinging. For these investigations, revealing a (110) surface plane of (mostly) GaAs, it has been found empirically that it is possible to measure on a cleavage plan for about a week. After this, the surface is too contaminated for stable high resolution imaging [39].

One limitation of cleaving samples for XSTM investigations is that high resolution STM investigations demand very flat surfaces. This limits the choices of crystal planes and structures that can be investigated by this technique. For example, in highly strained material systems, the success-rate of nicely cleaved surfaces can be very low and many and large steps may be induced by the cleavage. The crystal structure itself also influences which cleavage planes that can be created and the flatness of the revealed surface. There are surface planes that are more easily exposed than others. This is due to the density and strength of the bonds between different planes in the crystal structure. To reveal a plane that have a lower density of dangling or broken bonds is more easily done than to reveal one of higher density. The {110} planes are common cleavage planes for III-V semiconductor materials whereas the preferential cleavage plane is (111) for Silicon (Si). As was mentioned above, the XSTM studies performed in this work have involved cleaving sample to reveal the (110) surface. The substrate, as well as most of the
embedding material and the NWs is GaAs. I have therefore included a section in the Appendix (A2) which discusses XSTM imaging of this surface.

Finding the NWs in XSTM investigations can be compared to looking for the proverbial needle in a hay-stack considering the size of the total cross-sectional area of a cleaved sample surface and the cross-sectional area of a single NW. It is necessary to include materials in the growth (if not already included in the structure of interest) that can easily be distinguished from each other when imaged by STM in order to locate the NWs. In this work, a combination of AlGaAs and GaAs has been used to locate the epitaxially grown and interesting part of the samples. These materials are almost completely lattice matched. As was discussed in the work by Albrektsen et al in ref. [42], the Al content introduce an enhanced oxygen affinity of the AlGaAs layers compared to the GaAs. When imaged by STM the surface of AlGaAs is therefore often seen as rough in comparison to the surface of GaAs. Besides this effect, the difference in the electronic structure between the materials can show up as a difference in apparent topography when imaged in constant current mode [40, 42, 43]. The procedure of locating the NWs by the help of the AlGaAs material as a marker is described in Appendix (A1.2).

### 3.2 Scanning Electron Microscopy

In scanning electron microscopy (SEM) the sample is investigated by means of a scanned electron beam. The SEM consists of a closed system which includes one or several vacuum pumps to keep vacuum conditions during measurements. One of the main components of an electron microscope is the source for the electrons: the electron gun. There are two main types: the thermionic and the field emission gun. In the former, a filament (of most commonly tungsten (W) or lanthanum hexaboride (LaB6)) is heated and free electrons created through thermionic emission. For the second type, the field emission gun, a sharp tip-shaped single crystal of tungsten works as a cathode. By applying a large voltage difference (usually a few tens of kV) between this and an anode, free electrons are created and emitted from the tip by field emission. These free electrons are accelerated and transported towards a target (the sample) as a focused beam.
Figure 3.4: Possible interactions of an electron beam and a specimen. By detection of the secondary electrons (SE) a topographic representation of the sample can be visualized (conventional SEM imaging). From the recombination process of electron-hole pairs photons are emitted and these are detected in cathodoluminescence measurements, see section 3.3.

The beam is focused and controlled by electromagnetic lenses. When the electrons arrive at the sample, different processes may occur as a consequence of the interaction between the electron beam (e-beam) and the sample material, see Fig. 3.4. Some of the electrons will be inelastically scattered, thereby creating other free electrons within the material. When this interaction takes place in the surface region and up to about 50Å into the sample material, the created electrons may escape the material. These electrons are called secondary electrons (SEs). By detecting the SEs, together with the position of the scanned primary e-beam, a topographic image of the sample surface can be constructed. This is how SEM imaging is most often done, and also how it was done in this work. The yield of SEs is influenced by several
factors, such as the work function, doping, penetration depth, and geometry of the sample.

Electrons that are scattered back more or less elastically within the material are called backscattered electrons (BEs). These have much higher energy than the SEs, are much more sensitive to the chemical composition of the sample and can escape from further into the material compared to the SEs (roughly 1μm). In terms of intensity, however, the number of SEs will be much larger than the BEs and these electrons will therefore give a much stronger signal from the sample. Primary electrons will also be absorbed within the material and their kinetic energy will cause different electronic excitations within the material, resulting in for example the emission of X-rays and Auger electrons. Another effect is the generation of electron-hole pairs, which when recombining may give emission of light. This effect is called cathodoluminescence (CL) and will be discussed more in a separate section below.

SEM is very useful and rather fast technique to use for imaging nanostructures such as NWs. It can give a magnification up to 1000 000 times and has a resolution limit of around 10Å. The resolution is set by the wavelength of the electrons of the beam and the electromagnetic lenses, which are very inefficient in comparison to ordinary lenses used for optical microscopes. This is what ultimately limits the resolution in electron microscopes. The resolution and magnification for standard SEM:s are sufficient, and in many cases excellent, for studies of the NW morphology in terms of length, diameter, and in the high resolution cases; the orientation of the surface facets. Operating a standard SEM is rather simple to learn and imaging NWs by this technique is quickly done and will still give a lot of valuable information about the NWs. The SEM is most often the first tool used when evaluating the growth of NWs, and therefore also very much a crucial one. After a first look at the NWs in the SEM, a more detailed investigation of the NWs can be done by one or more of the other techniques discussed in this chapter.
3.3 Cathodoluminescence microscopy and spectroscopy

Today the effect of cathodoluminescence, the radiative recombination of electron and hole pairs created by energetic electrons, is not as widely used in our everyday life as it once was. The old types of TVs and computer screens, the thick ones, all had a cathode-ray tubes which utilize this effect. However, it is also a useful and interesting effect to study and explore in order to investigating the optical properties of materials. Cathodoluminescence microscopy (CL) is a method in which the effect of cathodoluminescence is induced by the e-beam from an SEM (or a TEM) [44, 45]. The intensity of the resulting photons are detected and monitored with respect to the position of the e-beam on the sample. Papers VI and VII concerns CL measurements on III-V NWs (note that the Supplementary Information for paper VII is included in Appendix A3).

The schematic set-up of the low-temperature CL system used in this work is shown in Fig. 3.5. The use of an e-beam in this technique means that some level of vacuum condition is required. The right part of Fig. 3.5, including the electron gun and the sample stage, is therefore kept at low pressure. Further, in the CL system there is a cryostat that can be used to cool down the samples using liquid helium. This has been used in the measurements presented here, giving a temperature of around 6-8 K during the CL investigations. This is done because the temperature is known to strongly affect the optical properties, as well as the electronic properties, of semiconductor materials [44]. The (energy) band structure for the electrons and holes is a function of the spacing between the atoms (i.e. the lattice spacing) and the temperature affects this (increased temperature involve lattice dilation) and thus the band structure. Also, thermal energy contributes to electron-phonon interaction. A lower temperature leads to less thermal broadening. Another benefit from performing measurements at low temperatures is that non-radiative recombination processes tend to slow down significantly with temperature, leading to more radiative recombination of electron and hole pairs.
In the CL set-up used in Lund, two different data acquisitions can be made: either (1) a cathodoluminescence intensity spectrum (intensity vs wavelength) in a spot or area of the sample or (2) cathodoluminescence spatial images for a specific area of the sample. In the later case, the intensity of the CL signal for a specific wavelength is recorded and displayed as a function of the e-beam position. For the CL measurements involved in this work, we mainly used a GaAs photomultiplier (PMT) with a photon energy detection range of 1.37 to 6 eV.

The spatial resolution in CL measurements is given by the e-beam radius, the generation volume of the electron-hole pairs (penetration
depth) and the lateral diffusion of the charge carriers [44]. Considering the magnitude of the above mentioned factors, the ultimate resolution is usually limited by the lateral diffusion length of the charge carriers, which commonly is in the order of a few μm. The radius of the e-beam and the generation volume are significantly smaller, the former around a few hundreds of Ångström and the later a few thousands of Ångström. The penetration depth is a function of the e-beam energy and the density of the material and thus can be varied by varying the acceleration voltage of the e-beam. In this way it is possible to tune the depth at which the material is being excited by the e-beam [44, 46]. Further, the penetration depth of the primary electrons and the diameter of the generation volume are coupled, where a larger penetration depth gives a wider generation volume.

