Abstract

This thesis describes growth, processing, characterization and photoluminescence (PL) spectroscopy of nanowire heterostructures. The nanowires were made of III-V semiconductor materials and were produced by Au-particle assisted growth. Axial heterostructures in the form of quantum dots (QDs) in the nanowires as well as radial heterostructures in the form of core-shell nanowires were studied.

Axial heterostructures in the InAs-GaAs and InAs-InP material systems were studied and it was found that the latter material system gave the best control of the QD dimensions and spectrum. In this system wurtzite InAs$_{0.85}$P$_{0.15}$ QDs with well defined dimensions were grown in wurtzite InP nanowires. QDs with diameters, $d$, between 9 and 22 nm were produced. By growing the heterostructures using only the In stored in the Au seed particle and AsH$_3$ from the gas phase a well controllable QD height of $0.35d$ was achieved for nanowires with diameters larger than the critical diameter for the Gibbs-Thomson effect, which was estimated to be 9 nm under the growth conditions used. The size dependence of the QD PL spectrum was studied. We found that the largest QDs were luminescing at the telecommunication wavelength of 1300 nm. With decreasing QD size the emission blue shifted and level splittings as well as the biexciton binding energy increased, illustrating strong confinement. A comparison of the experimental data to a strain dependent $k\cdot p$ model indicated that the band gap of InAs$_{0.85}$P$_{0.15}$ is 190 meV larger and the effective mass is a factor two larger in the wurtzite polytype compared to the zinc blende polytype.

Radial heterostructures, core-shell nanowires, were grown using low temperature, kinetically limited growth for the core to suppress lateral growth and high temperature growth for the shell. Core-shell nanowires in two material systems, GaAs-GaInP and GaAs-AlInP, were investigated. It was found that the shell increases the emission efficiency of the core two to three orders of magnitude by moving the surface states away from the core. The effect of strain, caused by a lattice mismatched shell, on the PL spectrum was investigated and the core emission was tuned over a range of 240 meV. It was also found that planar defects such as twins and stacking faults in the nanowire propagate into the shell during growth and that new twins and stacking faults are created due to $\{1,1,1\}$ faceted corrugations on the nanowire surface. A defect free shell therefore requires a defect free core without $\{1,1,1\}$ micro-facets. Furthermore, phase segregation due to capillarity effects during shell growth was studied. Cross-sectional transmission electron microscopy showed that Al rich domains are formed in the $<-2,1,1>$ directions in the shell. However, PL investigations indicated that In rich domains also exist, these are possibly associated with the corrugated nanowire surface.
Two other applications for the core-shell nanowires were also investigated. A growth scheme was developed where the shell growth was extended in order to completely embed the nanowires which could then be cleaved to enable cross-sectional scanning tunneling microscopy of the interior of the nanowires. Such studies of axial heterostructures revealed an asymmetry in the sharpness of heterostructure interfaces as a consequence of large amounts of group III material being stored in the Au particle causing memory effects following material switching. In the second application a process for conversion of core-shell nanowires into tubular nanowires which can be used for cell injection was developed. It was shown that these tubular nanowires can be used to efficiently deliver cell membrane impermeable molecules to macrophages.
List of Papers

I. Sharp exciton emission from single InAs quantum dots in GaAs nanowires
N. Panev, A. I. Persson, N. Sköld, L. Samuelson
This was the first report of optically active quantum dots in nanowires.
I took part in the planning and the photoluminescence measurements. I contributed to the writing of the paper.

II. Optical studies of tunable quantum dots in semiconductor nanowires
Manuscript
This paper presents the first study of quantum dots in nanowires where emission energies, level splittings and biexciton binding energies are tuned using only the size of the quantum dots.
I did the planning, developed the growth and did the photoluminescence measurements. I also took part in the interpretation of the $k\cdot p$ calculations and the TEM characterization. I am the primary author of the manuscript.

III. Growth and optical properties of strained GaAs-Ga$_x$In$_{1-x}$P core-shell nanowires
Nano Letters 2005, 5, 1943-1947
This was the first study of the effect of a passivating shell on the nanowire emission efficiency. It was also the first study where a ternary shell was used as a means to tune the strain in the nanowire.
I took part in the planning, developed the growth and did the steady state photoluminescence measurements. I was the primary author.
IV.
Phase segregation in AllnP shells on GaAs nanowires
Nano Letters 2006, 6, 2743-2747
This was the first study of phase segregation in the shell of a core-shell nanowire as a consequence of the surface curvature.
I took part in the planning, grew the samples, did the photoluminescence measurements and part of the analysis of the TEM characterization. I was the primary author.

V.
Growth and segregation of GaAs-Al_{1-x}In_{x-1}P core-shell nanowires
J. B. Wagner, N. Sköld, L. R. Wallenberg, L. Samuelson
Manuscript
This paper extends the discussion on the phase segregation in the shell. It also presents evidence of twin formation on the corrugated nanowire side facets during shell growth.
I took part in the planning and grew the samples.

VI.
Direct imaging of the atomic structure inside a nanowire by scanning tunneling microscopy
A. Mikkelsen, N. Sköld, L. Ouattara, M. Borgström, J. N. Andersen, L. Samuelson, W. Seifert, E. Lundgren
Nature Materials 2004, 3, 519-523
This was the first cross-sectional STM study of nanowires. Investigations of impurities and twin boundaries on an atomic level was presented.
I took part in the planning and the development of the growth.

VII.
GaAs/AlGaAs nanowire heterostructures studied by scanning tunneling microscopy
Nano Letters 2007, 7, 2859-2864
This was the first cross-sectional STM study of axial and radial heterostructures in nanowires. An asymmetry in the sharpness of the heterostructure interfaces was reported.
I took part in the planning and grew the samples.
VIII.

Nanofluidics in hollow nanowires
N. Sköld, T. Hernán, J. B. Wagner, W. Seifert, L. Samuelson, J. O. Tegenfeldt
Proceedings μTAS 2007
This was the first report of production of tubular nanowires in a configuration where they could be used as needles for cell injection.
I took part in the planning, developed the fabrication method and did the measurements. I was the primary author.

