InAs-InP Core-Shell Nanowires
Epitaxial Growth and Characterization

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Abstract
In this thesis investigations concerning the epitaxial growth and characterization of InAs-InP core-shell nanowire heterostructures are presented. These nanowires have a potential use as the conductive channels in a novel high mobility vertical transistor design, fabricated at Lund University’s department of Solid State Physics. The InAs nanowires as well as the InP shell are epitaxially grown in a Metal-Organic Vapor Phase Epitaxy (MOVPE) system where thickness control on the atomic scale is possible. Characterization of the nanowires is carried out with both a Scanning Electron Microscope (SEM) and an analytical Transmission Electron Microscope (TEM). In order to complement TEM investigations a model describing an X-ray Energy Dispersive Spectroscopy (XEDS) linescan is derived for the grown structure.

The results of the growth investigation show that the total reactor pressure of the MOVPE system has an important influence on shell-coverage and morphology. It is further demonstrated that it is possible to grow thin shells, with a thickness of 2-3 nm, without forming visible interface defects. The shell growth mechanism depends on the diffusion length of the adatoms, primarily controlled by substrate temperature. Evaluation with the derived XEDS model shows excellent correspondence with experimental data, confirming the grown structure.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AsH$_3$</td>
<td>Arsine, precursor for Arsenic</td>
</tr>
<tr>
<td>BF</td>
<td>Bright Field, a detection technique used in STEM</td>
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<tr>
<td>CBE</td>
<td>Chemical Beam Epitaxy, an epitaxial technique</td>
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<td>C-V</td>
<td>Capacitance-Voltage</td>
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<td>EBL</td>
<td>Electron Beam Lithography</td>
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<td>EELS</td>
<td>Electron Energy Loss Spectroscopy, an analytical TEM tool</td>
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<tr>
<td>FEG</td>
<td>Field Emission Gun, electron source used in electron microscopes</td>
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<tr>
<td>F-M</td>
<td>Franck-Van der Merwe, a 2-D growth mode</td>
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<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field, a detection technique used in STEM</td>
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<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
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<td>MBE</td>
<td>Molecular Beam Epitaxy, an epitaxial technique</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller, device used to control gas flow</td>
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<tr>
<td>ML</td>
<td>Monolayer</td>
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<tr>
<td>MOSFET</td>
<td>Metal-Oxide-Semiconductor Field-Effect-Transistor</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal-Organic Vapor Phase Epitaxy</td>
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<tr>
<td>PH$_3$</td>
<td>Phosphine, precursor for Phosphorous</td>
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<tr>
<td>QW</td>
<td>Quantum Well</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>S-K</td>
<td>Stranski-Krastanov, a 2-D + 3-D growth mode</td>
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<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy/Microscope</td>
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<td>TMGa</td>
<td>Tri-Methyl-Gallium, a metalorganic precursor</td>
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<tr>
<td>TMIn</td>
<td>Tri-Methyl-Indium, a metalorganic precursor</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy/Microscope</td>
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<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid, a nanowire growth mechanism</td>
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<tr>
<td>V-W</td>
<td>Volmer-Weber, a 3-D growth mode</td>
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<tr>
<td>WIGFET</td>
<td>Wrapped-Insulator-Gate Field-Effect-Transistor</td>
</tr>
<tr>
<td>Wz</td>
<td>Wurtzite, hexagonal close packed crystal structure</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-ray Energy Dispersive Spectroscopy, an analytical TEM tool</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Molar fraction, fraction of a precursor entering the growth reactor</td>
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<tr>
<td>Zb</td>
<td>Zincblende, cubic close packed crystal structure</td>
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1. Introduction

Nanotechnology is a field of science where the major disciplines chemistry, biology and physics have converged. By using knowledge and techniques from traditionally different parts of science entirely new phenomena can be discovered, studied, understood and finally utilized to improve everyday life. This thesis is written in the borderland between physics and chemistry and methods developed in both these fields are required to fabricate and study the nanostructures, also known as nanowires, described in the following chapters. Before we dive into the world of nano-science and technology a background describing the prerequisites for this thesis is presented.

The Metal-Oxide-Semiconductor Field-Effect-Transistor (MOSFET) has been the most crucial electronic component in the information technology revolution that has occurred over the past decades. Since it was realized for the first time in 1960 it has continuously been improved and downscaled which has resulted in an unprecedented performance increase and cost reduction. The scaling has followed a prediction made by Gordon Moore where he states that the number of transistors on a chip doubles every two years. The minimum feature size in a commercial microprocessor will in 2009 reach 32 nm and development is already underway to further reduce this. Eventually the downscaling, which has been so successful in the past, will run into obstacles as the size of device features enters the quantum regime. In order to continue the performance increase beyond the next decade new transistor designs are needed that addresses the upcoming issues with further MOSFET downscaling.

Nanowires are one of the new building blocks that are promising to use in future electronic devices where quantum effects such as electron confinement can be utilized to improve device performance. A vertically oriented nanowire transistor design, depicted in figure 1.1, has already been fabricated at Lund University, demonstrating the ability to control and process such a device. The device has been termed Wrapped-Insulator-Gate FET (WIGFET) due to its optimal wrapped gate geometry for charge control in the conductive nanowire channels.

Properties inherent to nanowires such as: defect free semiconductor heterostructures and III-V semiconductor integration with existing Silicon (Si) technology are only a few of the advantages nanowires offer.

Even though several advantages are presented when introducing novel designs and ideas, there are also several obstacles that must be overcome in order to compete with existing well developed technology. One of the main arguments for using III-V semiconductors instead of Si in electronic components has been the higher mobility of electrons in some of the III-V semiconductors. Indium-Arsenide (InAs) is the material of choice for the nanowires

![Figure 1.1 SEM image of a WIGFET. Image from Bryllert et al. [1].](image-url)
comprising the conductive channels in the WIGFET. When bulk properties of InAs and Si are considered, the electron mobility of InAs is 33000 cm$^2$/Vs compared to 1450 cm$^2$/Vs for Si [2], i.e., the electron mobility of InAs is more than 20 times higher.

The advantage of a high mobility has however not been as prominent with nanowires where mobility values of 3000-10000 cm$^2$/Vs [1], considerably lower than in bulk, have been reported. One reason for the low mobility values is the large surface to volume ratio which is unavoidable when the size of a structure is reduced. In a crystal the surface can be viewed as a defect since it interrupts the periodicity of the crystal, and as with any defect the atoms present at the surface can act as scattering centres for electrons travelling in the vicinity.

In this thesis a material with a higher band gap$^1$, Indium-Phosphide (InP), is epitaxially grown around InAs nanowires as a shell. By depositing a material around the conductive channel the electrons travelling inside it will be further away from the surface states that can scatter them. The use of a higher band gap material also helps to confine the electrons, further reducing the probability that they will scatter.

Since the InAs-InP nanowires eventually ought to be integrated into a device there are some restraints that must be considered. The InAs nanowires used in this study should not be dissimilar to the nanowires that are used in the WIGFET, i.e., they should be of similar length and diameter, and it must be possible to grow a thin InP shell that covers the entire wire. The shell should be thin since a thick shell would move the gate further away from the channel that it controls, thus reducing its ability to effectively control the flow of charge inside the channel.

This thesis is comprised of two major techniques, namely epitaxy and electron microscopy. In the second chapter general concepts of epitaxy along with a description of Metal-Organic Vapor Phase Epitaxy (MOVPE) are provided. After this general discussion on epitaxy, the third chapter specifically deals with the growth of nanowires. The role of Transmission Electron Microscopy (TEM) is then introduced in chapter 4 as an invaluable tool for characterization. In this chapter a model used for describing and verifying the grown structures is also derived. The following chapter presents the results of experimental investigations and chapter 6 contains a discussion of the results. Finally chapter 7 gives a short summary of the thesis.

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$^1$ InAs has a band gap of 0.35 eV compared to 1.34 eV for InP [2].
2. Semiconductor Epitaxy

2.1 General Concepts of Epitaxy

Electronic applications often have a very high demand on crystal quality since crystal defects act as scattering centres for charge carriers and therefore degrade device performance. A minimum amount of crystal defects is obtained if the deposited film orders itself after the crystal structure and orientation of the substrate. This ordered growth of one crystalline material upon another is defined as epitaxy.

An ideal situation for epitaxy occurs if the atomic structure and lattice constant of the substrate match the atomic structure and lattice constant of the film material. This is of course achieved if a material is grown upon itself, i.e., homoepitaxy. A defect free interface and film can then be formed if the conditions are favourable. However, if film and substrate material are different, i.e., heteroepitaxy, a matching of the lattice constant (assuming the same atomic structure) can only be achieved when certain specific material combinations are used, for example In$_x$Ga$_{1-x}$As ($x = 0.53$) grown on InP. If the lattice constant of film- and substrate material do not match defects are formed if the films critical thickness is exceeded, since the interface between film and substrate must adapt to accommodate the built-up strain.

Crystal growth is governed by thermodynamics and a systems´ strive to reach equilibrium. In crystal growth at least two phases are present, a supply phase and a crystal phase. A system is at equilibrium when its Gibbs´ free energy ($G$) is at a minimum \cite{3}. The small change in $G$ that occurs when material ($N$) is added to a system is described by the chemical potential ($\mu$) defined in equation 2.1.

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} \quad (2.1)$$

The subscript $T,p$ denotes that the temperature and pressure in the system are kept constant. The difference in chemical potential between the supply phase and the crystal phase determines whether a crystal grows, dissipates to or is in equilibrium with the supply phase. This difference, termed supersaturation ($\Delta \mu$), can explicitly be written as:

$$\Delta \mu_{SC} = \mu_S - \mu_C \quad (2.2)$$

In equation 2.2 $\mu_S$ and $\mu_C$ denote the chemical potential of the supply phase and the crystal phase respectively. Crystal growth is thermodynamically allowed if the supersaturation $\Delta \mu_{SC}$ is positive, i.e., a driving force exists for adding material to the crystal phase. A continuous supply of material to the supply phase ensures continued crystal growth as material incorporates into the crystal, i.e., a steady-state condition is achieved. If no more material is supplied the supersaturation would decrease, and the supply and crystal phase will at some point reach equilibrium where no chemical potential difference exists between them, i.e., $\Delta \mu_{SC} = 0$.

Even though thermodynamics govern the possibility of crystal growth kinetic factors also play a crucial role in determining the final quality and structure of the deposited film. Kinetic
factors control the rate at which processes occur and a good example of a kinetic factor is the diffusion of growth material on a crystal surface.