3.3.1 Cathodoluminescence measurements on nanowires

CL studies of the optical properties of NWs are not widely used, especially not in comparison to photoluminescence (PL). The strength with using CL in combination with SEM imaging is that it makes it possible to have high spatial resolution of the measured area together with the emission intensity of the generated photons. In CL the detected light can be monitored with respect to where it was generated (i.e. where the electron-hole pairs where generated by the e-beam) and SEM images of the investigated sample area can be compared to the intensity and wavelength of the emitted light. This is different to PL measurements, in which the emission is detected with respect to where it was emitted. It is also possible to see if there is a lack of emission at special places of a structure or sample with CL. A drawback with CL is the high excitation density, where a single electron from the e-beam can generate 500-1000 electron-hole pairs. This can lead to a broadening of the emission peaks, and thereby a reduced spectral resolution.

In Fig.3.6, three different ways in which NWs can be studied in our CL system are illustrated (see also the figure of the CL system in Fig.3.5) [45, 46]. NWs can be studied by CL as grown on the substrate either in top-view, see Fig.3.6a), or a sample can be rotated and the NWs can be studied in side-view as seen in Fig.3.6b). It is also possible to break the NWs off from the substrate surface and deposit them onto another surface, see Fig.3.6c). The later alternative has the advantage that it removes any possible problems regarding separating between the emission coming from the substrate and the
Figure 3.6: Illustrating three different ways to study NWs by CL: in top-view (a) or side-view (b), still attached to the substrate. The NWs can also be studied after being broken off and deposited onto another substrate surface (c). Photons emitted from the interaction with the incoming e-beam are indicated here by the blue arrows. d) An SEM image of NWs, recorded using the set-up shown in c). e) Here there are actually two images, superimposed onto each other. The inverted SEM image in d) (blue) and a CL image (yellow) taken simultaneously over the same sample area (see more in the text).

emission coming from the NWs. In the situations where NWs are grown from the same type of material as the substrate, the emission of the substrate can dominate the measurements when the NWs are still left on the substrate. SEM and CL images from measurements on NWs of the type illustrated in Fig.3.6c) are shown in Fig.3.6d) and e).
The inset in the SEM image in d) shows schematically how two materials were combined in these NWs. These NWs are axial heterostructures with segments of a lower bandgap material (InGaAs) inserted in a higher bandgap material (GaAs) (see section 4.4.1 and papers VI and VII).

This shows one of the major strengths with studying NWs using CL. It also illustrates how a major part of the CL measurements have been done in this work. The Fig.3.6e) is actually two different types of images. Here a CL image has been measured and then this data has been superimposed onto the inverted SEM image displayed in Fig.3.6d). The SEM image is presented in the blue-scale while the CL image is presented in the yellow-scale to be able to compare the detected emission of light with the topographic view of the same area. This particular CL image was recorded at an energy which corresponds to emission coming from the segments within the NWs and so the yellow regions indicate the location of the lower bandgap segment in the NWs.

By varying the acceleration voltage of the e-beam it is possible to vary the penetration depth and to some extent tune which parts of the NWs that are to be studied. For example, if the NWs have a shell, enough voltage needs to be applied to have significant excitation in the NW core if this material is to be investigated. If the voltage is set to high, however, the electrons may go through the NW and excite the substrate and the emission of photons will come from the substrate material instead [46].

3.3.2 Charge carrier diffusion length measurements in nanowires using cathodoluminescence

As mentioned above, the light that is emitted and detected in a CL measurement is not necessary emitted from the same place as the electrons and holes were created. The diffusion of charge carriers within the studied samples may result in emission also from other regions. In general this has a negative effect on the measurement by reducing the spatial resolution. The recombination centre is usually located at the spatial region with the highest emission intensity. However, diffusion effects can also be put into use by performing measurements of diffusion lengths of charge carriers. For example, non-radiative defects, which show up as black dots or stripes in the CL images, as well as defects (or other spatially restricted regions) that have well defined luminescence energies can be used for such measurements. However, it is
necessary that these defects withhold at least one lower energy state for the charge carriers, as compared to the surrounding material. In other words, they need to be working as sinks or traps for the charge carriers. In the case of non-radiative defects, the CL intensity (the emission intensity in a CL measurement) will decay as the e-beam gets closer to the defect and more of the charge carriers reach it by diffusion and thus get “trapped”. The opposite will happen to the CL intensity in the other case, the CL intensity for a specific energy (related to the defect) will increase as the beam gets closer. In both situations, the dependence of the intensity on the distance to the defects can be used to determine the diffusion length of the charge carriers.

Further, for the transport of charge carriers in NWs, the shape of the NWs (length-to-diameter ratio commonly very large) give that this can be considered to take place in only one dimension. Therefore the concentration of charge carriers, which due to diffusion is found away from the excitation volume, can be expressed as [47]:

\[ C(x) = C_0 e^{-x/L} \]

Here \( C(x) \) is the carrier concentration at location \( x \), \( C_0 \) the concentration at \( x=0 \), and \( L \) the diffusion length. Thus, the concentration of charge carriers at location \( x \) is proportional to \( e^{-x/L} \). The CL intensity can be approximated as proportional to the carrier concentration, and thereby proportional to \( e^{-x/L} \). Measuring the CL intensity as a function of distance from the emission area will show an exponential dependence which can be used to determine the diffusion length.

By fabricating axial heterostructures within NWs, CL investigations of the ambipolar diffusion length can be performed. This was done in papers VI and VII (see also Appendix A3) and is schematically illustrated in Fig.3.7. Here, a lower and a higher bandgap material are combined axially within a NW core, see Fig.3.7a). The CL signal coming from parts of the lower bandgap material (the yellow segment in this figure) can be measured as a function of the e-beam position on the parts of the higher bandgap material. The electron and holes created in the higher bandgap material parts of the NW will diffuse. Depending on the distance to the lower bandgap material parts of the NW, some of the recombination will take place here, see Fig.3.7b). The intensity of the signal coming from the lower bandgap
Figure 3.7: a) An axial heterostructured NW with a segment of a lower bandgap material. b) Charge carriers created in the higher bandgap material part of the NW may diffuse and recombine in the lower bandgap segment. By measuring the CL intensity of the emission coming from this segment as a function of the e-beam position on the NW, the ambipolar diffusion length can be determined.

Material parts will thus depend exponentially on the distance from the e-beam position and these regions of the NW. Plotting the natural logarithm of the intensity as a function of position and by fitting a straight line to it, the diffusion length can be determined as it will be the reciprocal of its slope (see the equation above). Note that this will give the ambipolar diffusion length and thus the combined diffusion of electrons and holes. However, it is probably the charge carrier type which has the shortest diffusion length that effects the measurements the most.

More details about this set-up for diffusion lengths measurements in NWs are found in Appendix A3, which is the Supplementary Information to paper VII.
3.4 Transmission Electron Microscopy

In Transmission Electron Microscopy (TEM), most of the imaging is done by detecting electrons that have been transmitted through a sample or specimen. This means that only very thin samples can be investigated using this type of microscope. NWs are excellent specimens for TEM investigations, having diameters of only some tens of nanometers. The basic parts of a TEM are an electron gun, electromagnetic lenses and detectors. The basic principle is similar to a conventional (transmission) optical microscope. However, instead of light, electrons are used, and instead of conventional glass-lenses, the electrons are focused by electromagnetic lenses. The human eye can detect light and can therefore be used as a “detector” in an optical microscope, but not when the light is replaced by electrons.

The electrons are, as in an SEM, created and accelerated by an electron gun (acceleration voltage is usually around a few hundreds of kV). A set of condenser lenses focuses and direct the electrons from the electron gun into a parallel beam, which “hits” the specimen. Objective lenses are placed after the specimen to project a magnified image of the sample using the transmitted electrons. The image produced by these electrons can be detected and recorded using an electron-sensitive CCD camera. It is also possible to detect the electrons using a phosphorous-covered screen, which lights up (cathodoluminescence) at the locations where it is hit by electrons. However, this screen can only be used to observe the image, not to record it. Images are typically recorded using the CCD camera or photographic film. In this work, the TEM images have been recorded using a CCD camera.