The following papers are not included due to content beyond the scope of this thesis.

IX.

Nanowire growth and dopants studied by cross-sectional scanning tunnelling microscopy
A. Mikkelsen, N. Sköld, L. Ouattara, E. Lundgren
Nanotechnology 2006, 17, S362-S368

X.

Growth of one-dimensional nanostructures in MOVPE
Journal of Crystal Growth 2004, 272, 211-220

XI.

Semiconductor nanowires for 0D and 1D physics and applications
Physica E 2004, 25, 313-318

XII.

Semiconductor nanowires for novel one-dimensional devices
L. Samuelson, M. T. Björk, K. Deppert, M. Larsson, B. J. Ohlsson, N. Panev, A. I. Persson, N. Sköld, C. Thelander, L. R. Wallenberg
Physica E 2004, 21, 560-567
Preface

This thesis summarizes my work as a PhD student at the division of Solid State Physics at Lund University during the years 2003-2008. It covers growth and optical characterization of axial and radial nanowire heterostructures, including nanowire quantum dots and core-shell nanowires, as well as the production of tubular nanowires for life science applications. The thesis contains eight research papers preceded by an introductory section. Chapter 1 serves as a general introduction to low-dimensional structures and their optical applications. Chapters 2 and 3 are introductions to epitaxy and nanowire growth respectively while chapter 4 is a more detailed discussion on nanowire heterostructures. Chapter 5 discusses the photoluminescence studies performed on the nanowires. Both chapter 4 and chapter 5 are divided into two parts; one covering axial heterostructures and one covering radial heterostructures. Chapter 6 deals with tubular nanowires and cell injection. In addition to photoluminescence studies other methods have also been used to characterize the nanowires, mainly transmission electron microscopy (TEM) and cross-sectional scanning tunneling microscopy (STM). The results of these measurements are included in this thesis but as the measurements were performed by others than me the techniques are only described briefly in the appendix.

This work would not have been possible without the help of a large number of people whom I gratefully acknowledge. First I would like to thank my supervisors Prof. Lars Samuelson, Prof. Mats-Erik Pistol and Prof. Werner Seifert.

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Niklas Sköld
Lund, August 2008
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Chapter 1

1. Introduction

Semiconductor nanostructures, such as nanowires and quantum dots, are low dimensional structures with optical and electrical properties governed by quantum confinement. These properties differ drastically from the properties of macroscopic structures and depend sensitively on the dimensions of the nanostructure. Apart from being excellent models for studies of quantum mechanical phenomena, the nanostructures have several technological applications due to their tailored properties. This chapter serves as an introduction to low dimensional structures in general and nanowires and quantum dots in nanowires in particular.

1.1 Low-Dimensional Structures for Optics

Quantum confinement occurs in a semiconductor crystal that is reduced to a size comparable to the electron wavelength (the de Broglie wavelength) [1]. A confining structure can be constructed as a heterostructure, which is a combination of materials where the charge carriers are confined in a low band gap material surrounded by a large band gap barrier. A thin slice of low band gap material sandwiched between barriers of large band gap material is termed a two-dimensional (2D) structure, as the charge carriers are free to move in two dimensions while confined in the third. Similarly, in a one-dimensional (1D) structure, the charge carriers can only move freely in one direction and in a zero-dimensional (0D) structure they are fully confined. 2D, 1D and 0D structures are called quantum wells, quantum wires and quantum dots respectively. The size limit where weak confinement effects can be seen is generally around 100 nm, but it is not until the size has been reduced to around 10 nm that strong confinement occurs [2]. The eigenenergies and wavefunctions for a single charge carrier are given by the solutions to the Schrödinger equation:

\[
H_0 \Psi(r) = \left[ -\frac{\hbar^2}{2m^*} \nabla^2 + V(r) \right] \Psi(r) = E \Psi(r)
\]  

(1.1)

where \( H_0 \) is the single particle Hamiltonian, \( r \) is the spatial coordinates of the system, \( \hbar \) is Planck’s constant, \( m^* \) is the charge carrier effective mass and \( V(r) \) is
1.1 Low-Dimensional Structures for Optics

the confining potential. \( E \) is the charge carrier energy and \( \Psi(r) \) is its corresponding wave function. In the two limiting cases the charge carrier is either free or fully confined. For a free charge carrier the energy spectrum is a continuous band:

\[
E = \frac{\hbar^2}{2m^*} \left( k_x^2 + k_y^2 + k_z^2 \right)
\]

where \((k_x, k_y, k_z)\) is the wavevector of the free charge carrier. For a charge carrier confined by an infinite hard-wall potential, shaped as a box with lateral extension \( L_x, L_y, L_z \), the solution to the Schrödinger equation is:

\[
E = \frac{\hbar^2 \pi^2}{2m^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)
\]

where the principal quantum numbers are \( n_{x,y,z} = 1, 2, 3... \) The energy spectrum is quantized and subband edge positions and level splittings are proportional to \( 1/L^2 \). Transition energies can therefore be tailored by controlling the confinement. The optical emission corresponds to the band gap, \( E_{bg} \), plus the quantization energy.

Except for shifting the subband edges quantum confinement also affects the density of states (DOS) of the energy spectrum. For a bulk semiconductor the DOS increases as \((E-E_{bg})^{1/2}\) and vanishes at the band edge, as seen in Figure 1.1(a). For a quantum well, the confinement splits the bulk energy spectrum into a series of subbands, each with a finite DOS at the subband edge, Figure 1.1(b). For a quantum wire each subband edge leads to a singularity in the DOS, Figure 1.1(c), and for a quantum dot the energy spectrum is fully discrete and the DOS is described by delta functions, Figure 1.1(d). This pile-up of DOS at the band edge is in large part why confinement enhances optical performance \[2\] as more transitions can contribute to the optical response at a given energy. For this reason semiconductor lasers are made from quantum well structures, since the enhanced transitions at the band edge reduces the threshold current, and development is driven towards devices of even lower dimensionality.