An atomistic model of crystal growth provides a complementary insight into the understanding of the growth process. In this model the adatoms\(^2\) are viewed as building blocks that incorporate into the substrate crystal. In the growth process, the adatoms are first supplied to the substrate by a supersaturated supply phase. The adatoms can then diffuse on the crystal surface and either incorporate into the crystal or desorb back into the supply phase. In order for an adatom to be incorporated it has to form a sufficient number of bonds to keep it from desorbing. Some sites on the substrate surface will be more favoured for incorporation than others. Incorporation preferentially occurs at atomic steps or kinks where the possibility of several bonds exists. On an atomically smooth surface incorporation can also take place once a nucleus\(^3\) has formed. A nucleus can form if a sufficient number of adatoms bond to make it stable.

### 2.1.1 Surface Transport

Adatoms can arrive at a nucleation/growth site either by direct impingement from the supply phase or by diffusion on the surface. The diffusion length \(\Lambda\) of an adatom on a surface can be related to the deposition flux \(J_r\) and substrate temperature \(T\) by equation 2.3 [3].

\[
\Lambda = A \sqrt{\frac{1}{J_r}} e^{-E_s/2RT} \tag{2.3}
\]

This equation holds as long as \(T\) is low enough that film evaporation is not significant. In equation 2.3 \(A\) relates to the surface on which the diffusion occurs, \(E_s\) is the activation energy for the surface diffusion and \(R\) is the gas constant. The most important factor in this expression which can be controlled is the substrate temperature \(T\). An increase in substrate temperature leads to longer diffusion lengths which can be important in order for the adatoms to reach the nucleation or growth site. It should be noted that equation 2.3 is valid when only one type of adatoms is present. However, similar temperature behaviour can be expected when two types of adatoms are present. When a compound semiconductor is grown the two different types of adatoms can have different diffusion lengths on the substrate and in growth of InAs it is believed that In adatoms have the longest diffusion length on the substrate. Often it is the adatom with the longest diffusion length that is most important in order to understand the growth results.

### 2.1.2 Nucleation and Growth Modes

Nucleation and growth of an epitaxial film can proceed by two principal growth mechanisms. If a crystalline substrate has a series of atomic steps, created for example by cutting the substrate at a slight angle away from a crystal plane, growth can proceed by a step flow mechanism. The steps act as preferential incorporation sites and as growth proceeds the steps “flow” forward creating an epitaxial film. On the other hand, if the substrate is an atomically smooth surface growth must be initiated by the formation of a nucleus which will spread and

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\(^2\) Adatoms are mobile atoms present on the substrate surface which hasn’t yet incorporated.

\(^3\) A nucleus is a stable cluster of adatoms.
grow larger. The nucleus then acts as the preferred site for incorporation of adatoms. This mechanism is referred to as birth and spread. Three different growth modes that describes nucleation and continued growth are introduced below.

Franck-Van der Merwe (F-M) growth mode, illustrated in figure 2.1, proceeds in a layer by layer process, i.e., the epitaxial film wets the substrate forming a smooth film. This growth mode is termed 2-D since the growth of one layer only proceeds once the preceding layer has reached a certain size, determined by the diffusion length of the adatoms.

![Figure 2.1 Franck-Van der Merwe growth mode](image)

In the Volmer-Weber (V-W) growth mode, illustrated in figure 2.2, it is not energetically favourable for the adatoms to directly bond with the substrate and the adatoms instead primarily bond to the nuclei forming 3-D islands. This growth mode is termed 3-D since the growth of one layer is not preceded by the completion of the previous.

![Figure 2.2 Volmer-Weber growth mode](image)

The final growth mode is Stranski-Krastanov (S-K), illustrated in figure 2.3, which describes a combination of the two previous, i.e., 2-D + 3-D growth. In S-K growth the first layers of the epitaxial film wets the surface on top of which islands form.
Figure 2.3 Stranski-Krastanov growth mode. The initial layers are formed in a layer by layer process but after a certain film thickness has been reached 3-D islands start to form.

Which growth mode is favorable for a given system is primarily determined by the relation between film and substrate surface energies as well as a possible difference of lattice constant. These factors are further discussed in the next section on heteroepitaxy.

2.2 Heteroepitaxy

The ability to grow epitaxial films of different materials upon one another has been critical to realize high performance electronic, optoelectronic and photovoltaic devices. Heteroepitaxy represents a way to create devices with desired characteristics by making it possible to tailor the band structure of the grown material. This type of band structure engineering can be used to confine and control the transport of electrons through a material.

One of two important factors for achieving successful high quality growth of one material upon another is that a favourable relation exists between the surface and interface energies of the substrate free surface ($\gamma_s$), substrate-film interface ($\gamma_i$) and the film free surface ($\gamma_f$). 2-D growth is achieved when $\gamma_s > \gamma_f + \gamma_i$ since the formation of the film free surface and substrate-film interface is more energetically favourable than retaining the substrate free surface. If instead the inequality $\gamma_s < \gamma_f + \gamma_i$ is fulfilled, island formation is favoured resulting in 3-D growth.

The second factor which determines by which growth mode the growth proceeds is the lattice mismatch $f$, defined by equation 2.4.

$$f = \frac{(a_s-a_f)}{a_s} \quad (2.4)$$

In equation 2.4 $a_f$ and $a_s$ represent the lattice constants of the epitaxial film and substrate, respectively. This equation is only valid for comparing materials with the same crystal structure. In order to achieve high quality growth $f$ normally has to be small.

If $\gamma_s > \gamma_f + \gamma_i$ is fulfilled at the same time as a lattice mismatch exists between the substrate and film S-K growth can occur. The initial monolayers wet the surface, since this is energetically favourable, but after a certain critical thickness the built up strain is too big to accommodate and islands can form to relax it.
2.3 Metal-Organic Vapor Phase Epitaxy
The technique used to grow core-shell heterostructured nanowires in this thesis is MOVPE. This technique is a form of Vapor Phase Epitaxy, in which the growth material is supplied to the growth reactor as a vapor and chemical reactions occur in order to deposit growth material on a substrate. As the name MOVPE implies, some or all reactants, also called precursors, are supplied in a metal-organic form.

The main components of a MOVPE system, depicted in figure 2.4, are the precursor supplies, the hydrogen carrier gas, the mass flow controllers (MFCs) and the reactor. The precursors are supplied either from a gas bottle as a hydride or from a so called bubbler in metal-organic form. Metal-organic precursors are preferred for the group III elements, for example In where the metal-organic compound Tri-methyl-indium (TMIn) is used. The group V elements, P and As, are supplied in vapor form as hydrides, i.e., Phosphine (PH₃) and Arsine (AsH₃). It should be noted that the above mentioned sources are the ones used in this thesis and that other MOVPE systems may have other sources, such as metal-organic precursors for group V elements. The carrier gas consists of highly purified hydrogen (H₂), which helps to transport the reactants to the reactor as well as transporting bi-products away from it. MFCs are used to control the flow of gas, thus controlling the amount of material supplied to the reactor. A metal-organic bubbler offers extra possibilities to control the amount of material supplied, for example by changing the pressure or temperature inside the bubbler.

**Figure 2.4** Schematic of a MOVPE system. Additional sources can be added if needed, for example PH₃. Arrows indicate the flow direction.

Compared to other epitaxial growth techniques such as Molecular Beam Epitaxy (MBE), the growth mechanism in MOVPE is conceptually more complex due to the numerous chemical reactions involved, but it also presents many advantages. In MBE elemental sources of for example P, As and In are used to supply the growth material. The growth is carried out in ultra high vacuum where the mean free path of the atoms is much longer than the growth chamber size, thus the growth material is supplied by molecular beams to the substrate. For some applications where extreme control of the epitaxial film is required MBE is advantageous to use, however in most applications MOVPE possesses several desirable advantages and some of these are listed below:
1. A possibility of high growth rates makes MOVPE suitable for implementation in an industrial growth process.
2. MOVPE is very versatile and growth of virtually all III-V and II-VI semiconductor compounds and alloys is possible due to a high number of available precursors.
3. The possibility of long diffusion lengths for adatoms prior to incorporation enables high quality overgrowth of complex structures, allowing several sequential growth and processing steps.

Of course, some parts need special attention when using an MOVPE system. For instance the temperature dependent decomposition of precursor gases and unintentional doping by impurities, due to the presence of methyl groups inside the reactor, can be problematic. For the application in growth of core-shell heterostructured nanowires MOVPE is the most suitable technique since complex structures (nanowires) are present on the surface, and a uniform and controlled growth of the shell is critical. Growth of a shell in MOVPE also gives the possibility to eventually upscale the process in an industrial environment.

Another very important aspect of an MOVPE system is concerns with safety precautions. All used precursors are highly toxic and some, for instance PH₃ and TMIn, combust spontaneously in air. AsH₃ is the most dangerous gas because only a few ppm is lethal and since it does not burn in air leak detection is not as obvious. Due to these risks several safety measures are employed to ensure that no precursor gases leak into the ambient atmosphere. Leak detectors are coupled to the machines built in automatic safety system along with sound and visual alarms inside the lab. If a leak is detected all precursor supplies are immediately closed and the machine goes into a safe state. The entire system is purged with nitrogen to trap remaining toxic gases in a dedicated container, and an alarm is sounded to evacuate the lab. A detailed training is also required for all personnel working independently with the machine. The lab staff is also thoroughly trained to deal with emergency situations and evacuation procedures are regularly tested.

**2.3.1 Precursor Decomposition**

The chemistry of the involved precursors is very important for understanding the actual growth conditions. Even though a controlled flow of precursors enter the reactor, the chemical reactions and thermal decomposition of the precursors are determining factors for the amount of material available for crystal growth, especially when the growth temperature is low. There are some investigations concerning these reactions but the chemistry is complex, since there are at least two precursors (for a binary compound), a carrier gas and catalytic surfaces involved. For example when Tirtowidjojo et al. theoretically analysed MOVPE growth of GaAs they included 60 species involved in 232 reactions in the gas phase and 19 species involved in 115 processes on the surface [4]. Due to the complexity of the chemistry involved no intermediate chemical reactions between the precursors will be discussed in this thesis. Instead a qualitative analysis of the temperature behaviour in the different material systems will be presented. For further information and discussion concerning the intermediate reaction steps I refer to the references mentioned in the following paragraphs.
The decomposition of precursors can either be homogeneous or heterogeneous. A precursor decomposing homogeneously decomposes in the gas phase without involving a solid surface. A precursor decomposing heterogeneously decomposes with aid of a solid surface, catalysing the decomposition.