Below I will give a short description of the TEM modes that have been used to characterize the NWs discussed in several of the appended papers (III-V and VIII-IX). The interested reader will find the textbook of Williams and Carter [48] suitable for more in-depth reading about TEM. In addition, TEM studies of NWs in particular are extensively discussed in the chapter by Gustafsson et al in ref. [46, 48].

In HRTEM, the projected atomic rows in a crystal can be imaged and the crystal structure of for example a NW can be investigated. Imaging with such a high resolution is possible due to the wave nature of the
electrons. Though it can appear so, in this mode of TEM it is not the transmission versus absorption between different regions of the sample that lies behind the image formation. Instead in HRTEM it is the interference between the transmitted electron waves themselves that makes up the images. The way electron waves (also applies to light waves) are transmitted through a crystal depends also on its crystal structure. Generally, the term high resolution imaging (by TEM) is used to refer to imaging of the lattice of the specimen under investigation, rather than to an absolute resolution.

Inelastic scattering of the electrons within the specimen will also result in the emission of X-rays, see Fig. 3.1. The X-rays can be detected by an energy dispersive detector and such measurements are called X-ray energy dispersive spectroscopy (XEDS). (Note that there are also other abbreviations used for this: EDS and EDX) Different elements give rise to different characteristic peaks in such a spectrum and elemental information can be extracted from the specimen using the detection of the X-rays. In addition, the intensity of the peaks is related to the amount of that particular element present in the sample, and the composition can thus be calculated from this type of measurements. As mentioned earlier, inelastic scattering can also lead to CL, which can also be studied in the TEM.

Scanning TEM (STEM) is a TEM mode in which the e-beam is focused into a small spot rather than the parallel beam used for HRTEM. This beam can have a dimension close to, or below, the distance between atoms in a crystal. This beam is scanned over the specimen, similar to how the e-beam is scanned in an SEM, while different signals coming from the sample can be recorded and thus be related to localized points of the specimen. STEM can for example be used to extract compositional data using XEDS measurements and localized regions can be analysed in terms of type of element and concentration. In addition, peaks in the spectra that are related to a specific element may be used to map the element in a certain region of the specimen. Further, it is also possible to record maps of different elements. By using a range of detectors it is possible to detect different signals. The detection of the transmitted electrons is referred to as bright field imaging (BF), while the detection of scattered electrons is called dark field imaging (DF). When only electrons scattered at high angles are collected it is called high angle annular dark field (HAADF).
4. Epitaxial growth

Epitaxial growth is ordered growth of crystalline material on a substrate surface. The substrate surface can be seen as a template, whose crystallographic order strongly affects the order of the material that grows on it. To model or describe epitaxial growth, the important processes that take place can be divided into those governed by kinetics and by thermodynamics. G.B. Stringfellow writes in his book “Organometallic Vapor-Phase Epitaxy; Theory and Practice”: Thermodynamics underlies the epitaxial growth process for all techniques, including MOVPE, since epitaxial growth is simply a highly controlled phase transition [49]. What is meant here is that thermodynamics describes the driving force for epitaxial growth and ultimately limits what is possible to achieve in terms of different phases and chemical compositions. Thermodynamics defines the equilibrium microstructure and composition of, for example, a solid material, when formed under a certain set of conditions. However, it is important to know the kinetic limitations at different growth conditions in order to predict the outcome of the growth and to understand the growth results. Such knowledge can also be used to control the growth by accessible growth parameters.

Kinetics defines the rates of the different processes that take place and is used to describe the reactions paths that lead to the epitaxial growth. It may also in some situations hinder the most thermodynamically stable phase or composition from being reached. For example, if the
temperature during growth is low, this may hinder or significantly slow down some important reactions and processes at the substrate surface. In this way, the phase which is most thermodynamically stable may be unreachable due to kinetic hindrance. Neglecting the reactions that are kinetically hindered, or which are too slow, by the use of a so called “hindered” equilibrium may help to get a more realistic picture of the final state of a system during or after growth [49]. Some important kinetically-controlled processes occurring during epitaxial growth include precursor decomposition kinetics and surface diffusion.

The aspects of epitaxial growth that are described and discussed in this chapter are chosen from the perspective of particle-seeded NW growth by metal-organic vapour phase epitaxy (MOVPE). For a thorough and general description of epitaxial growth, see for example [50, 51]. Further, the papers III-IV and VIII concern and discuss the crystal structure formed during particle-seeded NW growth with respect to the thermodynamic stability of these and nucleation kinetics.

4.1 Thermodynamic aspects of epitaxial growth

Epitaxial growth is, as mentioned above, a phase transition and if possible such transitions always move towards equilibrium, i.e. the lowest energy state for the system. The direction of a phase transition will thus be to reduce the energy of the system. If two phases, $\alpha$ and $\beta$, are not in equilibrium, the driving force that strives towards equilibrium (i.e. governs the phase transition) is given by the difference between the chemical potentials ($\mu$) of the two phases:

$$\Delta \mu = \mu_\alpha - \mu_\beta$$  \hspace{1cm} (1)

This difference, $\Delta \mu$, is called the supersaturation [50] and at equilibrium this is 0 (i.e. $\mu_\alpha = \mu_\beta$). The chemical potential of a phase $\alpha$, $\mu_\alpha$, is a measure of the change of the Gibbs free energy, $G$, if adding a small amount of material, $n$, to this phase at constant pressure ($P$) and temperature ($T$):

$$\mu_\alpha \equiv \left( \frac{dG}{dn} \right)_{P,T}$$  \hspace{1cm} (2)
Further, the chemical potential for a single-component ideal gas can be expressed as [50]:

$$\mu = \frac{dG}{dn} = RT \ln P$$  \hspace{1cm} (3)

where $R$ is the ideal gas constant. In most cases, epitaxial growth involves vapour and solid (condensed) phases. The supersaturation between the vapour phase and the condensed phase of a component $i$ in a gas mixture can thus be expressed as [51]:

$$\Delta \mu = \mu_v - \mu_c = RT (\ln P^i_p - \ln P^i_v) = RT \ln \frac{P^i_p}{P^i_v}$$  \hspace{1cm} (4)

Here $\mu_v$ is the chemical potential for the vapour phase and $\mu_c$ for the condensed phase, and $P^i_p$ and $P^i_v$ stand for, respectively, the actual partial pressure and the equilibrium vapour pressure of the component $i$. $P^i_p / P^i_v$ is sometimes referred to as the supersaturation ratio. When there is a continuous supply to the vapour phase and $P^i_p / P^i_v > 1$, the condensation will continue. If $P^i_p / P^i_v < 1$, the volume of the condensed phase will instead decrease because the material is vaporized, and if it is equal to 1 there is equilibrium between the phases. For phase transitions between a liquid and a solid phase, or between different solid phases, the pressures in Eq. (4) are replaced by concentrations. For a more thorough, and general, derivation of the chemical potential and the supersaturation, see for example ref. [49, 52].

To summarize, in order to determine which phase transitions that are possible from a thermodynamic point of view, one turns to the chemical potential differences between the involved phases. In addition, Eq. (4) is a very useful expression which may be used to calculate the supersaturation between different phases for a certain set of conditions. The work presented in paper III concerns how the supersaturation can be varied and how this affects the crystal structure of GaP NWs.

4.2 Kinetic aspects of epitaxial growth

In growth by MOVPE, the species to be incorporated during growth are supplied as precursor molecules. For example, the growth of GaAs is commonly performed using the precursors trimethylgallium (TMG) and arsine
(AsH₃) as sources for the Ga and As atoms. Before the atoms can be incorporated as new crystalline material on the substrate, these molecules must be decomposed or cracked by pyrolytic reactions. This means that several important reactions governed by kinetics are needed before growth can actually start. In order to break the bonds of the precursor molecules during the pyrolysis, enough heat must be provided. If the temperature is too low, the decomposition of one or more of the precursor molecules can be the rate limiting step in the overall growth. The rate of decomposition will in this case set the limit for the growth rate as the supply of growth species is limited by these reactions. Low growth temperature may also result in the incorporation of impurities as a result of incomplete precursor decomposition. One common example is the unintentional incorporation of carbon in III-V materials grown by MOVPE [49]. When the temperature is high enough, the reactions to decompose the precursors will be fast and it will be the mass transport of the precursors to the substrate surface or to the growth interface that will limit the growth rate. In this situation, the growth rate will be temperature-independent.