Quantum dots (QDs) are of particular interest due to their fully discrete energy spectrum that makes them similar to atoms, they are therefore sometimes called artificial atoms. Each state corresponds to a certain spectral line in the light emission and by studying the emission from dots of varying sizes and shapes the effects of confinement on a specific state can be probed. Electric and magnetic fields can also be applied to study Zeeman and Stark effects on the energy spectrum \[3\]. As the total angular momentum is conserved for optical interactions, the spin of the confined electrons and holes are linked to the polarization of the emitted or absorbed photons. Thus the spin state of the QD can be probed and manipulated using polarized light.
Chapter 1. Introduction

**Figure 1.1:** The density of states for (a) bulk, (b) a quantum well, (c) a quantum wire and (d) a quantum dot.

From a technological point of view QDs have several potential applications. Highly efficient lasers can be produced using QDs as active medium [1]. QDs can also be used for quantum computation. The spin states of an electron confined in a QD is a two-level system which is a natural candidate for the realization of a qubit where the state can be initiated, manipulated and read out using magnetic fields and optical transitions [4]. Another application motivating many research groups is the prospect of using QDs as single photon sources for quantum key distribution [5]. QDs emit antibunched photons meaning that there is a dead time between successive photon emission events as the dot first need to be repopulated. This is in contrast to a classical light source which displays a photon bunching behavior, i.e. the photons tend to be emitted in bunches rather than individually. To create a single-photon-on-demand-source the QD is excited by a short laser pulse, creating several electron-hole pairs that are confined in the QD. The QD will then emit a number of photons (corresponding to the number of electron-hole pairs created per pulse) but as every state corresponds to a specific emission line a certain transition can be selected, e.g. the last emitted photon, using a monochromator. Thereby one single photon per pulse can be produced. If single photons are to be transmitted in an optical fiber it is of course essential to minimize losses and emission should be tuned to one of the telecommunication windows at 1.3 or 1.55 μm where scattering and absorption in the fiber are minimized.
1.2 Nanowires

Nanowires are epitaxially grown freestanding rods of semiconductor material with a diameter smaller than 100 nm. Most often they are grown using an Au seed particle that enhances growth locally, but other methods such as selective area growth on a masked substrate [6] can also be used. The nanowires described here were grown using Au seeds and the focus of this thesis will therefore be on this system. Au assisted nanowire growth was discovered 1991 by Hiruma et al. who in an attempt to produce nanowires by selective area growth accidentally contaminated their samples with Au during an etching step prior to growth [7, 8]. As they realized that all the nanowires had an Au particle at the top they recalled the work by Wagner and Ellis [9] who studied Au assisted growth of wires in the micron range, called whiskers, already in the 60’s and developed the so called vapor-liquid-solid (VLS) growth model. Hiruma therefore attributed the nanowire growth mechanism to VLS growth from nm sized Au droplets on the substrate surface. Today Au assisted growth is by far the most common and versatile method to produce nanowires, so in the words of Richard Buckminster Fuller “There is no such thing as a failed experiment, only experiments with unexpected outcomes”.

As the nanowires are not embedded and their diameters are small, strain is allowed to relax laterally during growth. This enables material combinations that are not possible using conventional planar epitaxy due to lattice mismatch. Nanowires of direct band gap III-V material which are good light emitters can be integrated on cheap Si substrates [10, 11] and lattice mismatched axial heterostructures can be formed without dislocations [12]. This offers a versatile approach to create QDs with well controlled dimensions within the nanowire which can easily be individually contacted [13, 14]. QDs in nanowires have shown confinement effects with discrete optical spectra [15, 16] and efficient single photon emission [17].

Since the nanowires are freestanding in air their huge surface-to-volume ratio makes them extremely sensitive to their surroundings. Nanowires have therefore been used to construct chemical sensors capable of detecting single molecules ans viruses on the nanowire surface [18, 19]. For optical applications surfaces however degrades the emission efficiency since the large amount of surface states creates non-radiative recombination centers. Therefore it is important to protect the nanowire surface with a radial heterostructure. In such a core-shell nanowire the surface states are moved away from the charge carriers confined in the core which significantly enhances the emission efficiency [Paper III], [20].

Core-shell nanowires can furthermore be converted into nanotubes by selectively etching out the core [21], [Paper VIII]. This is an interesting approach to produce well defined tubes for nanofluidic applications. Tubular nanowires have been used to produce nanofluidic channels narrow enough to enable single molecule detection [22] and solution field effect transistors [23].
Chapter 2

2. Epitaxy

The ordered growth of a crystal which adopts the structure of a single crystalline substrate is called epitaxy. Growth of one single material is called homoepitaxy while a sequential combination of different materials is called heteroepitaxy. Ideally the growth proceeds in a layer-by-layer fashion and atomically sharp interfaces of the heterostructures can be produced. The growth species can be supplied to the substrate from a liquid phase, a vapor phase or as a molecular beam; liquid phase epitaxy (LPE), vapor phase epitaxy (VPE) and molecular beam epitaxy (MBE) respectively. Most of the nanowires discussed in this work were grown by metalorganic vapor phase epitaxy where the growth material is supplied by metalorganic- (group III material) and hydride precursors (group V material) in vapor phase. The precursors are compounds that decompose when heated, pyrolyse, to elemental group III and V material. For example GaAs is grown from trimethylgallium, (CH₃)₃Ga, and arsine, AsH₃.