TMIn has the lowest decomposition temperature [5] of the precursors used in this work. A graph showing decomposition vs. temperature in a Deuterium (D₂) atmosphere is shown in figure 2.5. The two curves represent different amount of In covered surface available inside the reactor. Due to the small difference between the curves it is concluded that the decomposition of TMIn is not dependent on the amount of In surface present. TMIn thus decomposes homogeneously and can be fully decomposed at temperatures as low as 360°C.

![Figure 2.5 Thermal decomposition of TMIn in a D₂ atmosphere. The two different graphs represent different reactor sizes with different amount of In covered surface available. Figure from Buchan et al. [5].](image)

Decomposition of hydrides is more complex, especially at lower temperatures, since it involves both chemical reactions with other precursors and heterogeneous decomposition on available solid surfaces. Decomposition in the TMIn-PH₃ system has been investigated by Larsen et al. [6] and the results are shown in figure 2.6. The figure shows a large dependence, of the decomposition behaviour, on the amount of TMIn present. The investigation also showed that when no TMIn was present, the decomposition temperature was lowered several hundred degrees centigrade in the presence of an InP surface. From figure 2.6 one can conclude that chemical reactions between the two precursors determine the decomposition behaviour at temperatures below 400°C. After all of the TMIn is consumed, any remaining PH₃ decomposes heterogeneously. The heterogeneous decomposition is very low at temperatures below 400°C.
No study has been found describing the decomposition of AsH₃ together with TMIn. However, a study of AsH₃ decomposition in the presence of Tri-Methyl-Gallium (TMGa) [7] shows a similar behaviour as that of TMIn-PH₃. The heterogeneous decomposition of AsH₃, without TMGa, takes place at lower temperatures than for PH₃, without TMIn, and can be complete just above 500°C. The presence of TMGa lowers the decomposition temperature further and the dependence on the TMGa:AsH₃ ratio indicates that the decomposition is dependent on chemical reactions between the precursors at low temperatures, similar as for the case of TMIn-PH₃ decomposition.

The low growth temperature of nanowires, typically 400-500°C, increases the importance of precursor decomposition behaviour. At this low temperature much of the precursor material goes through the reactor without adding to the growth. It can be especially hard to achieve a large surplus of P when InP is grown, since the decomposition temperature of PH₃ is high compared to the growth temperatures used in this thesis.
3. Epitaxial Growth of Nanowires

Nanowires, previously called nanowhiskers, are quasi one-dimensional structures that have introduced a possibility to fabricate semiconductor devices with superior control and properties. Since the end of the 1990s several research groups around the world have directed much attention towards growing [8, 9] and studying [10] nanowires. The next step in nanowire evolution is fabrication of devices where the new properties, inherent to nanowires, are utilized. Some of these new advantageous properties are listed below:

1. Fabrication of axial heterostructures in nanowires with a large lattice mismatch is possible without formation of defects. This possibility is offered since the geometric shape and small dimensions of nanowires gives a possibility for radial strain relaxation, thus avoiding relaxation via formation of dislocations.
2. Nanowires can be fabricated by a bottom-up approach which enables superior control of size and a possibility to tailor electronic and structural properties.
3. The one-dimensional nature of nanowires changes the physical properties of the materials involved, which combined with the above mentioned properties enables realization of high quality low-dimensional semiconductor devices, such as resonant tunnelling diodes and single electron transistors.

A common procedure for III-V nanowire growth (with a seed particle) employed in this thesis is written below and illustrated in figure 3.1.

1. Size selected Au aerosol particles are deposited on a substrate.
2. The substrate is heated to the desired growth temperature with an overpressure of the group V element, i.e., As or P, to avoid decomposition of the substrate due to the high vapor pressures of the group V elements.
3. Once the growth temperature is reached the desired flow of group III precursor material is introduced into the reactor. The growth rate under the Au particle is enhanced, lifting the particle upwards and forming a nanowire. The diameter of the nanowire is controlled by the size of the Au particles.
4. After a certain time the nanowires have grown to the desired length. At this point the sample can either be cooled down or a change in growth parameters and precursor material can promote growth of a shell covering the nanowire.
3.1 Nanowire Growth with a Seed Particle

In 1992 Hiruma et al. [11] were the first to report the successful growth of InAs nanowhiskers on InAs and GaAs substrates. The nanowires were 20-40 nm in diameter and had a particle with similar diameter at the top. It was concluded that a thin layer of Au formed Au nanoparticles when the substrate was annealed prior to growth. Under the particles the growth was enhanced compared to the bulk resulting in the one-dimensional structures. It was proposed that the growth mechanism was the same as one reported almost 30 years earlier by Wagner et al. [12], termed the Vapor-Liquid-Solid (VLS) mechanism.

The VLS mechanism was proposed to explain the growth of Si whiskers assisted by Au seed particles. The whiskers had a diameter in the range of 100 nm – 200 μm and the seed particle could be composed of different materials, including Au, Pt, Ag, Pd, Cu and Ni. The VLS mechanism focused on explaining the one-dimensional growth by investigating the role of the Au particle and its interaction with the vapor and substrate. It was concluded that the Au particle forms a liquid alloy droplet with the growth material at a temperature above the Au-Si eutectic, which then becomes supersaturated and solid Si is deposited at the interface between the alloy droplet and the solid Si surface. It was not clear why the growth rate was enhanced, but it was suggested that either the alloy droplet acts as a sink for the supplied Si atoms or that it catalyzed the chemical processes involved in the growth.

3.1.1 InAs Nanowire Growth

In this thesis nanowires of the binary compound semiconductor material InAs have been grown. This material consists of the group III element In and group V element As and is thus a III-V semiconductor compound. Although bulk InAs crystallizes in the cubic close packed zincblende (zb) crystal structure, InAs nanowires often grow in the closely related hexagonal close packed structure wurtzite (wz) or a mixture of the two [13].

The nanowires investigated in this thesis preferentially grow in a [111]B direction. In the <111> directions (which are normal to the close packed bi-layers) the difference between the
two crystal structures, wz and zb, is found in the stacking sequence. The stacking sequence in zb can be written as ABCABC whereas the wz structure instead has the stacking sequence ABABAB. A, B, and C here denotes the close packed bi-layers of the crystal structure. Since these two structures are very similar in the preferred growth direction, nanowires can often exhibit a mixed structure composed of wz and zb segments. If the segment is only one bi-layer thick it is known as a stacking fault.

Even though InAs is a compound semiconductor and not an elemental semiconductor, such as Si, the VLS mechanism was proposed to explain this nanowire growth [11]. In order to understand the mechanism behind InAs nanowire growth the properties of the Au particle in the presence of In and As has to be considered. The lowest melting temperature (455°C) possible for Au in the presence of In and As occurs when a certain amount of In alloys with the Au and forms an eutectic melt [14]. This property poses an inconsistency between the nanowire growth and the VLS mechanism, pointed out by Dick et al. [15]. They observed that no Au seeded particle nanowire growth was possible in their system when the growth temperature reached the eutectic temperature. This shows that a liquid Au particle is not necessary for InAs nanowire growth. It has further been shown that the activation energy for GaAs nanowire growth is the same as that in planar GaAs growth [16] and since it is also possible to grow nanowires in MBE [17] where no precursor decomposition is involved it can be concluded that catalytic effects by the Au particle, either assisting incorporation or precursor decomposition, are not required for nanowire growth.

Attention is now directed towards a more general mechanism to explain nanowire growth, where a liquid particle is not necessary. The seed particle is, in this model, considered to be a collector of material and acts as a preferential site for nucleation [18, 19]. The preferential nucleation takes place at the triple phase line at which all three phases (supply, collector and substrate) are present. The enhanced nucleation locally increases the growth rate under the collector particle and a one-dimensional structure, a nanowire, can form.

3.2 Nanowire Growth without a Seed Particle

In collaboration with Bernhard Mandl, at the department of Solid State Physics, InAs nanowires were grown without using a particle to seed the growth. These wires were grown on an InAs substrate on top of which a thin layer of SiOx had been deposited. The SiOx layer had a thickness of 1-2 nm and it partially covered the surface. The growth procedure for these wires is slightly different than for the seed particle assisted growth. Once the substrate is loaded into the reactor the temperature is increased without supplying AsH3, thus an overpressure of As is not achieved. This means that the InAs surface starts to decompose as the As starts to evaporate. The free In atoms do not evaporate as easily [20] and can start to diffuse on the surface possibly forming In particles/droplets. Growth is initiated by turning on both the TMIn and AsH3 flows simultaneously when the desired growth temperature is reached. When the growth is finished an overpressure of As is kept inside the reactor to avoid evaporation of the wires.
3.3 Heterostructured InAs-InP Nanowire Growth

Two basic types of heterostructures exist for nanowires. The first type consists of a heterostructure grown axially, i.e., a change in material is present along the length of the wire (see figure 3.2a). The other type of heterostructure is when a different material is grown on the nanowire side facets, a so called core-shell heterostructure (see figure 3.2b).

![Figure 3.2](image)

**Figure 3.2** Illustration of different type of heterostructures in nanowires: (a) axial heterostructure and (b) radial heterostructure also called a core-shell heterostructure.

The ability of nanowires to form defect-free heterostructure interfaces (mentioned in the beginning of this chapter) is only true for the axial heterostructure where radial strain relaxation is possible. The core-shell heterostructure on the other hand should have similar constraints as layer by layer growth, i.e., a lattice mismatch would introduce crystal defects if the critical thickness is exceeded.

InAs has a lattice constant of 0.606 nm and the lattice constant of InP is 0.587 nm which gives a lattice mismatch of 3.1% (calculated with equation 2.4). This large mismatch should eventually lead to formation of dislocations or other crystal defects once a certain critical thickness is reached. Experimental studies show that a critical thickness of 2-3 nm can be expected [21] when growing on a planar surface.

In previous studies Au seeded GaAs nanowires with lattice matched shells have successfully been fabricated. The materials used to grow the different shells have been ternary alloys of Ga_xIn_{1-x}P [22] or Al_xIn_{1-x}P [23] which with the correct composition (x) is lattice matched to GaAs. When growing a shell around a GaAs nanowire the parameter which is changed to favour shell growth is temperature. Both of the above mentioned shells were grown at a temperature above 600°C which should be compared to the nanowire growth temperature around 450°C.

Before effort was directed towards nanowire research, heterostructures in the InAs-InP materials system were grown on planar substrates. The aim was then to grow strained quantum wells (QW) with a thickness of a few monolayers (ML). Schneider Jr et al. [24] successfully fabricated an InAs QW, i.e., an InP-InAs-InP heterostructure, in a MOVPE system. Compared to nanowire growth temperatures planar growth is often carried out at higher temperatures (550-600°C) which makes comparison of growth parameters difficult due to the temperature dependant decomposition of precursors. The strain relationship is also different compared to the growth investigated in this thesis since InAs is grown on InP resulting in compressive strain instead of tensile for the epitaxial film.