For a reaction governed by kinetics, such as for example the (chemical) reactions responsible for the decomposition of the precursors, the reaction rate constant \( (k) \) depends on the temperature and the activation energy \( (E^*) \) for the reaction. The activation energy for a chemical reaction (or for a physical process) is the energy barrier that needs to be overcome for the reaction/process to take place. The reaction rate constant, \( k \), is expressed by the Arrhenius equation:

\[
k = Ae^{-E^*/RT}
\]

(5)

Where \( A \) is a pre-exponential factor which depends on the type of reaction [51]. In the case of decomposition of the precursors, \( k \) will be the rate constant for molecule dissociation and \( E^* \) the energy cost associated with this.
Figure 4.1: The curve here is drawn to show schematically an Arrhenius-plot behaviour of the growth rate \( r_g \) versus growth temperature \( T \). Two types of growth regimes can be seen here: the mass-transport limited regime (yellow) and the surface-reaction limited regime (green). In the former the growth rate is temperature-independent and in the later it follows the expression of Eq.(5), increasing exponentially with increased temperature.

In Fig. 4.1 a schematically drawn Arrhenius-plot behaviour is shown, illustrating how the growth rate \( r_g \) can depend on temperature \( T \). The two different growth regimes, the mass-transport limited growth regime and the surface-reaction limited growth regime (sometimes also referred to as the kinetically limited growth regime), are also indicated in this figure (the former yellow and the later green). NWs grown by MOVPE using Au particles are commonly grown in the latter regime and thus the growth rate usually increases with temperature. As the plot is drawn in Fig. 4.1, the linear behaviour of the curve in the green region indicates that the growth rate is mainly controlled by one specific reaction or process in this temperature-interval. However, a more realistic situation during growth is perhaps when
different reactions (or steps in a reaction) limit the growth in different temperature-intervals. In that case, this type of plot would show changes in the slope of the $\ln(r_g)$ versus $T^{-1}$ curve [51]. Each change in slope would correspond to a change from one reaction (or reaction step) being rate limiting to another one.

Usually there are many reactions taking place simultaneously, and most processes involve several reactions steps and different pathways. For a series of reactions it is the slowest step that controls the overall reaction rate. When different reactions are carried out in parallel pathways, it is the slowest step in the fastest pathway that will control the overall reaction rate.

Further, to explore how complicated things can become when different reactions or processes dominate in different temperature regions I will use surface diffusion as an example. If $k$, $A$ and $E^*$ in Eq. (5) are, respectively, the surface diffusion rate constant ($k_D$), the pre-exponential factor for surface diffusion ($A_D$), and the activation energy for surface diffusion ($E^D$), the equation will describe the diffusion of the species along the surface. (Note that $E^D$ may be different for different facets and this can lead to anisotropic growth.) However, as the temperature increases the rate of desorption (or re-evaporation) will increase and this will at some temperature affect the surface diffusion by shortening the life-time of the species on the surface. In order to know how, for example, the diffusion length is affected by changes in temperature, it is therefore necessary to consider two types of temperature-regimes. First, if the temperature is sufficiently low and the species are more likely to diffuse until they are finally incorporated and buried – increasing the temperature will increase the diffusion length exponentially (called the burial regime [51]). The life-time (i.e. average life time) is in this case given by [51]:

$$\tau_b = \frac{n_{ads}}{J_{dep}}$$

Here $n_{ads}$ is the number of adsorption sites per area unit and $J_{dep}$ the deposition flux of species per area unit and second. The average life-time here is then the average time the species can spend diffusing along the surface to find their most energetically favourable sites before being incorporated and becoming “un-mobile” (buried). The mean distance the species diffuse before being incorporated, the diffusion length ($A$), is then given by [51]:

- 58 -
\[ \Lambda = a \sqrt{k_D \tau_b} = a \sqrt{\tau_b A_D e^{-E_D/RT}} = a \sqrt{\tau_b A_D e^{-E_D/2RT}} \]  \hspace{1cm} (7)

where \( a \) is the distance between sites on the surface and \( k_D \) is the surface diffusion rate discussed above. In this case, as was mentioned above, increasing the temperature will increase the diffusion length exponentially.

Secondly, in an interval where the temperature is sufficiently high for the desorption process to be faster than the burial process (i.e. the rate of re-evaporation is significant), the diffusion length will instead decrease exponentially with increased temperature (called the desorption regime [51]). Here the average life-time of the species on the surface is limited by the process of re-evaporation. In this situation the life-time is instead given by the reciprocal of the reaction rate of desorption:

\[ \tau_{des} = \frac{1}{k_{des}} = \frac{1}{A_{des}} e^{E_{des}/RT} \]  \hspace{1cm} (8)

The diffusion length in this regime is thus expressed as [51]:

\[ \Lambda = a \sqrt{k_D \tau_{des}} = a \sqrt{\frac{A_D}{A_{des}} e^{(E_{des} - E_D)/2RT}} \]  \hspace{1cm} (9)

The activation energy for desorption is always greater than the one for diffusion \( (E_{des} > E_D) \) and in this regime the diffusion length will therefore decrease exponentially with increased temperature. The NWs studied in this work have in general been grown at low temperatures, where the re-evaporation is not significant, and so the diffusion length should in general increase with increased growth temperature.

4.3 Metal-Organic Vapour Phase Epitaxy

There are three major epitaxial techniques that are used for the growth of III-V NWs: metal-organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE). CBE is, however, much less used than the other two. MOVPE has the advantage of being a very flexible technique in terms of type of materials that can be grown, and for epitaxial growth in general it is considered more suitable for large-scale production [49]. As mentioned earlier, the structures that are studied and discussed in this work
were grown using solely MOVPE and so this technique is the focus here; descriptions of other techniques are beyond the scope of this thesis. The interested reader may find references [53] and [54] useful regarding growth by, respectively, MBE and CBE. Also, in ref. [49] (which focuses on MOVPE) the above mentioned epitaxial techniques, as well as others, are briefly explained and compared.

### 4.3.1 The basic operation of an MOVPE reactor

In this section I will go through the basic principles for the operation of an MOVPE reactor, using the overall set-up that is illustrated in Fig. 4.2.

The source material is supplied as metalorganic and hydride precursors in a flow of an inert and ultra-pure carrier gas, in our case H₂. The metalorganic-sources for the group III species are most often liquid; a few, such as trimethylindium (TMI), are solid. The containers for the metalorganics, also called bubblers, are kept in temperature-controlled baths. An inert gas is transported in a thin pipe and released below the liquid level, thereby forming bubbles within the metalorganic-liquid. The saturated vapour-pressure of the metalorganic and the total pressure of the bubbler are thus preserved within the container while some of the metalorganic-vapour and carrier-gas mixture is transported away through the pipes during growth. Electronic-pressure-controllers (EPC), situated on the pipe leading from the bubbler, measure and control the pressure in the bubblers. Mass-flow-controllers (MFC) adjust the flows in the different pipes to set-point values. The group V sources are most often hydrides and thus gaseous sources which are kept in gas bottles. These are, when the proper valves are open (red valve), released into the pipes leading to the reactor cell (pink valve open = to run line) or to the exhaust (green valve = vent line) by the pressure difference of the hydride gas bottles and the pressure in the pipes. During growth, the red valves for the sources to be used are open. The precursors are sent to either the run-line (pink valves open), leading to the reactor-cell, or the vent-line (green valves open).

Commonly, the pipes are prepared by opening the sources that are to be used before actually starting the growth, sending the flows from the different sources to the vent-lin. In this way, there is some time preserved for the flows to adjust to their set-point values and the lines to be filled. When a
Figure 4.2: The overall principle of the set-up of an MOVPE machine. The valves are colour coded in the following way: red valves are open when the source is to be used and blue are closed, and vice versa when the source is not to be used. When a pink valve is open, the corresponding green valve is closed and the flow is sent to the run line. In the opposite situation, the flow is by-passed the reactor and sent to the exhaust through the vent line.

source is to be used during the growth, the flow is then redirected from the vent-line to the run-line.