Epitaxial growth is governed by thermodynamics and the parameter of interest is the chemical potential, \( \mu \), which is defined as the derivative of the Gibbs free energy, \( G \), with respect to the number of particles in the system, \( n \), at constant pressure, \( p \), and temperature, \( T \) [24]:

\[
\mu = \left( \frac{\partial G}{\partial n} \right)_{p,T}
\]

The chemical potential is other words the work needed to add one atom to a specific phase. When two phases are at equilibrium they have the same chemical potential and there is no net exchange of matter or energy over the phase boundary. If they are not at equilibrium there is a difference in the chemical potentials called the supersaturation, \( \Delta \mu \), and the system will strive towards equilibrium by precipitating material from the high \( \mu \) phase to the low \( \mu \) phase to minimize the free energy of the system. The supersaturation is thus the driving force in epitaxial growth and material is precipitated from a supersaturated liquid or vapor phase with high \( \mu \) on the crystalline substrate. The supersaturation of a vapor is:

\[
\Delta \mu = kT \ln \left( \frac{p}{p_0} \right)
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( p \) is the partial pressure of the growth specie in the gas phase and \( p_0 \) is the equilibrium partial pressure, which is the vapor pressure of the solid precipitated phase.
2.1 Metalorganic Vapor Phase Epitaxy

Metalorganic vapor phase epitaxy (MOVPE) makes use of the surface reactions of metalorganic compounds and hydrides at the substrate with methane as a rest product. The precursors are transported in an ultra-pure carrier gas, H₂, N₂, or Ar, to the reactor cell. A laminar gas flow over the substrate forms a well defined boundary layer over the surface across which the precursors diffuse perpendicular to the flow [25]. In our two systems the substrate is placed on a susceptor which is heated by a radio frequency coil outside the reactor cell or by halogen lamps, respectively. To ensure that the chemical reactions only take place at the substrate surface the walls of the reactor cell are kept cold. Waste material and unreacted precursors are transported out of the reactor cell and burned.

![Figure 2.1: Schematic illustration of our MOVPE system. Group V material is supplied from hydrides while group III material is supplied from metalorganic (MO) precursors. The flows are regulated by mass flow controllers (MFC).](image)

The metalorganic precursors used in this work are: trimethylindium (TMI), trimethylgallium (TMG) and trimethylaluminum (TMAI). The hydride precursors are: arsine (AsH₃) and phosphine (PH₃). Hence any alloy of In, Ga, Al and As, P can be grown. The carrier gas is H₂. All flows are regulated by mass flow controllers and pneumatic valves switch the gases between the reactor and a vent line. Figure 2.1 schematically illustrates the system.

Although thermodynamics define the equilibrium state and the driving force of the growth process it does not provide information about the time required to attain that state. For MOVPE the processes that limit the growth rate is divided into two
main parts, surface kinetics and mass transport [25], which correspond to two different temperature regimes. At low temperatures surface kinetics limit the epitaxial growth. This can be both physical processes such as surface diffusion and nucleation as well as chemical reactions. The chemical reactions can to some extent occur in the gas phase (homogeneous reactions) but for MOVPE, surface reactions (heterogeneous reactions) are dominating and it is generally the rate of the chemical reactions needed for the pyrolysis of the precursors that determines the growth rate. For example: before a Ga atom can be incorporated into the crystal lattice it has to loose the three methyl groups. In an exothermic chemical reaction products have a lower energy than the reactants but to reach the product state the reactants have to temporarily form an activated complex requiring an activation energy. Therefore the reactants need a certain amount of thermal energy to overcome this activation barrier and the growth rate, \( R \), increase with temperature in the following way:

\[
R = R_0 \cdot e^{-E_A/kT}
\]  

(2.3)

where \( E_A \) is the activation energy of the rate limiting (slowest) reaction and \( R_0 \) is a temperature independent constant. At higher temperatures (for normal operating pressures above 550°C) the activation barrier is overcome and surface reactions are no longer the rate limiting step but rather mass transport through the gas phase [25]. Gas phase diffusion is essentially temperature independent and the growth rate levels out to a constant value.

### 2.2 Heterostructures and Strain

An important issue in heteroepitaxy is lattice matching between the substrate and the epilayer. Materials cannot be arbitrarily combined since they generally have different lattice constants resulting in lattice mismatch \( m \) defined by:

\[
m = \frac{a_{\text{epi}} - a_{\text{sub}}}{a_{\text{sub}}}
\]  

(2.4)

where \( a_{\text{epi}} \) and \( a_{\text{sub}} \) are the lattice constants of the epitaxial film and the substrate respectively. For lattice mismatched materials the epitaxial film will elastically deform to adopt the substrate lattice and create a pseudomorphically strained layer. If the epilayer has a nominally larger lattice constant than the substrate, Figure 2.2(a), it will be compressed in both directions parallel to the interface while it relaxes in the direction normal to the interface as shown in Figure 2.2(b). Assuming a thick substrate and a thin epilayer all the strain will be accommodated by the latter and the areal strain energy density will increase linearly with the film thickness (since the strain energy is proportional to the volume of the strained material). At a critical thickness it surpasses the dislocation energy density and
dislocations are formed to relieve the strain [26] as shown in Figure 2.2(c). The physical deformation of the semiconductor crystal leads to a distortion of the atomic positions which in turn affects the band structure. Strain can therefore be used for band structure engineering to tune the band gap and the effective masses of the charge carriers. The band gap will increase for a compressively strained epilayer and decrease for tensile strain. Dislocations on the other hand are generally harmful to optical device properties as they create deep levels in the semiconductor band gap which acts as non-radiative recombination centers [27].

Another way for the system to reduce the strain energy is to change growth mode from layer-by-layer growth to island formation as shown in Figure 2.2(d). This will result in a larger surface area and thus a larger surface energy. The islands are however not constrained on the sides and can relax laterally to reduce the strain energy resulting in a net reduction of the system’s energy. This growth mode is called Stranski-Krastanow growth and occur for large lattice mismatches, \( m > 2\% \). If growth continues dislocations are again formed but it is possible to grow a thin low band gap island layer dislocation free and subsequently cap it with large band gap material to form so called self-assembled QDs [28].