Nanowire core-shell heterostructures of InAs-InP have been reported in several articles where different growth techniques have been used. A wide variety of schemes has also been
employed to promote shell growth; however no systematic investigation of InP shell growth has so far been published.

By using Chemical Beam Epitaxy (CBE), Zanolli et al. [25] demonstrated growth of InP shells with various thicknesses. CBE is a technique similar to MBE but uses the same type of precursors as in MOVPE. However, CBE employs thermally assisted decomposition of precursors which eliminates many of the temperature dependant decomposition issues present in MOVPE. It was thus possible to reduce the growth temperature and introduce a kinetic hindrance for the adatoms mobility on the nanowire side facets, i.e., the diffusion length is shortened. The shorter diffusion length promoted shell growth over axial nanowire growth. However, this article does not present anything concerning the morphology or growth mechanism of the shell. Zanolli et al. also only grew thicker shells between 10-20 nm which is more than the theoretical critical thickness of an InAs-InP heterostructure. The core-shell nanowires were evaluated with photoluminescence measurements which showed an increased luminescence efficiency when an InP shell passivated the InAs surface.

Jiang et al. [26] successfully fabricated a 2 nm thick InP shell around an InAs nanowire by a thermal evaporation and vapor transport technique. Since only a thin InP shell was fabricated, below the critical thickness, a high quality interface was expected. TEM investigation showed no visible dislocations near the InAs-InP interface. The nanowires were further characterized by nanowire FET measurements and theoretically extracted values for the mobility showed an increase compared to previously reported values. The mobility had a lower bound of 11500 cm²/Vs which is very promising and a strong argument why these structures need to be investigated further. One should note that in the article by Jiang et al. the core and shell were grown in two separate steps and not completed in situ, since the growth material had to be changed to grow the shell.

A more advanced process based on the core-shell geometry considers remote doping of the core via the shell. By introducing dopants in the InP shell the charge carrier concentration in the InAs core can be increased without introducing ionized impurities, similar to the modulation doping employed for achieving a 2-dimensional electron gas. This remote doping has been accomplished by Li et al. [27], who successfully fabricated a 7 and 20 nm thick InP shell. While growing the shell, p-type dopants were introduced by flowing di-ethyl-zinc in the growth chamber. This type of modulation doping will also be possible to implement in the growth conducted in this thesis once a good knowledge and understanding of the growth has been acquired. The InAs wires by Li et al. were fabricated on an InP substrate in a MOVPE system. In order to promote radial over axial growth, thus forming a shell, the growth temperature was increased from 420°C, which was the nanowire growth temperature, to 500°C. This change in shell growth temperature is the opposite (increase instead of decrease) of that used by Zanolli et al. in CBE. In MOVPE, temperatures below 400°C may seriously affect the decomposition of precursors since no thermally assisted decomposition is used. If temperature instead is increased the decomposition is enhanced and depending on the axial nanowire growth rate dependence on temperature, radial growth may be favored.
When growing seed-particle-free nanowires the prerequisites are quite different compared to the seed particle assisted growth. Seed particle free growth of an InP-InAs-InP core-multishell heterostructure has been accomplished by Mohan et al. [28]. They concluded that when growing the outermost InP shell, radial growth was favored by a high P coverage since a lower P coverage resulted in more unwanted axial growth. The outermost InP shell in this study was grown at a temperature of 600°C, not too different from the InP core growth temperature of 625°C.

The short bibliographical study presented above shows that even though some work has been done on radial-heterostructure InAs-InP nanowires there is a lack of knowledge concerning the growth mechanism as well as structural characterization. In the above presented articles the nanowires have been characterized either by optical or electrical measurements, which showed promising results. The thorough investigation in this thesis concerning the growth of InAs-InP core-shell nanowires should provide a better understanding of shell formation and a possibility to further improve the properties of the surface passivated and quantum-mechanically confined InAs nanowires. This is interesting for realizing a new generation of high mobility FETs based on vertical nanowire wrapped gate technology.
4. Transmission Electron Microscopy
A Transmission Electron Microscope (TEM) is an invaluable tool for studying nanostructures. In a TEM an electron beam is transmitted through a sample and interactions between the electrons and the sample give rise to several different image forming mechanisms. Besides the formation of an image, a TEM can also provide chemical information if it is equipped with analytical tools enabling X-ray Energy Dispersive Spectrometry (XEDS) or Electron Energy Loss Spectrometry (EELS). Before discussing the image formation and analytical capabilities of a TEM a brief description of the actual instrument is given below.

Figure 4.1 shows a typical TEM column with indicated components. The top of the column consists of an electron gun, in this case a Field Emission Gun (FEG). This type of electron gun extracts electrons by applying an intense electric field over a fine tip of ZrO₂ coated W. The emitted electrons are then accelerated by a set high voltage, 300kV in the microscope used. Once the electrons are accelerated they reach the first set of electromagnetic lenses, called condenser lenses. Theses lenses shape the electron beam either as a parallel beam, used in TEM mode, or as a fine probe, used in Scanning-TEM (STEM) mode. In TEM mode the image is formed by the objective lenses after the parallel electron beam has gone through the specimen. Imperfections in the objective lenses, such as spherical aberration, set the limit for how high resolution the microscope is capable of. The newest generation of TEMs have extra lenses to compensate for aberrations improving resolution considerably. The last major set of lenses are the intermediate and projector lenses, which magnify the formed image from the objective lenses and projects it onto the viewing equipment, such as a fluorescent screen or a CCD camera.

Figure 4.1 Schematic of a TEM column.
Image formation in TEM or STEM mode is dependent on interactions between the incident electron beam and the sample. The charge of the atomic nuclei and electrons present in the sample can scatter electrons travelling through it. This scattering can be divided into two different types: elastic and inelastic. An elastic scattering event will change the direction of an incident electron without the electron losing energy. When an inelastic scattering event occurs the incident electron will change direction and also transfer energy to the sample. The amount of scattering is dependent on the thickness of the sample and its elemental composition, since atoms with a higher atomic number give rise to more scattering than atoms with a lower atomic number.

The scattering of electrons gives rise to the concept of diffraction which is an important aspect of image formation and an additional source of information in a TEM. A diffraction pattern is formed in the back focal plane of the objective lens and can be used to determine the crystallinity and atomic structure of a sample. If the sample is crystalline only certain scattering events will be allowed and thus the diffraction pattern will consist of a number of well defined diffraction spots. These spots will have a specific position determined by the crystal structure and orientation of the sample.

The Fourier transform of a High Resolution TEM (HRTEM) image gives the same information as a diffraction pattern. If the sample is crystalline only certain frequencies corresponding to the different spacings of atomic planes in the image will be present in the transform. If different spacings along one direction exist in the image, for example originating from materials with different lattice parameter, the area containing the different spacings can be isolated by filtering the frequencies in the Fourier transform, and then inverse transform the filtered Fourier transform. This procedure, known as Fourier mapping, has successfully been used to isolate InAs-InP axial heterostructures [29].

4.1 STEM and XEDS
With STEM, image formation occurs without the use of either the objective lens or the intermediate/projector lenses. Once the condenser lenses has shaped the electron beam into a fine probe, usually 0.6 nm or less in size, the formed probe is scanned over an area of interest. The electrons interact with the sample and some of them scatter. An image is formed by measuring the intensity of the electrons at a certain angle after the sample. The intensity is related to the position of the electron probe before the sample thus forming an image. Several different detectors can be used to form an image displaying the desired information.

If a detector is placed directly under the incident electron beam a so called Bright Field (BF) image is formed. The limited size of the detector ensures that only electrons which have not scattered or only scattered in a small angle are detected. This means that volumes in the sample where electrons are highly scattered will appear dark in the BF image, while areas through which electrons are easily transmitted will appear bright.

Instead of placing a detector in the middle of the column, detecting electrons which have not scattered (or scattered very little), a detector can be placed as a circle around the BF detector

---

4 A diffraction pattern is the distribution of electrons in reciprocal space.
thus detecting electrons that scatter in a certain angle. This detector is called an Annular Dark Field detector, or if the detector is placed at an even higher angle, a High Angle Annular Dark Field (HAADF) detector. When an image is formed by this type of detector volumes that scatter electrons most will appear brightest, opposite to a BF image. A HAADF detector is ideal to use if contrast between different elements is desired.

The inelastic scattering events that occur can be used to obtain chemical information. When an incident electron transfers energy to an electron in the sample the electron can be excited, leaving its energy state. The free state can be filled by an electron in a higher energy state thus lowering the total energy of the atom. When the higher energy electron changes state the excess energy can be emitted as a photon or be transferred to another electron which can leave the atom, a so called Auger electron. The energy of the emitted photon will be equal to the difference between the two energy states and, is thus characteristic to the element involved. The photons detected by the XEDS detector in an analytical TEM may have energies from a few keV up to tens of keV, i.e., in the x-ray range. These photons can be used to determine the elemental composition of a sample by performing quantification at a point, or to determine the spatial position of different elements by relating the electron probe position with the amount and energy of the detected photons. In this thesis a so called linescan is frequently used to analyze the structure of core-shell nanowires. In a linescan, the variation in relative quantity of an element is determined along a line by scanning the electron probe along a specified line and relating the x-ray signal to the electron probe position. In order to evaluate the geometric structure and composition of the investigated samples a model describing a linescan of a core-shell nanowire is derived below.

4.2 XEDS Model
Several methods could be considered for detection and characterization of a shell covering a nanowire. Detection of a shell around a nanowire in a TEM, when the core and shell consist of different materials, can be accomplished by use of XEDS, EELS or by utilizing the contrast between elements arising when a HAADF detector is used. Since the shell covers the entire nanowire, detection and thickness determination are more complex than detecting and determining the length of segments in an axial nanowire heterostructure. The analysis of a core-shell structure by XEDS can be accomplished by performing a linescan in STEM mode, obtaining a profile for the amount of each material present as function of position. If the wire is covered with a shell material, this material will give an x-ray signal over the entire width of the wire, while the core material should only give an x-ray signal in the middle of the wire.