The substrate is situated on the susceptor inside the reactor cell when the machine is in operation. The susceptor is heated using a radio-frequency coil or infra-red lamps, or by resistive heating. At a certain temperature, if the sources are directed into the reaction cell, the precursor molecules will decompose at the substrate surface and epitaxial growth will take place. The residual vapours and the rest products from the chemical reactions taking place are pumped out through the exhaust line. Here the residual vapours and gases are either burned or filtered away.
MOVPE is carried out in the pressure range from atmospheric pressure (1013 mbar) down to a few tens of mbar. When MOVPE is performed at pressures below atmospheric pressure it is called low-pressure MOVPE (LP-MOVPE). The growth carried out in this work was performed using LP-MOVPE, at a pressure of 100 mbar.

4.4 MOVPE growth of III-V semiconductor nanowires from gold-particles

Growth of one-dimensional rods or wires, also called whiskers, using seed-particles has been carried out for over a half century [55, 56]. Au as particle-material clearly dominates the field of particle-seeded NW growth. NWs from a wide variety of materials and growth conditions have been realized using Au particles. Messing et al [57] discuss this in a recent review paper, in which the focus is partly to understand why Au in particular has been so successful. The authors suggest that it is a collection of beneficial properties of Au, rather than one specific property, that makes this material advantageous for seed-particles. This thesis is mainly focused on growth from size-selected Au aerosol-particles generated by an evaporation/condensation method [58]. However, Au seed-particles can also be defined and fabricated using other methods, for example by electron beam lithography (EBL), from the annealing of a thin Au film deposited onto the substrate and it is also possible to buy commercial fabricated Au colloids dispersed in an aqueous solution. These and more fabrication and deposition methods for Au particles are discussed and briefly described in ref. [57]. Further, in paper V the results from a study focusing on the influence of Au seed-particle preparation method on GaAs NWs grown by MOVPE are presented and discussed. Below it is described how NWs have been grown using MOVPE and Au aerosol seed-particles in this work. For a thorough review of seed-particle NW growth, see [55].

First, the Au seed-particles are deposited onto a substrate surface (Fig. 4.3 a)). In most cases, the substrate is of the same material as the NWs that are to be grown and the substrate surface is (111)B. Other surface orientations may also be used, as will be discussed later on. The substrate with the deposited Au particles is then placed onto the susceptor in the reactor cell of the MOVPE machine (see section 4.3.1.). The substrate is then usually annealed for a period of time at a temperature around 600-650°C in order to
Figure 4.3: a) Au particles are deposited onto a substrate surface. b) This illustrates how a substrate orientation of (111)B results in vertically grown NWs while c) show how the NWs grown from (001) substrate surfaces still usually grow in an <111> direction and thus grow with an angle of around 35° with respect to the surface plane. By changing the sources during growth, axial heterostructures as in d) can be grown. e) and f) show, respectively, how a change in growth condition (increased temperature) gives the possibility to grow radial heterostructured NWs or even embed the NWs to facilitate XSTM investigations.

remove the surface oxide. In some cases, the substrate is brought up directly to the desired growth temperature, which is usually somewhere around 400-500°C, without any pre-growth annealing. The influence of the pre-growth annealing was one of the things studied in the work presented in paper V.

For III-V semiconductor materials, increasing the temperature easily desorbs the material due to the high vapour pressure of the group V species, which are volatile at the temperatures usually used for growth of NWs. A flow of the group V species is therefore provided to the reactor cell when the temperature is increased and then maintained until growth is finished and the temperature has been decreased to around 300°C.

To nucleate (i.e. to start) the growth of the NWs, the flow from the group III source is directed to the run line (see Fig.4.2 and section 4.3.1). Now, when both group V and group III species are available in the reactor cell, and the temperature is sufficient, NW growth is nucleated at the interface between the seed-particle and the semiconductor surface. Growth is favoured at this interface and will proceed much faster here then elsewhere on the
substrate surface. More about the mechanisms of NW growth and why growth is favoured underneath the seed-particle is discussed in a separate section (see section 4.4.3).

The NWs usually grow in an $<111>$B direction, resulting in vertical NWs in the case of an (111)B oriented substrate (see Fig. 4.3 b)). The $<111>$B growth direction has been shown to be the most favoured one, almost irrespectively of the substrate surface orientation. For example, in the case of growth from a $<001>$ oriented substrate, as in papers I and II, the NWs still grow preferentially in a $<111>$B oriented direction. This means that the NWs grow in an angle of $35.3^\circ$ from the substrate surface plane, as illustrated in Fig. 4.3 c). As is discussed in the paper by B. Wacaser et al [59], the lowest energy interface between the semiconductor material and the Au particle for the NWs should be the $\{111\}$ surfaces. This may be understood by looking at which surface plane or planes of ZB and WZ structures that correspond to the least number of broken bonds. That is, one must look at which surface plane or planes of these crystal structures that can be created from bulk by cutting the least number of bonds. In addition, the top part of the semiconductor material of the NW, which is in contact with the seed-particle, is usually a $\{111\}$B oriented surface (at least from what has been observed post-growth). Furthermore, even in the case of NW grown from a (111)A oriented surface, there is still a significant proportion of the NWs that grow in a $<111>$B direction [60]. It should be noted that chemical surface pre-treatment, pre-growth annealing conditions (or the exclusion of an pre-growth annealing step) and material combination between the NW and substrate materials have been observed to influence the favoured growth direction. See for example a recent review by Fortuna and Li [61] which focuses on the control of growth directions for particle-seeded growth.

As the NWs are grown, new surfaces are formed: the surfaces of the NWs themselves. Some growth on the NW side-facet surfaces (radial growth) usually takes place, although growth in the axial direction (underneath the Au particle) of the NWs is in general much faster. The growth on the NW sides commonly results in a slightly tapered shape instead of a uniform rod-like shape, i.e. the bottom of the NWs becomes wider than its top part. If this growth is significant, it can even give a really pronounced tapered shape of the NWs.
In most cases the growth rate on the NW sides, as well as on the substrate surface, is increased at higher temperatures. It is thereby possible to increase the temperature and thus intentionally induce a faster growth onto the substrate and NW surfaces. In this way radial heterostructures (also called core-shell heterostructured NWs) can be grown, see Fig 4.3 e). Such NW structures were grown and studied in paper VI and paper VII, and growth of heterostructured NWs will be discussed in the following section. It is feasible to embed larger parts of the NWs by growing a thicker layer onto the substrate surface, see Fig 4.3 f). A scheme to embedded large parts of the NWs can be used to enable XSTM measurements of the interior of NW-structures [39, 62]. As mentioned earlier, results from this type of measurements are presented in papers I-II (see also Appendix A1).

4.4.1 Growth of heterostructured nanowires

Axial heterostructured NWs, which are heterostructures formed along the NW length (see Fig. 4.3 d)), can be grown by changing the type of III and V sources supplied to the reactor cell during growth. Further, as mentioned in the previous section it is possible to increase the growth rate on the NW sides and substrate surface by increasing the growth temperature, and in this way realize radial/core-shell heterostructured NWs (see Fig. 4.3. e)) [63-65]. However, both types of heterostructures are complicated by the coupling between radial and axial growth, and it is in generally problematic to find conditions under which solely axial or radial growth takes place. This is an important point addressed in paper VII. Although for example changes in the growth temperature are useful to enhance/suppress strongly either radial- (higher temperature) or axial- (lower temperature) growth, it could be that it is actually impossible to find the right conditions in order to grow solely on the NW sides or solely axially underneath the seed-particle for most III-V semiconductor materials [66].