**Figure 2.2:** Schematic illustration of pseudomorphic strain. When an epitaxial layer with larger lattice constant than the substrate, (a), is grown it pseudomorphically compresses and adopts the substrate lattice constant in the substrate plane while relaxing in the direction normal to the interface, (b). At a critical thickness dislocations are formed to relieve the strain, (c). For large lattice mismatches it can be energetically favorable to change growth mode to Stranski-Krastanow island formation (d).
2.3 Capillarity Effects and Growth on Non-Planar Surfaces

Surface atoms at the interface between two phases have a surrounding that is not characteristic of either phase. The surface of the condensed phase is therefore associated with an extra energy called the surface energy, $\gamma$ [29]. For a liquid or amorphous particle $\gamma$ is not orientation dependent but for a crystal, different facets have different $\gamma$ depending on the density of the unsaturated bonds at the surface, the so called dangling bonds. Surface energies thus increase the chemical potential of the surface and thereby also change the supersaturation which therefore becomes dependent on the geometry of the surface. Effects of the surface curvature on thermodynamic properties are called capillarity effects as they were first studied experimentally in fine glass tubes called capillaries.

Equilibrium vapor pressures are generally tabulated for planar surfaces but as a particle reduce in size the equilibrium vapor pressure increase. The Gibbs-Thomson equation [29] gives the size dependent vapor pressure of a spherical particle with radius $r$:

$$p_r = p_\infty \exp\left(\frac{2\gamma \Omega}{r k T}\right)$$  \hspace{1cm} (2.5)

where $p_r$ is the radius dependent vapor pressure, $p_\infty$ is the vapor pressure of a planar surface (i.e. $r = \infty$), $\Omega$ is the atomic volume in the condensed phase, $k$ is Boltzmann’s constant and $T$ is the temperature. The Gibbs-Thomson effect modifies the vapor pressure and the chemical potential for nanoparticles and non-planar surfaces and is therefore important to consider for nanowire growth. Atoms on the surface of a small nanoparticle or at the crest of a sharp edge are not as tightly bound to the condensed phase as if they were situated at a flat surface and the vapor pressure/chemical potential increase. An expression for the surface dependent chemical potential during alloy growth that includes both capillarity- and strain effects was derived by Biasiol and Kapon [30, 31]. According to the model the chemical potential of the component $i$ can in one dimension ($X$) be described as:

$$\mu_i = \mu_0 + \Omega \left[ \sigma_t(X) \right]^2 / 2E + \Omega [\gamma(\Theta) + \gamma'^*(\Theta)]k(X) + kT \ln x_i(X)$$  \hspace{1cm} (2.6)

where $\sigma_t$ is the tangential surface stress, $E$ the elastic modulus, $\gamma(\Theta)$ the (orientation dependent) surface energy, $k$ the surface curvature and $x_i$ is the component molar fraction. The second term corresponds to surface strain effects arising during growth of lattice mismatched materials. The third term accounts for capillarity effects and the fourth term is a contribution due to the entropy of mixing. $k$ is defined as the reciprocal radius of the surface structure, positive for convex surfaces and negative for concave surfaces so that $\mu$ increases as the surface structure sharpens [32].
Chapter 3

3. Epitaxial Nanowire Growth

3.1 Particle Assisted Nanowire Growth

The particle assisted nanowire growth mechanism is commonly explained by the vapor-liquid-solid (VLS) model which was proposed by Wagner and Ellis [9]. In this model a metal particle forms a liquid alloy with the substrate above the eutectic temperature. The metal droplet, generally Au is used, acts as a collector of material from the vapor phase, it supersaturates and precipitates material at the liquid-solid interface. The Au thus acts as a local seed or catalyst and growth occurs mainly underneath the Au forming a nanowire with a diameter defined by the diameter of the droplet. The Au droplets can be produced simply by evaporating a thin Au film on the substrate and melting it. Droplets produced this way however have a certain size distribution and a high density. Therefore size selected Au aerosols or colloids are generally used to achieve a homogeneous size distribution and a well controllable density. The position of the Au particles and thereby the nanowire position can also be controlled using electron beam lithography [33].

Although the VLS model is commonly used to describe nanowire growth it has been found that a liquid particle is not a prerequisite for growth. Solid Au particles have also been used to produce nanowires [34, 35] and for InAs and InP nanowires it has actually been found that growth only occurs below the Au-In eutectic melting temperature, i.e. the particle is in its solid state [35]. Furthermore the catalytic effect of the Au is not entirely understood. According to the definition; a catalyst is a substance that increases the rate of a reaction by lowering the activation energy of the rate limiting step, in the case of MOVPE grown nanowires the pyrolysis of the precursors. Growth studies have not been conclusive and there have been reports both on activation energies similar to planar growth [36, 37] (i.e. no catalytic effect) as well as significantly lowered activation energies [38]. It has been argued that the role of the Au particle isn’t catalytic but that it acts as a collector of material [37]. In and Ga has a high solubility in Au at the temperatures used for growth [35] and the Au particle supersaturates. If growth on the substrate surface and the nanowire side facets is kinetically hindered the Au-semiconductor interface is the only point where supersaturation can be reduced and the group III material precipitates out underneath the particle, combining with group V material from the gas phase.
3.1 Particle Assisted Nanowire Growth

A schematic of the growth used for the nanowires in this thesis is shown in Figure 3.1. Size selected Au aerosols are deposited on a (111)B substrate as this is the preferential growth direction for nanowires (a). The substrate is then annealed at a high temperature, around 600°C, in order to desorb native surface oxides and alloy the Au particles with the substrate, a group V overpressure prevents the substrate from desorbing (b). The temperature is subsequently reduced and growth commences when the group III precursor flow is turned on. Typical growth temperatures are in the range 400-450°C where the growth rate on the side facets is very low due to the kinetic hindrance of the surface reactions (c). By switching precursors during the nanowire growth axial heterostructures can be produced (d). Radial heterostructures can be produced by changing growth conditions to overcome the kinetic hindrance of the surface reactions and increase the side facet growth. This can be done by utilizing homogeneous pyrolysis of the precursors in the gas phase by pre-heating the precursors before they reach the substrate [39] or by increasing the temperature altogether [20, 40], [Paper III]. In this work the latter method is used and the shell is grown at a temperature of 600°C or above (e). At this high temperature, the Au loses its “catalytic” effect as growth becomes mass transport limited. Growth therefore occurs on the side facets and on the substrate as well as underneath the Au.