The nanowire is assumed to be rod shaped and lying flat on a TEM grid with the electron beam impinging perpendicular to the TEM grid (see figure 4.2). In this model both nanowires with circular and hexagonal cross sections are considered. A linescan signal from a wire with hexagonal cross section will depend on how the wire is oriented relative to the electron beam and in this model both orientations depicted in figure 4.2b-c are considered. For ease of derivation, a wire with circular cross section is used as an example in the text below.
Figure 4.2 Cross section of a core shell nanowire with (a) a circular cross section, (b) a hexagonal cross section and (c) a rotated hexagonal cross section.

A linescan is performed by scanning the electron beam, along a line, in the x-direction. The x-ray intensity of the relevant elements is recorded in every point, with a certain resolution, and a graph of the x-ray intensity vs. length is plotted. The x-ray intensity at one point of the linescan will be proportional to the volume of the material irradiated with electrons, weighted by the density of electrons in that volume:

\[ I \sim \iiint f(x,y,z) \cdot g(x,y,z) \, dx \, dy \, dz \]

Here \( f(x,y,z) \) describes the geometric shape of the material and \( g(x,y,z) \) describes the shape and density of the electron beam. If the electron beam were assumed to be point like, the x-ray intensity from every point would only depend on the geometry of the structure. However, since the lengths of interest are the same order of magnitude as the size of the electron beam, the finite size of the electron beam must be taken into consideration. In order to construct a full model, the convergence angle of the electron beam along with scattering of electrons within the sample could be taken into account. In the present model only the convergence angle of the electron beam will be taken into consideration since studies by Thomas et al. show that the effects of electron scattering within a nanowire is negligible in most cases when this type of model is applied [30]. Here it is assumed that no generated x-rays are reabsorbed by the sample. If the sample were very thick this absorption might influence the result and the detector position would have to be accounted for in the model.

The irradiated volume \( g(x,y,z) \), i.e., the electron beam, can be described by a two dimensional Gaussian distribution [31] in the x-y plane. The convergence angle of the electron beam, represented by a wider and flatter Gaussian distribution where the beam isn’t focused, is accounted for in the standard deviation and amplitude of the beam. This means that the electron beam is described by a Gaussian function in the x-y plane with an amplitude and standard deviation dependent on \( z \). This gives the following representation:

\[ g(x, y, z) = A(z)e^{-\frac{(x-x_0)^2+(y-y_0)^2}{2\sigma(z)^2}} \]
\[ \sigma(z) = \sigma_0 + z \cdot \tan(\alpha) \]

\[ A(z) = \frac{1}{\iint_{-\infty}^{+\infty} e^{-\left(\frac{x^2+y^2}{2\sigma(z)^2}\right)} \, dx \, dy} \]

Where \( A(z) \) is the amplitude, \( \sigma(z) \) is the standard deviation of the distribution with minimal value \( \sigma_0 \) and convergence semi-angle \( \alpha \), and \((x_0,y_0)\) is the center point of the electron beam. \( A(z) \) is included in order to normalize the distribution, i.e., the electron current is preserved.

In order to extract the different signals for the core and shell material two different functions describing the geometry of these structures must be considered. Since the wire is assumed to be rod shaped and infinitely long, the shape functions describing these structures will only depend on \( x \) and \( z \). The core of a wire with circular cross section is described by:

\[ f_c(x, z) = \begin{cases} 1, & x^2 + z^2 < R^2 \\ 0, & \text{otherwise} \end{cases} \]

The shell of a wire with circular cross section is in a similar manner described by:

\[ f_s(x, z) = \begin{cases} 1, & R^2 < x^2 + z^2 < (R + d)^2 \\ 0, & \text{otherwise} \end{cases} \]

In the equations above \( R \) is the core radius and \( d \) is the shell thickness, as defined in figure 4.2. Similar expressions for a hexagonal cross section is a bit more tedious to express and derive and is therefore left as an exercise to the interested reader. The hexagonal structure is however implemented in the model, in both forms depicted in figure 4.2b-c.

The x-ray intensity acquired at one point \((x_0,y_0)\), for the core and shell material respectively, in the linescan can now be expressed as:

\[ I_c \sim \iiint_{-\infty}^{+\infty} f_c(x, z) \cdot A(z) \cdot e^{-\left(\frac{(x-x_0)^2+(y-y_0)^2}{2\sigma(z)^2}\right)} \, dx \, dy \, dz \]

\[ I_s \sim \iiint_{-\infty}^{+\infty} f_s(x, z) \cdot A(z) \cdot e^{-\left(\frac{(x-x_0)^2+(y-y_0)^2}{2\sigma(z)^2}\right)} \, dx \, dy \, dz \]

A linescan profile can now be obtained by sweeping the position \((x_0,y_0)\) and relating the position \((x_0,y_0)\) with the acquired intensity \(I_s\) or \(I_c\). The calculated values are only proportional to the real intensities. In order to determine the real intensities beam current, acquisition time and a material/instrument specific constant that dictates how effective x-rays of a certain material are emitted/collection must be included in the model.
4.2.1 Practical Aspects when Implementing the Model

The above described model was implemented in a MATLAB environment. In order to find the shape functions $f_C(x, z)$ and $f_S(x, z)$ describing the geometry of the investigated nanowire, a Least Square fitting procedure was employed to evaluate linescans obtained with different shape functions, i.e., shape functions that have different core diameters, shell thicknesses and geometric structures. Since the calculated values do not have the correct intensity or position relative to the experimental data these two variables were first fitted in an iterative way, after which the calculated and experimental linescans could be compared. The best fit between experimental data and theoretically calculated values was obtained by minimizing the sum:

$$
\sum_{x=1}^{n} [X_x - (I_C/S)_x]^2
$$

Where $X_x$ is the experimental data in position $x$, $(I_C/S)_x$ are the theoretically calculated values at corresponding position $x$ and $n$ is the number of data points in the experimental linescan.

In order to minimize the time required to analyze one linescan profile, symmetries in the model were used to reduce computation time. The symmetries used are:

1. Only a quarter of the nanowire cross section was “scanned” with the electron beam, i.e., the quadrant where $x < 0$ and $z > 0$.
2. The electron beam consisted of only a half 2-D Gaussian distribution, i.e., the part where $y > 0$.

The use of these symmetries does not affect the shape of the linescan profile but only the overall intensity, i.e., the calculated profiles are proportional to the ones that would be obtained without using any symmetries.

4.2.2 Examples of Calculated XEDS Linescans

Figure 4.3 shows examples of calculated XEDS linescans of a wire with a diameter of 35 nm and a shell thickness of 10 nm with a circular (figure 4.3a) or hexagonal (figure 4.3b-c) cross section. The relative intensity between the core and shell signal is not the one that would obtained in an experimental situation, since several factors not included in the model affect this.
Figure 4.3 Calculated XEDS linescans of a core-shell nanowire with a circular (a), hexagonal (b) or rotated hexagonal (c) cross section. The corresponding structures are depicted in figure 4.2(a-c) respectively. The linescan was calculated by using a standard deviation of 0.5 nm and a convergence semi-angle of 10 mrad for the electron probe. The core diameter is 35 nm and the shell thickness is 10 nm.
5. Growth Investigation

In order to investigate growth parameters that affect axial vs. radial growth, shell morphology, shell growth rate and shell growth mode several investigative series were completed. All investigated samples were characterized with a Scanning Electron Microscope (SEM) and some selected samples were further investigated with an analytical TEM. TEM investigations are necessary to confirm the grown structure and to be able to resolve the thinnest shells.

The investigation covers InAs-InP heterostructure nanowires grown with a seed article on both InAs and InP substrates. By growing InAs nanowires on an InP substrate, high frequency operation of the WIGFET is possible since InP is a semi-insulating material which reduces parasitic capacitances. Section 5.5 discusses results where nanowires were grown without a seed particle.

All investigations, unless otherwise specified, were carried out with 30 nm Au aerosol particles deposited with a density of 1 or 2/μm². Growth was carried out on both (111)B InAs and (111)B InP substrates in an AIXTRON 200/4 MOVPE system with a total flow (carrier gas plus precursors) of 13 l/min.

The amount of precursor that enters the reactor is given in molar fraction (χ), i.e., how many moles of the total molar flow consists of that precursor. From this the volume flow or partial pressure inside the reactor of a precursor can be calculated by multiplying χ with the total flow or the total reactor pressure respectively.

5.1 Initial Investigation of Growth Parameters

5.1.1 InAs Reference Nanowires on an InP Substrate

In order to evaluate shell thickness and axial vs. radial growth, a reference sample of Au aerosol seeded InAs nanowires on an InP substrate with no shell was grown. Before starting the growth the samples were annealed at a temperature of 530°C for 5 min since this recipe is optimized for lithographically defined seed particles. This step is usually not necessary when growing Au aerosol seeded nanowires, but it is critical when growing lithographically defined arrays of nanowires. The wires were nucleated by growing a short InP section (<100 nm) under the Au particle before growing the InAs wire. The nanowires, shown in figure 5.1, are of uniform length and have a slightly tapered base due to the InP section. The growth parameters are summarized in table 5.1. These previously optimized growth parameters were used for all InAs nanowire growth on InP substrate in this thesis.
5.1.2 Temperature Investigation of Shell Growth

Several previous investigations [25, 27] concerning the growth of an InP shell has indicated that temperature is an important parameter that influences shell growth (see section 3.4). Figure 5.2 shows a temperature series with 20°C increments. Table 5.2 gives reference shell growth parameters that were utilized in the temperature, PH₃, TMIn and reactor pressure series below, i.e., in the temperature series all parameters specified in table 5.2 were kept constant except for temperature.

**Figure 5.1** InAs reference nanowires on an InP substrate.  
**Table 5.1** Growth parameters used for reference InAs nanowires on InP substrate.

<table>
<thead>
<tr>
<th>Growth parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth time</td>
<td>10 minutes</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>420°C</td>
</tr>
<tr>
<td>$X_{AsH_3}$</td>
<td>$3.1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$X_{TMIn}$</td>
<td>$2.8 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>100 mbar</td>
</tr>
</tbody>
</table>
Figure 5.2 SEM images of samples in temperature series with a shell growth temperature of (a) 360°C, (b) 380°C, (c) 400°C, (d) 420°C, (e) 440°C, (f) 460°C and (g) 480°C. Other relevant growth parameters are summarized in table 5.2.
When the shell growth temperature is 440°C or below a shell consisting of several segments is clearly visible. The number of segments increase as temperature is decreased. A comparison between the two samples with the lowest growth temperature, i.e., 360°C and 380°C shows a decrease in shell growth rate when growth temperature is reduced. This is consistent with the decrease in decomposition efficiency for TMIn discussed in section 2.3.1.