An important part of fabricating heterostructures in general is to be able to make abrupt interfaces. Since it is known that at least the group III material is incorporated into the seed-particle during NW growth, when the source is turned off there can be a memory effect due to the material still stored in the particle in growth of axial heterostructured NWs. In paper I it is discussed how the material stored in the particle can continue to incorporate into the NW after the source is turned off, thereby forming unsharp interfaces
in axial heterostructured NWs. It is, however, possible to limit this effect by including a pause for a period of time inbetween the growth of the different materials [67]. During this time most of the stored material should “flush” out from the seed-particle as the NW continues to grow from the material stored in the seed-particle. However, abrupt interfaces in heterostructured NWs have been reported to be limited by another effect also, which also relates to the involvement of a seed-particle. In the work by Dick et al [67], different IV and III-V materials were combined in axial heterostructured NWs and the resulting NW-morphology was studied. It was found and explained how some combinations lead to kinked NWs while some lead to perfectly straight NWs. They observed that although one material, A, could be grown on another material, B, to give straight NWs, the combination B on A would not give the same morphology. Thus the order in which the material was grown axially influenced whether the NW grew to be straight or not. In addition, their study showed that unlike to thin film heterostructures, there was not a direct connection between a large (or in some cases any) lattice mismatch between the two materials and whether they grow straight or kink. For further explanation, see ref. [67] and the more or less simultaneously appearing report by Paladugu et al [68].

Further, radial heterostructures can suffer from problems related to inhomogeneous composition or thickness of the shell. As was shown in paper I, irregularities in the crystal structure of the NWs can result in an inhomogeneous thickness. It is known that for example twinning of the crystal structure (see chapter 2) results in a microfacetted NW morphology [69, 70]. When a new material is to be grown onto such NW side surfaces, the microfacetted morphology is smoothed out and, for sufficient radial growth, replaced by nearly flat NW side facets. This gives so called side-pockets of the shell material in the cavities that have formed in the twinned NW core (see figure 5 in paper I).

For binary III-V materials, the shell should in principle be homogeneous in terms of composition. However, for ternary shells there might be significant gradients or fluctuations in the shell composition due to the non-planar shape of the NW side facets [71]. In addition, the diffusion lengths are usually different for different atom species (and molecules). This can result in a variation of the shell composition along the NW length as the incorporation of
one or more of the species is influenced (or even limited) by the diffusion of atoms or molecules from the substrate surface.

4.4.2 MOVPE growth at low temperatures

NWs are grown at low temperatures compared to the temperatures used for conventional layer growth by MOVPE. For example, GaAs NWs are usually grown somewhere around 400-500 °C whereas layer growth of GaAs is typically performed in the temperature regime around 600-650 °C [49]. The decomposition of the precursors is strongly dependent on the temperature, especially in the temperature range usually used for NW growth. It has been shown in pyrolysis experiments that the decomposition of the precursors can be greatly enhanced when both hydride and metalorganic precursor molecules are present simultaneously. This has been shown for trimethylindium (TMI) + phosphine (PH₃) [72] and trimethylgallium (TMG) + arsine (AsH₃) [73], indicating that this is probably also the case for other combinations of these precursors as well as other similar metalorganics, for example trimethylaluminium (TMA), in combination with either of the above mentioned hydrides. In addition, in the same studies it was shown that the substrate surface strongly influences the amount of decomposed species (linear dependence on substrate surface area) which lead to the conclusion that at low temperature the pyrolysis is mainly heterogeneous (i.e. the decomposition takes place at the surface). In both of these studies, it was found that the two hydrides start to decompose at significantly lower temperatures in the presence of the metalorganic molecules. The PH₃ was found to start to decompose at around 175°C, which is over 200°C lower than when it decomposes alone (400°C) [49, 72]. Similarly, for AsH₃ the decomposition was found to start at a temperature of roughly 100°C lower, at around 300°C, compared to decomposition alone [49, 73]. Also the metalorganics were found to start to decompose at lower temperatures. The temperature of TMI was found to be 50°C lower when combined with PH₃ and roughly the same was found for TMG in the presence of AsH₃. The decomposition of TMG was found to be complete at around 430°C when combined with AsH₃ and for the unmixed situation it has been found to be around 500°C.

These results clearly show that the decomposition of the metalorganic and the hydride molecules are probably strongly connected also during NW growth, which indeed is usually performed at low temperatures. It
is however necessary to take into account that the situation of growth by MOVPE differs from the one in the experimental set up used in pyrolysis experiments. For example, the temperature readings are most likely not directly transferable between a pyrolysis experiment and a growth done by MOVPE. It has been found that when comparing the two situations that the pyrolysis studies are shifted to lower temperatures [49]. The temperature needed during MOVPE growth to reach similar decomposition efficiency as found from pyrolysis experiments is therefore probably significantly higher.

A very important conclusion from the studies in ref. [72] and [73] is that at low temperatures, because the decomposition of the hydride and the metalorganic are characterized by a joint pyrolysis reactions, the actual V/III ratio of the decomposed species is unity. This means that increasing either the V or the III molar flow/supply will not change the true V/III ratio – it can only increase the amount of both. Normally, the nominal input V/III ratio is larger than 1 (group V precursor is in excess) during MOVPE growth of III-V materials. At low temperatures, increasing the molar flow of the group V precursor will not change much but increasing the group III would lead to more III AND V molecules being decomposed and thus increase the growth rate. However, the V/III ratio of the decomposed species would not change. It should be noted that in this reasoning, low temperature implies a temperature lower than the temperature at which the decomposition of the precursors alone (without being mixed with the other type) is significant.

Increasing towards the temperature at which one of them can be decomposed without the assistance of the other leads to a complicated situation. Then, it needs to be considered whether these molecules are likely to decompose by themselves before having the chance to assist the decomposition of the other type. The surface coverage of adsorbed molecules of each species and their diffusion on the surface can then strongly influence the rate of decomposition of both types of precursors. In practice, the metalorganics usually start to decompose at a lower temperature than the hydrides when unmixed. Therefore, reaching the temperatures at which the decomposition is significant for the metalorganics alone the efficiency of the decomposition of the hydrides could in principle actually go down for some growth conditions.

The discussion given above is intended to show that the input parameters during growth by MOVPE, especially at the low temperatures
usually used for NW growth, don’t necessarily describe the actual situation at the growth interface at the substrate surface (at least not in a straightforward way). Thus, to understand how and why changes in the molar flows and the temperature influence the resulting growth is not completely straightforward. It should also be pointed out that the substrate surface itself influences the reactions taking place, including the decomposition and the diffusion of both the precursor molecules and the decomposed species. This means that the detailed arrangement of the atoms in the surface, which may vary with parameters such as temperature, pressure and partial pressure of different species present, can influence the growth in a non intuitive way.

4.4.3 Describing the particle-seeded growth mechanism

The first model to describe the growth mechanism using seed-particles was proposed in the mid 60s by Wagner and Ellis [56]. At that time the wires had diameters in the range of micrometers. This first model, the vapour-liquid-solid (VLS) model, describes the anisotropic growth behaviour in the formation of wires by the use of a liquid impurity alloy droplet. The droplet is thought to act as a preferred site or a sink for deposition of material from the vapour, which thereby causes the droplet to become supersaturated with the material supplied as a vapour. Growth is then explained to take place as the material, entering from the vapour, precipitates at the interface between the alloy droplet and the solid substrate. As this model was further developed and discussed, it became more pronounced that the liquid alloy was considered to be acting as a catalyst for the chemical processes taking place [55].

Today the VLS model is still used to explain growth of NWs but it has also become clear that it fails to describe all situations of growth of NWs using seed-particles. Many experimental results do not fit with this model, and additional models have been proposed to explain the situation where the VLS model fails. For example, growth of NWs has also been shown with a solid seed-particle (vapour-solid-solid model proposed by Persson et al [74]) and different experimental results have shown both that the seed-particle/droplet does or does not act as a catalyst for the growth in different situations [55]. However, there are some things that seem to be general in the growth of wires from a seed-particle: the seed-particle forms an alloy with at least one of the material species that the growing wire is composed of, and the particle-wire interface is a preferential area for the material to precipitate.
There are more recent models which explain the growth mechanisms by a preferred nucleation at the interface beneath the seed-particle/droplet (see [59] and references within). This approach does not depend on the phase of the particle/droplet, nor does it rely on the seed-particle/droplet working as a catalyst, which is probably not true for all situations of particle/droplet seeded NW growth [55, 75]. Such an approach is promising also for describing the formation of twins and the wurtzite phase in NWs of materials that are commonly arranged according to the ZB phase in bulk. In this approach the anisotropic growth of the NWs is thus explained from a preferred nucleation at the seed-particle/droplet-NW interfaces, and a kinetical hindrance of nucleation and growth on the substrate and NW side surfaces at the lower temperatures typically used for NW growth. Wacaser et al [59] suggest the term preferential interface nucleation (PIN) for this mechanism.