The shell growth can be extended to a point where the nanowires become completely embedded. This makes it possible to cleave the sample and study the interior of the nanowires using cross-sectional scanning tunneling microscopy (STM). Such studies are extremely important as they provide atomic scale information of defects, impurities and heterostructure interfaces within the nanowires and are thereby supplemental to transmission electron microscopy (TEM) which gives an image averaged over several hundred atomic planes. Cross-sectional STM studies on embedded GaAs nanowires were presented in Paper VI and VII. For this work the nanowires were grown on (0,0,1) GaAs substrates instead of (1,1,1)B as the film growth rate on a (1,1,1)B substrate is very low. The nanowires however still grow in the preferential <1,1,1>B directions at an angle of 35° to the substrate. AlGaAs was chosen as the embedding material in order to avoid lattice mismatch and dislocations. Initially the entire embedding was AlGaAs, Paper VI, but as the Al readily reacts with residual oxygen in the STM chamber forming Al₂O₃ that easily adheres to the STM tip the image quality rapidly deteriorates after a couple of scans. Therefore the growth scheme was later changed so that only a thin AlGaAs shell was grown to give contrast to the GaAs nanowire sides and the wires were subsequently embedded in GaAs, Paper VII. A schematic illustration of the growth of embedded nanowires is shown in Figure 3.2. The AlGaAs forms a thin shell around the nanowire but also grows underneath the Au particle thus forming a radial as well as an axial heterostructure.
Chapter 3. Epitaxial Nanowire Growth

Figure 3.1: Schematic illustration of Au assisted nanowire growth. (a) Au particles are deposited on the substrate. (b) The sample is annealed at a high temperature. (c) Growth takes place at a reduced temperature where side facet growth is kinetically hindered. (d) Axial heterostructures can be produced by switching precursors during growth. (e) Radial heterostructures are grown at elevated temperatures.

Figure 3.2: Schematic illustration of the growth of embedded nanowires. (a) GaAs nanowires are grown on a (0,0,1) substrate. (b) AlGaAs is grown at an elevated temperature forming both a shell and an axial heterostructure. (c) The wires are embedded in GaAs.

3.2 Growth Rate

Growth species arrive at the Au particle not only directly from the gas phase but mainly by surface diffusion. The nanowire growth rate therefore does not only depend on precursor flows but also on the surface area that is collecting material for the particle. Precursors adsorb on the semiconductor surface and diffuse a mean distance of one diffusion length, \( \lambda \), before they either desorb into the gas phase again or reach the Au. The Au collects material from all surface within a distance
of $\lambda$, including both the nanowire side facets and, as long as the wire is shorter than $\lambda$, part of the substrate surface. Figure 3.3 schematically illustrates the collection area of the nanowires.

![Figure 3.3](image)

**Figure 3.3:** Schematic illustration of the growth species collection area within one diffusion length ($\lambda$) from the Au particle: (a) In the initial stage of growth material from the substrate surface reach the Au, when collection areas overlap the wires compete for material. (b) When the wires are longer than $\lambda$ they only collect material from the side faces. Catalytic synergy effects can increase the growth rate of neighboring wires.

At given growth conditions (temperature, precursor flows) the following two nanowire parameters affect the collection area and the growth rate:

1. **Nanowire separation:** In the initial phase of the nanowire growth the growth rate is high as the Au collects a lot of material from the substrate surface, Figure 3.3(a). However, if the collection areas of two nanowires overlap they will compete for material. This will result in a variation in growth rate depending on nanowire separation and well separated wires will grow faster than those close together [41]. In order to achieve good control of the dimensions of a heterostructure within the nanowire it should either be positioned at a height of more than one diffusion length or the nanowire separation should be well defined by patterned growth. It should however be noted that it has been reported that the catalytic effect of the Au can synergetically enhance the growth rate of closely separated nanowires [38]. Thus a situation can occur where wires that were originally competing for material instead assist each other in catalyzing the precursor pyrolysis when their collection areas are no longer overlapping.

2. **Nanowire diameter:** When the nanowire reaches a height of one diffusion length it only collects material that directly hits the Au particle or diffuses from the side facets, Figure 3.3(b). A surface diffusion model explaining the size dependent growth rate of the nanowires has been presented by Seifert et al. [42] and Johansson et al. [43] Approximating the nanowire as a cylinder with radius $r$ and the Au
particle as a hemisphere, also with radius \( r \), the nanowire growth rate, \( R_w \), can then be described by:

\[
R_w = \frac{2\pi r^2}{\pi r^2} R_{Au} + \frac{2\pi r\lambda}{\pi r^2} R_{Side}
\]  

(3.1)

where \( R_{Au} \) and \( R_{Side} \) are the arrival rate of precursors per surface site of the Au surface and side facets respectively. The prefactor \( 2\pi r^2/\pi r^2 \) is the ratio between the Au hemispherical surface area collecting material and the area of the growing interface. Similarly \( 2\pi r\lambda/\pi r^2 \) is the ratio between the nanowire side facet surface area collecting material and the area of the growing interface. Assuming that \( R_{Au} \approx R_{Side} = R \), i.e. that the collection efficiency is equal for the Au and the side facets, equation 3.1 reduces to:

\[
R_w = 2R(1 + \lambda/ r)
\]  

(3.2)

\( R \) is in turn given by the Herz-Knudsen equation which modified for the Gibbs-Thomson effect on the Au is:

\[
R(r) = \frac{p - p_r}{\sqrt{2\pi mkT}} = \frac{p - p_x \exp(2\gamma\Omega/ rkT)}{\sqrt{2\pi mkT}}
\]  

(3.3)

where \( p \) is the reactant pressure and \( p_r \) is the radius dependent vapor pressure of the reactant dissolved in the Au as defined by equation 2.5. \( m \) is the mass of the reactant, \( k \) is Boltzmann’s constant and \( T \) is the temperature.