The higher temperature samples, i.e., 440 - 480°C show formation of a shell primarily at the nanowire base. All of the high temperature samples show significant growth under the Au particle as well, either as a continuation of the wire or as a “lump” growing in another direction (kinked) than the initial wire. Attempts to grow an InP shell at 500°C or higher were not successful, since very few wires survived such a high temperature.

The increase in axial growth as temperature increases can be explained by an increased diffusion length for the adatoms that limits the growth. In this case the important adatoms are In, as the diffusion length of P on the surface is negligible in this temperature range. As equation 2.3 states the diffusion length will increase with increasing temperature and this increase in diffusion length leads to a larger area from which the Au particle can be supplied with growth material, thus increasing axial growth. In MOVPE the impingement flux may also change with temperature, since precursor decomposition is temperature dependant, which also can influence the diffusion length. The fact that the diffusion length has changed significantly is also indicated by the increase in nucleation density when temperature is lowered. The lower temperature samples contain more shell segments implying that more nucleation events have occurred on the nanowire side facets, which is evidence of a shorter diffusion length.

STEM and XEDS investigation of the sample with a shell temperature of 480°C are shown in figure 5.3. The XEDS linescan profile for P is typical for a shell structure. The investigation shows an inhomogeneous shell with a thickness of ~7 nm on the left side and ~4 nm on the right side, at the position where the linescan was conducted. This uneven shell explains the slight bending of the wires seen in figure 5.2g and figure 5.3. As the shell grows thicker on one side, more strain is caused on that side resulting in a bent wire. The resulting strain profile further enhances nucleation on the thicker side since it will create more energetically favorable incorporation sites. XEDS quantification also confirmed that the top “lump” under the Au particle consists of InP, as expected.

<table>
<thead>
<tr>
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<td>Growth temperature</td>
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</tr>
<tr>
<td>$\chi_{PH_3}$</td>
<td>$2.6 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$\chi_{TMIn}$</td>
<td>$2.8 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>100 mbar</td>
</tr>
</tbody>
</table>

Table 5.2 Reference shell growth parameters from which the different parameter series were completed.
Figure 5.3 STEM image accompanied by an XEDS linescan of sample with a shell growth temperature of 480°C. Scale bar is 100 nm in the left picture and 50 nm in the right picture.

A closer investigation of the sample grown at 440°C, shown in figure 5.4, reveals the shape of the grown shell. In this sample the shell only partially covers the wire and a cross section of the shell is visible. Figure 5.4 shows a hexagonal shell with the same side facets as the nanowire.

Figure 5.4 Higher magnification image of sample grown at 440°C. The shell has the same shape and facets as the original wire.
5.1.3 Molar Fraction Influence on Shell Growth

Another parameter that influences the diffusion of In on the surface is the amount of P present. In order for In adatoms to incorporate into the substrate P atoms must be supplied to bond with the In adatoms. An increase in PH$_3$ flow should make it easier for the In to incorporate. However, the high decomposition temperature of PH$_3$, compared to the nanowire and shell growth temperatures used, decreases this effect. SEM images where the flow of PH$_3$ is varied between 50 sccm$^5$ and 450 sccm giving a nominal V/III ratio$^6$ of 1000 to 9000 are depicted in figure 5.5. Figure 5.6 shows a plot of total wire length vs. $\chi_{PH_3}$. The nanowires in the reference sample, depicted in figure 5.1, had a mean length of 1150 nm. Comparing this length with the lengths of the nanowires from the PH$_3$ molar fraction series, seen in figure 5.6, it is evident that some InP always grows under the Au particle under these conditions and more grows if the amount of PH$_3$ is reduced. Axial growth of InP is not desirable since this will make it more difficult to contact and process the wires for implementation into the WIGFET design, and it will also be harder to grow thicker shells. Within each sample the nanowire length could vary quite a bit, resulting in the large error bars in figure 5.6. The variation is not easily explained but can be related to different amounts of growth material present in the vicinity of different wires.

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5 Sccm – Standard Cubic Centimetres per Minute is a measurement of volume flow at a specified standard temperature and pressure

6 V/III ratio denotes the ratio between group V and group III molar fraction entering the reactor. A V/III ratio of 9000 means that 9000 times more group V precursor molecules are present inside the reactor
Figure 5.5 SEM images of samples in PH₃ molar fraction series with following $\chi_{PH₃}$, V/III ratio in brackets: (a) $2.8 \cdot 10^{-3}$ (1000), (b) $8.5 \cdot 10^{-3}$ (3000), (c) $1.7 \cdot 10^{-2}$ (6000) and (d) $2.6 \cdot 10^{-2}$ (9000).

Figure 5.6 Total wire length vs. molar fraction PH₃. The reference sample where no shell was grown had a mean length of 1150 nm.

Figure 5.7 Top view of sample grown with a V/III ratio of 3000. A triangular shape of the shell segments can be observed on the two wires in the lower part of the image.

A comparison between the images in figure 5.5a-d shows differences in shell growth and morphology. When the V/III ratio is 1000 the shell grows with a more uniform shell thickness but with a considerable amount of tapering resulting in a thicker shell at the base.

The shape of the shell does not necessarily follow the shape of the original wire (hexagonal) as can be seen in figure 5.7, where a top view image of the sample with a V/III ratio of 3000 shows triangular shell segments. This interesting change of morphology has previously been observed by Verheijen et al. [32] in the GaAs-GaP materials system. They determined that facet formation was governed by the actual V/III ratio at the growth site. The actual V/III ratio can be controlled by temperature and supply of precursor material. A low amount of group V
material can affect the formation of polar facets resulting in an uneven growth rate on different side facets of the nanowire. This is in agreement with the observations made in this thesis where a low amount of group V material can result in a triangular shell.

Figure 5.8a-c shows SEM images where the InP shell has been grown with different amounts of TMIn flow. As can be seen in the plot in figure 5.8d the shell thickness\textsuperscript{7} increases with an increasing amount of TMIn. This means that the shell growth is limited by the amount of TMIn present, which is reasonable since there are several thousand times more PH\textsubscript{3} than TMIn inside the reactor. The morphology of the shell does not seem to improve since segments are still visible, but the segments have grown larger and has thus grown into each other.

\textbf{Figure 5.8} SEM images of $X_{TMIn}$ series (a)-(c) with accompanying shell thickness statistics (d). TMIn molar fractions with V/III ratio in brackets are: (a) $2.75 \cdot 10^{-6}$ (9000), (b) $8.24 \cdot 10^{-6}$ (3000) and (c) $2.47 \cdot 10^{-5}$ (1000).

\textsuperscript{7} The shell thickness has been calculated by measuring the widths of the nanowires with a shell and subtracting the mean width of the reference nanowires with no shell, and then dividing by two.
5.1.4 Influence of Total Reactor Pressure
The investigation of molar flows and temperature has so far not resulted in an InP shell with an optimal morphology and a reasonably low axial growth rate. It was therefore decided to investigate the influence of the total reactor pressure on shell growth. The total reactor pressure is traditionally a constant parameter (100 mbar in the system used) during an MOVPE growth run. Figure 5.9a-d shows a reactor pressure series. By changing the reactor pressure several changes are made simultaneously, for example a change in reactor pressure changes the partial pressures of the precursors and can also increase the interactions between the precursors, thus promoting a more efficient decomposition [33]. The change in reactor pressure also changes the coverage of growth material on the surface since the impingement rate changes when the partial pressure and decomposition of precursors change. These factors also influence the diffusion length of the adatoms.

![SEM images of samples grown with different reactor pressures](image)

**Figure 5.9** SEM images of samples grown with different reactor pressures, (a) 100 mbar, (b) 250 mbar, (c) 500 mbar and (d) 1000 mbar.
From figure 5.9 it can be observed that the shell coverage increases as the reactor pressure is increased. When the reactor pressure is increased to 1000 mbar (figure 5.9d) more bending of the wires is observed, indicating an inhomogeneous shell as discussed previously. The optimal growth conditions are achieved when the reactor pressure is 500 mbar (figure 5.9c) resulting in straight and un-tapered wires with good shell coverage. Some wires are still bent but the bending occurs at the base of the wires where the shell growth is different than further up along the wire, due to the presence of the substrate. The shell does however still seem to have some variation in thickness and steps are also present. Figure 5.10 shows a STEM-HAADF image and XEDS linescan profile of the core-shell nanowires where the shell is grown with a reactor pressure of 500 mbar. From figure 5.10 it can be concluded that a difference exists between the shell thicknesses on either side of the core. The shell thickness is measured to 6 and 10 nm on the left and right side respectively.

Another important aspect is the amount of axial growth that occurs simultaneously as the shell grows. Length measurements of the nanowires from the sample depicted in figure 5.9c indicate that axial growth is limited to the top “lump”. This is further investigated in the next section.

5.2 Evaluation of Shell Growth Mechanism

5.2.1 Comparison of Shell Growth on InAs and InP Substrates

In order to characterize the core-shell nanowires electrically they had to be grown on an InAs substrate since the substrate then can be used as a contact to the core of the wire. This homoepitaxial InAs/InAs (111)B growth is also the one currently used in the WIGFET project at the department. First a reference sample of InAs nanowires with no shell on an InAs substrate was grown (depicted in figure 5.11). Relevant growth parameters are summarized in table 5.3.
Growth parameter | Value
--- | ---
Growth time | 15 minutes
Growth temperature | 460°C
$X_{AsH_3}$ | $3.1 \cdot 10^{-4}$
$X_{TMIn}$ | $2.8 \cdot 10^{-6}$
Reactor pressure | 100 mbar

Figure 5.11 Reference InAs nanowire grown on an InAs substrate.

Table 5.3 Growth parameters used for reference InAs nanowires on InAs substrate.

Figure 5.12 shows a comparison between the InP shell growth on InP and InAs substrate. The shell was grown with the same parameters that were determined optimal on InP substrate, i.e., the same as those summarized in Table 5.2 but with a reactor pressure of 500 mbar. Comparing the two images reveals no significant difference, indicating that the core-shell morphology is not drastically affected by possible differences in diffusion length on the different substrates.

Figure 5.13 shows STEM-HAADF images with accompanying XEDS linescan profiles of two nanowires from the same sample as depicted in figure 5.12b.

Figure 5.12 SEM images for comparing shell growth on InP (a) and InAs (b) substrate.
Figure 5.13 STEM-HAADF images and XEDS linescans of InAs-InP core shell nanowires grown on an InAs substrate. (a) Shows a linescan in the middle of the nanowire while (b) shows the elemental composition at the top part of the wire. Scale bar is 20 nm in (a) and 50 nm in (b).