Recently, focus has been on explaining and understanding the crystal phase or phases formed during particle-seeded NW growth, not so much on general growth mechanisms. Still, several questions remain to be answered and a complete understanding of seed-particle growth mechanisms does not exist. For example, what is the composition of the seed-particle during growth and which species are actually present in the particle during growth.
5. Outlook

Today it is in principle impossible to keep track of everything reported about III-V NWs. In recent years, this research area has been very active and successful. Much focus has been on controlling the crystal structure within the NWs. Most recent advancement in engineering the crystal phases within single NWs is promising and I believe this will be a hot topic in the coming years. The results presented in paper IX clearly show that techniques involving supply interruptions during particle-seeded NW growth have great prospects for engineering polytypic NWs. I suggest that significant efforts are put into investigating the applicability of using the same approach for other III-V materials. This paper is not the first work in which this type of technique has been employed, but I believe the presented results are among the most promising so far. It will most likely lead more research groups to continue in the same direction.

More investigations are needed in order to understand why the crystal structure of NWs changes with different conditions during growth. It is known that the local supersaturation in the seed-particle probably influences this in many cases, but it may also be the case that the surface reconstruction of the NW side-facets is highly important. In addition, much is still unknown about the state and composition of the seed-particle during growth. Previously, it has been assumed that only the group III species are dissolved in the seed-particle, but it is actually not known if the group V species are present in the particle or not. Recently this possibility has been discussed more [76-78], and I think it is important to investigate this thoroughly in order to understand the particle-seeded NW growth mechanisms.
I have consequently used the term “seed-particle” in this thesis, which may suggest that the seed-particle is solid during NW growth. As mentioned earlier, in section 4.4.3, it is not completely clear whether the particle is solid or if it is a liquid droplet during NW growth, and most likely it is liquid in some situations and in other it is solid. Both the state and the composition of the particle (or liquid droplet) during NW growth is still very much unknown. In order to evolve more detailed models of NW growth and to fully understand the growth mechanisms, it may turn out to be necessary to investigate the phase and the composition of the particle at different growth conditions carefully.

It is necessary to perform more investigations on how twin planes, stacking faults and the phase of the crystal structure influence the properties of the NWs. I expect that the great advances in controlling the crystal phases and twin plane density which have been made lately will lead to very many such investigations the coming years. However, it is possible that the results are not completely straightforward to interpret. It could be that it is complicated to separate between the influence of the morphology/side-facets of the NWs and the influence of their crystal structure. The side-facets of the NWs depend on their crystal structure and these will not be the same on NWs (or parts of a NW) that is of the ZB phase as on NWs of the WZ phase (see paper IV). Because the surface-to-volume ratio of NWs is large, most of their properties are probably highly influenced by their surface.

I believe that with the increased control of making polytypic NWs it will be important to find the answer to the question posed in the end of chapter 2: How many layers must be stacked according to one specific crystal phase before it becomes reasonable to assume that this volume of material has identical, or close to identical, energy band structure as when the stacking sequence continues infinitively?

It is difficult to de-couple axial and radial growth for particle-seeded NWs and I do not know if it is possible to completely solve this issue. An interesting approach is to remove unintentional radial growth by some type of in situ etching during growth [66]. It is likely rather important to investigate this approach further. Unintentional overgrowth can be a severe problem, in particular since the overgrowth depends on the surface orientation of the side-facets. I believe this can complicate the interpretation of many types of
measurements performed on NWs. The growth rate is different on different surface orientations and this causes diameter variations along polytypic NWs. In addition, differences in the surface orientation on the NW side-facets may also lead to compositional variations in the growth of ternary materials and may influence, for example, the incorporation of carbon in the case of binary III-V NWs. Especially for heterostructured particle-seeded NWs it is necessary to investigate thoroughly how to de-couple between the axial and the radial growth.
Appendix

A1 XSTM investigations of embedded nanowire structures

Here I will first briefly describe the growth scheme used in papers I and II to embed NW structures. I will then also describe the method which was used to cleave the samples and how one may proceed to find the interior of the NWs within the cleaved surface.

A1.1 The embedding of the nanowire structures

First, the NW structures to be studied are grown from Au aerosols on an (001) substrate surface (see Fig. A.1a), b) and section 4.4). The NWs will grow in <111>B directions and they will therefore not grow perpendicular to the substrate surface as in the case of (111)B oriented substrates (see Fig. A.1b). Here they will instead be grown at an angle of 35.3° from the substrate surface.

After the NWs are grown, the group III source is turned off while group V is kept. The temperature is then increased from NW growth temperature (~450°C) to 630°C. When the temperature is stabilized, both TMG and TMA are switched on. The NWs will then continue to grow axially but at this temperature the growth on the NW sides and the substrate surface will also be significant, see Fig. A.1c) and the discussion in section 4.4.1. An AlGaAs shell will form on the NW cores and an AlGaAs layer will form on the substrate surface. The growth of the AlGaAs is then interrupted by switching of the TMA while keeping TMG and AsH₃. Growth on the NW sides and on the substrate surface is then continued for a sufficient time to allow for a thick GaAs embedding of roughly some μm to be realized, see Fig. A.1d).
Figure A.1: This schematically illustrates how the NWs are grown and then embedded by a combination of AlGaAs and GaAs to facilitate XSTM investigations, as in the work presented in paper I and II. The NWs are grown from aerosol Au particles from an (001) substrate surface and in \textless111\textgreater B directions.

A1.2 XSTM investigations of NWs – how to cleave and how to locate the NWs in the exposed surface

A small notch was done on each sample, as seen in Fig. A.2. Here it is also indicated how a small force is gently applied on the sample surface to cleave the sample along the direction of the notch. The cleaving of the samples was done when the sample had been mounted on a sample holder and put inside the protected environment of the UHV system.

The procedure of locating the NWs with help of the AlGaAs material as a marker is described in the steps below:
**Step 1**: The STM tip is placed in close proximity to the edge on the part of the sample where the epitaxial growth has taken place (position A in Fig. A.3c)). This can be done with the help of an optical microscopy.

**Step 2**: The tip is then moved towards the edge of the sample surface (direction of arrow at position A) until the tunnelling current between tip and sample drops to zero. In this way, the edge is found by observing when the tip-sample separation changes dramatically as the tip reaches and crosses the edge of the sample.

**Step 3**: It is possible to get a good approximation on how thick the embedding layer is (Δx in Fig. A.3c)) from the different growth parameters used to fabricate the structures. This, together with the knowledge of the edge position found in step 2, is used to place the tip above the cleaved surface plane of the substrate close to where the grown structure is believed to begin (position C in Fig. A.3c)).

**Step 4**: Next step is to find the interface between the substrate and the grown layers (interface B in Fig. A.3c)). While scanning with sufficient resolution to distinguish between layers of AlGaAs and GaAs material, the AlGaAs/GaAs

*Figure A.2: a) A specific cleavage plane can be induced by making a small notch with a diamond scriber. By carefully pushing on one part of such a sample (red arrow), while the other part is firmly attached into a special cross-section sample-holder, the sample can be cleaved inside the protected environment of the UHV system. A buried (or embedded) structure, as illustrated by the orange area in b), becomes in this way accessible for STM investigations.*
Figure A.3: In a) and b) it is illustrated how the notch and the cleavage of the samples were done to reveal a cross-section along the NWs. The steps in the text and c), explain the procedure we use to locate the cross-sections of the NWs. Following this procedure, the GaAs-"holes" in the AlGaAs-marker layer can be found. This is seen on the computer screen in d). This is a part of the interior or cross-section of a NW, surrounded by AlGaAs. In this STM image the NW growth direction is pointing downwards and the cleavage plane is (110).

interface can be identified as the tip is moved towards the edge (direction of arrow at position C). When the AlGaAs/GaAs interface has been located the next step is to find the NWs.