![Figure 3.4](image_url)

**Figure 3.4:** InAs and InP growth rate as a function of nanowire diameter. The Gibbs-Thomson (G-T) effect leads to a decreased growth rate for InAs nanowires with \( d<9 \) nm.
3.3 Nanowire Crystal Structure

For larger nanowires the Gibbs-Thomson effect can be neglected and as \( \lambda / r \gg 1 \) (\( \lambda \) will be quite short due to the low temperature used for nanowire growth but is still several hundreds of nm long compared to \( r \) which is around 10 nm) \( R_w \) will increase with decreasing \( r \) as \( R_w \sim 1/r \). For nanowires grown from small particles the \( r \) dependence of \( p_r \) dominates and \( R_w \) decreases with decreasing \( r \). Figure 3.4 shows the size dependence of the growth rate for InAs and InP nanowires that was used in Paper II. Both InAs and InP have a growth rate proportional to \( 1/r \) for thick wires and for InAs an onset of the Gibbs-Thomson effect is observed at a nanowire diameter of approximately 9 nm leading to a decrease in growth rate for thinner wires. The exact onset of the Gibbs-Thomson effect depends on the supersaturation and slightly higher values have been reported for InAs nanowires grown with chemical beam epitaxy where the supersaturation is lower [44].

3.3 Nanowire Crystal Structure

III-V semiconductors consist of atoms from group III and V in the periodic table which bind to each other by covalent sp\(^3\) hybrid bonds that are oriented in a tetrahedral manner. The covalent bonds can have more or less of an ionic character depending on the difference in electronegativity of the atoms. The atoms arrange themselves in either a zinc blende (ZB) or wurtzite (WZ) structure. These two crystalline structures are very similar but differ by a 60° rotation between two consecutive tetrahedral units around the [1,1,1] axis (the [0,0,0,1] axis for a WZ structure) giving rise to different stacking sequences of the atomic planes along this axis. Crystalline materials of the same chemical compound that differ only in the stacking sequence are called polytypes. When the bonds are more covalent in their character, ZB is the stable polytype. A rotation then occurs between each tetrahedral unit. For more ionic bonds the stable polytype is WZ and the tetrahedral units arrange themselves without any rotation to align ions of opposing charge [45]. The stacking sequence for WZ is described as ABAB as every second layer is identical in terms of atomic positions within the layer. For ZB the stacking sequence is ABCABC since every third layer is identical. For III-V semiconductors ZB is generally the most stable polytype with the exception of the nitrides for which it is WZ. Figure 3.5 is an atomic model of the stacking of ZB and WZ respectively.

Even though ZB is the stable polytype for most III-V semiconductors there is not a big difference in cohesive energy between ZB and WZ. For bulk GaAs the cohesive energy differs by 24 meV per III-V pair between ZB and WZ [46]. Due to the small energetic difference rotational twins can form during ZB growth in the <1,1,1> direction [47]. If the 60° rotation around the <1,1,1> axis between two consecutive tetrahedral units fail to come there is a reversion from ABCABCABC into ABCABACB stacking. In layer B the rotation is absent which causes the next
layer to position itself as A instead of C and so forth. As the nanowires grow in the <1,1,1>B direction these rotations are common and form stacking faults and twin segments within the wires. Figure 3.6 shows schematically how a 60° rotated segment forms a twin. If the twins occur very often, on every lattice plane, actual WZ segments, ABCABABABC, are formed.

Figure 3.5: Atomic model of the stacking of ZB and WZ. The two structures differ in the stacking sequence along the <1,1,1> axis (the <0,0,0,1> axis for a WZ structure). For ZB there is a 60° rotation between two consecutive tetrahedral units around the <1,1,1> axis, for WZ no rotation occurs.

Figure 3.6: Schematic illustration of a twin in a nanowire. Figure prepared by A. Mikkelsen.

It has also been found that nanowires sometimes exhibit a predominantly WZ structure. Due to the large surface to volume ratio of the nanowires the surface energies of the lateral facets cannot be neglected and cohesive energies will be modified from their bulk values. Assuming that the surface energies of the side facets are lower for WZ nanowires than for ZB the WZ structure will be favored below a certain critical diameter. For the nanowire materials studied in this work, GaAs and InP, critical diameters of 13 and 32 nm respectively have been reported.
3.3 Nanowire Crystal Structure

based on calculations of the energy difference $\Delta E_{\text{WZ,ZB}} = E_{\text{WZ}} - E_{\text{ZB}}$, where $E_{\text{WZ}}$ and $E_{\text{ZB}}$ are the system energies of WZ and ZB nanowires [48]. The GaAs nanowires studied here have diameters of 20 nm and up and indeed show a ZB structure with twins and stacking faults. The InP nanowires have diameters of 32 nm and below and show a WZ structure with stacking faults.
Chapter 4

4. Nanowire Heterostructures

4.1 Axial Heterostructures

Nanowires with a diameter comparable to the de Broglie wavelength result in confinement in two dimensions. A thin segment of low band gap material in the nanowire, an axial heterostructure, will confine the charge carriers also along the nanowire axis and thereby form a QD. Such QDs grown in nanowires are interesting as their dimensions, positions and surface densities are highly controllable. The most studied epitaxially grown QDs are the self-assembled QDs which are grown in the Stranski-Krastanow growth mode and form due to lattice mismatch between two semiconductors as described in section 2.2. Islands of low band gap material, typically a few nm high and a few tens of nm wide, are formed in order to relieve the strain induced by the lattice mismatch. The size, shape and density of these self-assembled QDs can to some extent be controlled by growth parameters such as temperature and deposition time [49] and they can be positioned using etched patterns where edges form preferential nucleation sites due to the balance between strain relaxation [50] and capillarity effects [51]. Nevertheless; formation of self-assembled QDs is a spontaneous strain induced process and controlling all properties independently is problematic. QDs grown in nanowires have in contrast shown great potential as a highly controllable system. Diameter and height are defined by the nanowire diameter and growth time respectively and can be chosen arbitrarily. The density depends on the nanowire density as defined by the Au seed particles while the position can be controlled lithographically.