The shell in figure 5.13a is slightly more homogeneous than the one in figure 5.10 and has a thickness of ~11 nm, roughly equal to that in figure 5.10. The XEDS linescan of the top part (figure 5.13b) reveals that axial InP is only present at the very top with a length of roughly 100 nm. This is a large improvement compared to the shell growth at lower pressures where axial growth was considerable.

5.2.2 Time Evolution of Shell Growth

A time series with the optimized parameters summarized in table 5.5, was carried out in order to see how the shell evolves with time and thus better understand the shell formation. These growths were conducted jointly with growth on patterned samples with Au particles defined by Electron Beam Lithography (EBL). For this growth another nanowire reference growth recipe (summarized in table 5.4), optimized for this purpose is used.

A time series with aerosol deposited particles is depicted in figure 5.14(b-h) along with the reference sample in figure 5.14a. SEM analysis of the time series resulted in the shell growth rate shown in figure 5.15.

<table>
<thead>
<tr>
<th>Growth parameter</th>
<th>Value</th>
<th>Growth parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth time</td>
<td>5 minutes</td>
<td>Growth time</td>
<td>Varied</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>460°C</td>
<td>Growth temperature</td>
<td>420°C</td>
</tr>
<tr>
<td>$X_{AsH_3}$</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$X_{PH_3}$</td>
<td>$2.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$X_{TMin}$</td>
<td>$4.6 \times 10^{-6}$</td>
<td>$X_{TMin}$</td>
<td>$2.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>100 mbar</td>
<td>Reactor pressure</td>
<td>500 mbar</td>
</tr>
</tbody>
</table>

Table 5.4 Growth parameters used for reference InAs nanowires in time series.  
Table 5.5 Growth parameters used for shell growth in time series.

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8 Nanowire dimensions of the samples in the time series were determined with the aid of a computer software written by Kristian Nilsson at the department. The width of the wires is determined as the mean width along the wire, not including the very top and bottom parts.
Figure 5.14 SEM images showing the time evolution of the shell. Shell growth time is (a) 0 min, (b) 0.5 min, (c) 1 min, (d) 2.5 min, (e) 5 min, (f) 10 min, (g) 20 min and (h) 40 min.

Figure 5.15 Shell thicknesses as function of shell growth time.

From figure 5.15 it cannot be confirmed that a shell covers the wire when the shell growth time is 30 s, since the mean width of these wires is slightly smaller than the mean width of the reference wires. However, in the sample with a growth time of 1 min the wires were wider than the reference indicating that a shell has grown. Comparison with the reference reveals that the shell thickness should be ~2 nm with a shell growth time of 1 min. The shell thickness as function of growth time does not seem follow a linear trend; instead it pans out as growth time is increased. This is consistent with a constant volume growth rate, since an increase in shell thickness increases the amount of growth material required to form the next layer of the shell.
5.2.3 TEM Investigation of a Thin Shell
It is not possible to characterize a thin shell by measurements in a SEM. Instead HRTEM along with Fourier mapping and XEDS analysis is used to evaluate shell thickness and quality. A HRTEM image of the sample in figure 5.14c with a shell growth time of 1 min is shown in figure 5.16.

![HRTEM image of a nanowire from the time series with a shell growth time of 1 min.](image)

**Figure 5.16** HRTEM image of a nanowire from the time series with a shell growth time of 1 min.

From this HRTEM image the presence of a shell cannot be confirmed by the contrast differences present, since these could be due to other effects, such as thickness. In order to separate a possible InP shell from the InAs core nanowire Fourier mapping of the image is carried out below.

Figure 5.17a and 5.17b shows two areas from which the Fourier transforms in figure 5.17c and 5.17d originate.
Comparing the Fourier transforms in figure 5.17c and 5.17d shows an elongation of the spots in figure 5.17d. This Fourier transform is from an area in the image (figure 5.17b) which would contain a possible shell which 5.17c is not (figure 5.17a). The elongation of the spots can thus be evidence of the presence of a shell. Figure 5.18a and 5.18b shows masks that isolates different frequencies of the Fourier transform and figure 5.18c and 5.18d shows the corresponding inverse transforms of the isolated frequencies.

**Figure 5.17** Fourier Transforms (c and d) of different parts (a and b) of the HRTEM image in figure 5.16.
In the Fourier transforms shown in figure 5.18a and 5.18b the frequencies increase from the center outwards. By isolating the part with a higher frequency (figure 5.18b) the presence of an InP shell should be evident, since the lattice constant of InP is smaller than that of InAs, thus corresponding to higher frequencies in the Fourier transform. Figure 5.19 shows the part of the original image from figure 5.17b, accompanied by an image where the inverse transforms have been overlaid.

From figure 5.19 it is evident that the outer most part of the nanowire is comprised of a thin shell with an approximate thickness of 2-3 nm, consistent with the theoretical value for critical thickness of an InP film on InAs. The interface between core and shell is epitaxial and without visible defects, such as dislocations. The red and green areas overlap, which is expected since the nanowire is viewed in transmission. Figure 5.20 shows the entire image which has been Fourier mapped in the same manner as figure 5.19.

**Figure 5.18** (c) Shows the inverse transform of the frequencies indicated by the white circles in (a). Similarly (d) shows the inverse transform of the frequencies indicated in (b).
Figure 5.19 Original image (a) and original image overlaid with color coded inverse transforms (b). Green corresponds to low frequencies, i.e., large lattice spacing, and red corresponds to high frequencies, i.e., small lattice spacing. Scale bar is 5 nm.

Figure 5.20 Original HRTEM image (a) and Fourier mapped image (b). Green corresponds to low frequencies, i.e., large lattice spacing, and red corresponds to high frequencies, i.e., small lattice spacing. Scale bar is 5 nm.

It has not been possible to use an XEDS linescan to confirm a shell as thin as the one shown in figure 5.20. An XEDS linescan was however performed on one of the nucleation sites along the wire (visible in figure 5.14c) where the InP shell has grown thicker. A STEM-HAADF image along with a XEDS linescan is shown in figure 5.21.
The P signal in figure 5.21 indicates the presence of a shell and the thickness is measured to ~5 nm. The sample with a growth time of 2.5 min has a thickness of ~5 nm which indicates that the nucleus is stable enough to propagate along the nanowire side facets and eventually cover the entire wire.

**5.2.4 Shell Growth Mechanism**

The shell growth mechanism of the nanowires in figure 5.14 appears to follow a birth and spread mechanism. Although the first few nm wets the surface, 3D nuclei start to form almost immediately (see figure 5.14b and 5.14c). These nuclei grow until they encounter another nucleus (see figure 5.14e) after which they grow into each other (see figure 5.14f). The growth then proceeds in what appears to be a layer by layer growth (see figure 5.14g and 5.14h). The initial growth thus consists of both a 2D wetting layer and formation of 3D nuclei, which can be caused by the strain present or by a too low mobility of the adatoms. Once the nuclei have increased in size and grown together forming a homogeneous shell, the growth seems to proceed in Franck-Van der Merwe growth mode (2D). The change in growth mode indicates that strain, caused by the lattice mismatch, is responsible for the formation of the inhomogeneous shell since a smoother shell is possible to grow once the shell is thicker. The thicker shell will thus have relaxed all the strain, probably by formation of crystal defects such as dislocations.

In the time series depicted in figure 5.14 the diffusion length of the In is shorter than the length of the wire. This is clear since nucleation sites are observed on the nanowire side facets. Figure 5.22 shows a time series where the diffusion length is longer than the length of the nanowires. The increase in diffusion length was accomplished by increasing temperature and new shell growth parameters are specified in table 5.6. The InAs nanowires were grown with parameters specified in table 5.4, i.e., the same as in the previous time series.
Figure 5.22 Time series of shell growth with growth parameters specified in table 5.4. Shell growth time is: (a) 2 min, (b) 5 min, (c) 6 min, (d) 7.5 min and (e) 10 min.

Table 5.6 Growth parameters used for shell growth of samples depicted in figure 5.22.

<table>
<thead>
<tr>
<th>Growth parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature</td>
<td>480°C</td>
</tr>
<tr>
<td>$X_{PH_3}$</td>
<td>$2.6 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$X_{TMn}$</td>
<td>$5.7 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>500 mbar</td>
</tr>
</tbody>
</table>
If growth parameters are changed in order to favor longer diffusion lengths the result is that no initial nucleation on the nanowire side facets is observed, as seen in figure 5.22a and 5.22b. Figure 5.22b also shows that the favored sites for incorporation of adatoms are under the Au particle and at the nanowire base. In figure 5.22c the shell, nucleating at the base, has propagated further up from the base of the wire until it in figure 5.22d covers the entire InAs nanowire. The shell thickness grows even thicker when time is increased more in figure 5.22e. The shell thickness in figure 5.22e can be more than 125 nm while the core InAs nanowire only has a diameter of ~35 nm. The rapid development of the shell between figure 5.22c and 5.22d is hard to explain, but the shell growth mechanism is different from the one encountered earlier. The shell starts at the wire base which acts as a favored site for incorporation. Once the step that forms at the base of the wire has reached a certain size it starts to propagate up along the InAs nanowire side facets. This forms a homogeneous shell with only a small amount of tapering. It is possible that steps continue to form at the nanowire base and then propagate upward, increasing the thickness of the shell even more. This growth is similar to step flow growth instead of the birth and spread mechanism proposed for the previously investigated growth.

5.3 Evaluation with XEDS Model

The XEDS model derived in section 4.2 is valuable in order to investigate the structure of grown core-shell nanowires. During the course of this project other methods for thickness determination, such as SEM, have proven more convenient. This XEDS model is however the best way to confirm that the grown structure is a core-shell, since this model takes the three-dimensional structure of the nanowire into consideration and has the capability to identify specific elements, which neither HRTEM nor SEM investigations can accomplish.

Figure 5.23 shows a HAADF image with accompanying XEDS linescan profile. This linescan profile will be compared to the XEDS model below.

![Figure 5.23 STEM-HAADF image with an XEDS linescan profile. Scale bar is 50 nm.](image-url)
The linescan profile in figure 5.23 is chosen since the wire is close to lying on one of its side facets and the profile has a good signal to noise ratio. The different possible structures depicted in figure 4.2 will be valid when the wire is oriented differently. If the wire is lying on one of its side facets (assuming the shell is hexagonal) the structure in figure 4.2b will be the best match. If it instead is rotated randomly the circular structure in figure 4.2a will probably be a close fit, and if it is rotated all the way to 30° the structure in figure 4.2c will provide the best fit. Figure 5.24 shows the best fit for circular, hexagonal and rotated hexagonal calculated linescan profiles (solid lines) together with the experimental data (dots).