**Step 5** : There are GaAs-"holes" in the AlGaAs layer that can be found. By scanning along the interface (see arrows at the position B in Fig. A.3c)), these GaAs-"holes" in the AlGaAs can be located. An example of this is shown on the "computer screen" in Fig. A.3d). At such a position, a GaAs NW has been
cleaved and the STM image shows the interior of the “root” of the NW surrounded by the AlGaAs capping material.

**Step 6**: When the “root” or beginning of the NW is found, the interior of this single semiconductor NW can be imaged and explored on the atomic scale.

**A2 XSTM imaging of the cleaved (110) GaAs surface**

The surface structure of a crystal may be different compared to the structure of the same plane in the bulk of the crystal. It can also be different depending on the conditions under which the surface was created and how it was created (if it was cleaved or epitaxially grown etc.). Annealing and the conditions during the annealing can also affect the surface dramatically. In this thesis, the main surface for the investigations has been the cleaved (110) GaAs surface, illustrated in Fig. A.4. It has been found that this surface retain the same periodicity as the bulk structure but has an inward (outward) relaxation of the cations (anions), as illustrated in Fig. A.4b) [45]. This surface has been intensively studied by STM since the beginning of the technique and it was actually the very first cleaved surface to be studied by STM [46]. Since 1987, when Feenstra et al published the first STM images for both positive and

![Figure A.4: A top view of the (110) GaAs surface is shown in a). b) shows a side view of the surface and illustrates the inward and outward relaxations of the Ga the As surface atoms respectively. (The larger Ga and As atoms are the surface atoms.)](image)
negative sample bias, it has been well established that the apparent atomic positions of the As atoms are imaged at negative sample bias and the Ga atoms at positive sample bias \[47\]. This is attributed to the difference in electron negativity between the Ga and the As atoms, as discussed in section 3.1.2. As the surface relaxes, the electrons in the dangling bonds of the Ga atoms are transferred to the As atoms.
A3  “Supplementary Information” to paper VII

Below is the “Supplementary Information” that is connected to paper VII included. However, some minor changes have been made in the formatting of the text and the figures. (Not that the references to this are included separately, in the end of A3.)

Supplementary information for “Diffusion length measurements in axial and radial heterostructured nanowires using cathodoluminescence”

Jessica Bolinsson, Kilian Mergenthaler, Lars Samuelson and Anders Gustafsson

S1 The principle of our measurements:

In this work, we have used cathodoluminescence imaging in a scanning electron microscope (SEM) to study the ambipolar diffusion length in nanowires (NWs) (see also ref. [1]). The approach we use is quite simple and illustrated in Fig. S1. It relies on the fact that the NWs to be studied have a segment with a lower bandgap than the main core, see the schematic illustration in Fig. S1a). By detecting the emission from the segment, it is possible to study the diffusion of the generated carriers from the higher-bandgap material parts of the NW core (green areas in Fig. S1) into the segment. It is important to point out that the segment acts as a “detector” for the diffusion. As the electron beam is moved along the NW core towards the segment, the intensity of the segment emission increases. This is because the distance that the generated carriers have to diffuse before they can recombine in the segment becomes shorter.

There is one general prerequisite for determining the diffusion length using CL measurements that is not often discussed. The emission from the local radiation center should have a near linear dependence on the excitation density. Anything else can result in a misinterpretation of the diffusion profiles. It is also important that the emission from the local radiation center does not saturate with increasing excitation density, as this would also affect the apparent shape of the diffusion profiles. It is therefore essential to keep the excitation low (a low probe current) in the measurements. Most of our structures show a near linear increase in the intensity with probe current.
and we have used 100-500nm long segments. We have observed that shorter segments, which show quantum dot behavior, have non-linear and saturation behavior and these have therefore not been used in this work [2]. In addition, any compositional gradients or electric fields in connection with the segments have to be negligible or at least on a shorter length scale than the measured diffusion lengths in these type of measurements. Otherwise the measured diffusion lengths may be influenced. We believe that the compositional variation near or in the segments in our measurements will not generate any significant gradients or electric fields as the In content in the InGaAs segment (or any possible Al gradient in or near the GaAs segment) is rather small.

Further, in our measurements we determine the diffusion lengths only from the excitation of charge carriers in regions of the NWs far

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**Fig. S1.** Here we schematically illustrate the experimental method we used in this work. 

a) a NW containing an axial heterostructure with a short segment of a lower-bandgap material “sandwiched” between a higher-bandgap material. 

b) the corresponding band structure along the NW. When the local excitation of the electron beam is moved towards the segment, the emission will increase due to the one-dimensional diffusion along the NW core.
enough away from the segments and thus we estimate that any effect from an electrical field is not influencing our measurements significantly.

Finally, it is important to know the background level in the measurements in order to make a proper exponential fit. In our measurements, the signal is zero outside the NWs and the black level in our images is the true zero level.

**S2 CL spectra for AlGaAs capped GaAs nanowires with an InGaAs segment:**

Fig. S2 shows a typical spectrum of the single NW used for the imaging in Fig. 3 in the paper. This is a GaAs NW with an InGaAs segment, capped with AlGaAs. The spectrum was recorded by scanning the beam over the NW. There are three main peaks. The emission from the GaAs core is centered at 1.48eV, the InGaAs segment at 1.42eV and finally the radial (InGaAs) quantum well (RQW) at 1.36eV. The 1.36eV area may not reflect the actual

![Typical spectrum from a single NW with a heterostructured (GaAs/InGaAs/GaAs) core, capped by an AlGaAs shell. The red line indicates the spectral resolution.](image-url)
peak of the emission, as the sensitivity of the detector used for this study drops in the region 1.33 to 1.40 eV. We strongly suspect that the actual emission peak is at an even lower energy.

When recording the emission from corresponding uncapped NWs, only the InGaAs segment emission is visible. The spectrum in Fig. S2 is an average spectrum of one NW with the beam scanning over the area of the NW. The energies of the images in Fig. 3 were chosen by varying the detection energy to obtain the highest local emission intensity in the various segments in the monochromatic images. The spectra were recorded with the beam scanning over an area containing one single NW. Because the single NWs covers less than 5% of the total scanned area, the signal-to-noise ratio is small in these measurements and thus the spectra are noisy. The area covered by the various segments is even less.

Fig. S3. Local area (1x1 μm²) spectra from a GaAs NW containing a GaInAs segment. The base (red) is dominated by the RQW emission, the middle (green) is dominated by the segment emission and the top shows only GaAs emission.
In order to show that the three emission peaks in Fig. S2 really come from different parts of the NWs, we recorded some local spectra from the top, base and the segment areas of a single NW. This was done by scanning the beam over a 1x1 μm² area of the NW. This is shown in Fig. S3 for a different NW coming from the same sample as the one in Fig. S2. The spectra shows that one peak dominates the emission in each area, confirming the results from the monochromatic imaging shown in Fig. 3 in the paper.

S3 Unintentional growth of a GaAs shell on the AlGaAs NW core:

Switching from growth of an AlGaAs core to a GaAs segment leads to the unintentional growth of a GaAs shell on the AlGaAs part on the core. As is discussed in the paper, this thin GaAs shell can be seen as a GaAs radial quantum well (RQW). Because GaAs is a binary compound, the segment and the RQW will have the same composition and the main difference in emission energy will be the quantization of the RQW. This means that there is a significant possibility that the emission from the two areas will overlap in energy. Fig. S4 shows an SEM image of NWs transferred to a non-emitting substrate and two corresponding CL images at two different energies: (b) recorded at 1.488eV and (c) at 1.518eV. The images illustrate two points. i) the emission from the segment and the RQW can be observed in both images. ii) as the detection energy is raised, the intensity from the base of the NW is increased and the intensity from the segment is decreased. (b) is recorded at the typical emission energy of our GaAs NWs. The spectral resolution in combination with relatively broad emission means that there is an overlap between the emissions from the two areas in the CL images.
References (for “Supplementary Information”)


References


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It has been great to be able to work closely with such an excellent CL expert as my supervisor Anders Gustafsson, you know the spectra for almost all GaAs/AlGaAs nanowires ever grown in Lund. Your broad and deep knowledge in physics has been highly valuable for a PhD student as me, especially since it also comes with a lot of patience and pedagogical skills.

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