Figure 5.24 XEDS model (solid lines) comparison with experimental data (dots). (a)-(b): Hexagonal cross section with 34 nm core diameter (CD) and 10 nm shell thickness (ST), (c)-(d): Circular cross section with 31 nm CD and 9 nm ST, (e)-(f): Rotated hexagonal cross section with 33 nm CD and 10 nm ST.
In figure 5.24 the characteristics of the electron probe are the same as those in section 4.2.2, i.e., a standard deviation of 0.5 nm and a convergence semi-angle of 10 mrad. Both the hexagonal and circular structures seem to fit reasonably well, however the hexagonal structure fits better on the sides of the profile and follows the experimental data very well. The rotated hexagonal structure has the worst fit which is most obvious in the shell comparison (figure 5.24f). The In signal has even better signal to noise ratio than the As (core) and P (shell) signal and therefore the In signal is compared with all three possible structures in figure 5.25. Naturally a core structure is used and the calculated diameter will be the total width of the wire.

The comparison in figure 5.25 confirms that a hexagonal structure provides the best fit for the investigated nanowire. The circular structure gives a descent fit and most notably quite a different diameter. It is therefore important, if comparison and determination of for example growth rate of a shell is undertaken with this model that investigated nanowires are tilted in the same crystallographic direction and the same structure cross section, i.e., hexagonal or circular, is used on all investigated wires. The rotated hexagonal structure provides the worst fit for this nanowire of the above compared structures but might be valid for a wire tilted in the correct direction.

![Figure 5.25](image-url) Comparison of an In signal in a XEDS linescan (dots) with calculated values (solid lines). (a) Hexagonal structure with a diameter of 54 nm (b) Circular structure with a diameter of 49 nm (c) Hexagonal rotated structure with a diameter of 53 nm.
5.4 Growth on EBL Patterned Samples

In collaboration with Kristian Nilsson, from Lund University’s department of Solid State Physics, electrical measurements were to be carried out on samples where the Au particles had been defined by means of EBL and subsequent lift-off technique. The growth recipe used for core and shell are the same as those optimized previously, summarized in table 5.4 and 5.5. Growth on patterned samples turned out to differ from aerosol deposited samples even when both EBL and aerosol deposited samples were grown simultaneously in the same growth run. A comparison of growth on the two different types of samples is shown in figure 5.26. The EBL defined Au particles has a diameter slightly larger than the aerosol deposited particles resulting in wires with a diameter of ~40 nm for EBL defined particles and ~35 nm for aerosol deposited particles, when no shell was grown.

![Figure 5.26](image)

**Figure 5.26** Comparison of growth with (a) EBL defined and (b) aerosol deposited Au particles. Shell growth time was 10 min and core wire growth time was 8 min.

From the SEM images in figure 5.26 it can be observed that both length and width is very different between the EBL defined and aerosol deposited samples. The EBL defined wires has a mean length of 3.4 μm and a mean width of 125 nm whereas the aerosol deposited wires have a mean length of 1.5 μm and a mean width of 60 nm, i.e., both length and shell thickness are approximately twice as large on the EBL defined wires. One reason for the apparent increase in growth rate on the EBL patterned sample can be attributed to the different history that this sample has been subjected to. Further investigation is however needed to conclusively state what the difference is caused by. The difference in growth rate may affect the growth conditions for both wire and shell growth and the parameters previously optimized may not give the same results as before even if the growth time is scaled accordingly. Figure 5.27a below shows the patterned reference sample and figure 5.27b-d shows a shell growth time series on patterned samples. These samples were grown in order to characterize the core-shell nanowires electronic properties.
Figure 5.27 Time series on patterned samples with growth times: (a) 0 s, (b) 15 s, (c) 30 s and (d) 60 s.

Figure 5.28 Shell thickness vs. growth time for the patterned samples depicted in figure 5.27.
Shell growth times were considerably reduced for this times series compared to the previous, in figure 5.14, where the same growth parameters were used. On all three samples where a shell was grown nucleation sites are present. It is however uncertain whether a thin wetting layer of 2-3 nm is present in the samples with the shortest shell growth time, and since it is not possible to characterize these wires with a TEM the only clue that can be obtained is by SEM investigations. Shell thickness vs. growth time from an SEM investigation is plotted in figure 5.28.

It is not possible to determine if a shell is present on the sample with the shortest growth time, i.e., 15 s. On the 30 s and 60s samples it is however evident that a shell is present with a mean thickness of 3 and 5 nm respectively. The electrical characterization was not finished in time to be printed in this report. Preliminary results from the measurements are however discussed in chapter 6, Discussion and Outlook.

5.5 Nanowires Grown without a Seed Particle
The nanowires grown without a seed particle differ in several aspects compared to the Au particle seeded nanowires discussed in the previous sections. Relevant growth parameters for a reference sample with InAs nanowires are summarized in table 5.6.

First of all it can be noted that the growth temperature of these wires is considerably higher than used for the Au seeded wires. The growth temperature is even higher than the temperature Au seeded wires survived, i.e., higher than 500°C. A SEM image of the reference sample without an InP shell is depicted in figure 5.29. It should be noted that the density of wires can vary some between samples and also in different areas on the same sample.

The nanowires in figure 5.29 has a length of 1.4-1.5μm and a diameter of 80-100nm. A SEM image of the first attempt to grow an InP shell around the InAs wires is shown in figure 5.30. The growth parameters are summarized in table 5.7.
Some of the nanowires in figure 5.30 are slightly bent which is a strong indication that a material with different lattice constant, i.e., InP, has grown around the InAs nanowire. Although these results looked promising further investigations of shell growth with seed particle free nanowires were halted due to an instability issue with the InAs nanowires. Attempts to grow an InP shell after this initial growth often resulted in wires that were shorter than the reference wires indicating that the InAs wires aren’t stable and start to decompose either as temperature or precursor flows are changed.
6. Discussion and Outlook

The growth investigation in chapter 5 shows that it is possible to grow an InP shell around an InAs nanowire while minimizing axial growth. It has further been shown that both thin (<5 nm) and thick (40-120 nm) shells are possible to grow with a good shell morphology. A reasonably good morphology seems harder to achieve with a shell of medium thickness (10-40 nm), due to multiple nucleation events along the nanowire side facets. Investigations in this thesis have however shown that it is possible to reduce the number of nucleation events (at least to zero) on the nanowire side facets. Continued optimization of growth parameters with the aim to grow a specific shell thickness might give better morphology results for wires with medium shell thicknesses. The number of nucleation events will mainly depend on growth temperature and length of the initial InAs nanowire. The amount of precursor material present also changes the diffusion lengths and may thus influence the number of nucleation sites. It should be noted that it is not the visual appearance of the wires that is critical but their electrical properties. An even shell is however important in order to control and reproduce device properties and to make sure that the entire wire is covered by the shell when the shell is thin.

TEM characterization along with the XEDS model derived in section 4.2 has proven invaluable during these investigations of core-shell nanowires. By using the XEDS model the geometric structure and composition of the nanowires could be deduced. It is normally hard to observe, in a TEM, whether the nanowire cross section is hexagonal, circular or any other conceivable structure, without the use of advanced preparation (cross sectional TEM) or imaging (3-D tomography) techniques that are very time consuming. Any type of geometric structure can be implemented into the derived model, for example a triangular shaped shell. The only issue that has to be considered is to tilt the nanowires in the desired direction in order to properly analyze them.

The thinnest shells are difficult to detect with XEDS and instead HRTEM along with Fourier mapping should be employed. One should however be careful when using such techniques on the edge of a nanowire since the edge itself might influence the nature of the Fourier transform, and since no well defined “diffraction spot” could be isolated during the Fourier mapping this investigation is not fully conclusive. During the course of this thesis it has not been possible to analyze thicker shells with HRTEM and Fourier mapping but such investigations would conclusively prove whether this analysis technique is valid to use. SEM measurements of the total nanowire width combined with Fourier mapping is however very strong evidence that a thin shell is present on the nanowires from the investigated sample.

Electrical measurements of the samples with EBL defined Au particles were completed shortly before my part in this project was finished. The measurement technique used is a type of Capacitance-Voltage (C-V) measurement explained by Roddaro et al. [34]. Preliminary results show no decrease in the amount of surface charge present. The results rather point in the other direction, i.e., the nanowires with an InP shell have more trapped surface charges than the reference InAs nanowires. Even though the preliminary results are discouraging the growth on patterned samples needs further optimization, since it turned out to differ from the samples with aerosol particles. By optimizing the growth parameters, a smoother shell might
be obtained which can improve the surface morphology possibly reducing the number of trapped charges.

The nanowires grown without an Au particle presented some problems that might be related to the growth mechanism of the wires. A shell heterostructure should be easier to achieve on seed particle free nanowires since the presence of a particle complicates the growth of a shell. Once the growth mechanism is thoroughly understood it is my belief that InAs-InP core shell heterostructures can be obtained and reproduced on these types of wires as well.

Another material that could be grown as a shell around an InAs nanowire is InP_xSb_{1-x} which with the correct composition is lattice matched to InAs. This material also possesses a larger band gap than InAs and may thus also improve the electrical properties by means of for example electron confinement. By growing a lattice matched shell the morphology may be improved resulting in a more homogeneous shell.

On a more personal note this project has given me a great insight into modern materials science and research in general. Much of my time during the course of this project has been spent learning techniques for epitaxial growth and electron microscopy as well as methods for interpreting the obtained results. My hope is that this project will continue and that core-shell nanowires eventually will be implemented into the WIGFET improving device performance.
7. Summary
This thesis has shown that it is possible to grow and characterize InAs-InP core-shell nanowire heterostructures. Shell growth parameters have been thoroughly investigated and the results show that the total reactor pressure has a major influence on shell-coverage and morphology. Along with the total reactor pressure, radial growth is also favored when a large amount of the P precursor PH₃ is supplied. Two different types of shell growth mechanisms have been investigated. The first type grew by a birth and spread mechanism and the second by a more step flow like mechanism. Which mechanism the growth proceeds with is dictated by the diffusion of adatoms on the nanowire side facets. TEM characterization has been carried out with aid of Fourier mapping and XEDS analysis. Fourier mapping was critical to identify a thin shell below the detection limit for XEDS. XEDS linescans in conjunction with a derived XEDS model confirmed the composition and 3-D structure of the grown nanowires. Growth of InAs-InP core-shell nanowires on patterns with EBL defined Au particles differed from samples with aerosol particles. The growth rate was twice as high on the EBL patterned samples and further investigation and optimization is needed to improve this growth.
8. References