Furthermore, the nanowire geometry makes it possible to stack two or more QDs on top of each other [52], separating them only by a thin barrier of high band gap material. The dots are then coupled via tunneling through the barrier and by controlling the barrier thickness the coupling can be tailored. If a single QD is termed an artificial atom a double QD can in analogy be termed an artificial molecule.

In order to fully control the position, height and interface quality of QDs grown in nanowires it is important to understand the mechanisms that govern the growth.
4.1 Axial Heterostructures

4.1.1 Nucleation

Due to the small diameter of the nanowires it is possible to grow highly lattice mismatched axial heterostructures without misfit dislocations. Since nothing constrains the mismatched material laterally during growth it is allowed to expand in this direction and thereby relieve the strain so that dislocations are avoided [53]. However, the nucleation process does not only depend on the strain energy but on all interface energies and island nucleation can still occur. If the heterostructure material nucleates as an island rather than in a layer-by-layer matter this can push the Au particle to the side and either cause the nanowire to kink in another crystalline direction than the initial \( <1,1,1> \) direction or crawl back down along the side facet of the wire [54]. Formation of 2D (layer-by-layer growth) or 3D (island formation) nuclei is determined by the interface energies, \( \sigma \), between the two heterostructure materials, material A and material B, and between A and B and the surrounding medium (in this case the Au): \( \sigma_{A-B} \), \( \sigma_{A-Au} \) and \( \sigma_{B-Au} \) respectively. When growing a heterostructure with material B on top of material A island formation will occur if \( \sigma_{A-Au} < \sigma_{A-B} + \sigma_{B-Au} \). The system will maximize the A-Au interface and thereby minimize the free energy by 3D nucleation of material B rather than growing a layer to create a large B-Au interface. Nucleation will occur at the edge of the Au where the group V material, which have a low solubility in Au, have the highest concentration.

In an extensive study Dick et al. [54] grew a number of different III-V heterostructures with different material combinations and found that if the heterostructures kinked it was always in one direction only, e.g. B on A but not A on B (a similar study with the same results was done by Paladugu et al. [55] for the InAs-GaAs material system). This indicates that \( \sigma_{A-Au} < \sigma_{A-B} + \sigma_{B-Au} \) (material B grown on A causes a kink) and \( \sigma_{B-Au} > \sigma_{A-B} + \sigma_{A-Au} \) (material A grown on B does not cause a kink). Therefore, \( \sigma_{A-B} \) is not the dominating term which would be the case for strain driven 3D nucleation (islands would form in both directions to minimize the strained, high energy, A-B interface). Straight heterostructures therefore require that \( \sigma_{A-Au} \approx \sigma_{B-Au} \) to avoid kinking altogether. Figure 4.1 schematically shows the nanowire heterostructure nucleation. If \( \sigma_{A-Au} \approx \sigma_{B-Au} \) layer-by-layer growth will be achieved on both interfaces (a). If \( \sigma_{A-Au} < \sigma_{B-Au} \) material B will nucleate as an island (b), which can cause the nanowire to kink (c).

Dick furthermore found that of the studied materials the only two material combinations that fulfilled the \( \sigma_{A-Au} \approx \sigma_{B-Au} \) criterion were the InAs-InP and GaAs-GaP systems and indeed these have been the most successful material systems so far in international research. As early as 2003 we presented the first optical study on QDs in nanowires [Paper I]. The material system then was InAs-GaAs and even though kinking was a problem it was possible to achieve a reasonable yield of straight nanowires. Photoluminescence measurements were then only performed on the nanowires that were straight. It is however reasonable to suspect that also the straight nanowires contained a 3D nucleated QD, although not big enough to force
the nanowire to kink, as shown in Figure 4.1(d). Such QDs are more similar to Stranski-Krastanow QDs (although not strain induced) and are not better controlled than the self-assembled QDs. Later we changed material system for the QDs to InAs-InP where well controlled small QDs can be produced without kinking. These results are presented in Paper II.

**Figure 4.1:** Schematic illustration of the heterostructure nucleation. (a) Layer-by-layer growth will be achieved when \( \sigma_{A-Au} \approx \sigma_{B-Au} \). (b) Material B will nucleate as an island if \( \sigma_{A-Au} < \sigma_{B-Au} \) which can cause the nanowire to kink (c). Even if the nanowire does not kink the QD dimensions are not well controlled.

### 4.1.2 Controlling Quantum Dot Size and Interfaces

As group III growth species need to pass through the Au particle before reaching the nanowire growth front an instantaneous switch in the gas phase does not necessarily correspond to an instantaneous switch at the heterostructure interface. Large amounts of group III material can be stored in the Au, between 5 and 40 atomic % depending on material and temperature [56], causing a memory effect. In order to achieve good control over the QD size and interfaces this memory effect needs to be considered.

In the cross-sectional STM measurements of axial GaAs-AlGaAs heterostructure interfaces in Paper VII the memory effect of Al stored in the Au particle was studied. An AlGaAs segment was grown using TMAI, TMG and AsH\(_3\), after which the TMAI was switched off and GaAs growth continued. Figure 4.2(a) shows a cross-sectional STM image of such a heterostructure and Figure 4.2(b) schematically shows the location of the image. It was found that the first interface was sharp while the second was diffuse, creating a tail of decreasing Al concentration. In Figure 4.2(a) the GaAs nanowire, the segment and the tail are marked. Figure 4.2(c) shows the Al concentration profile of the tail.

The sharpness of the first interface indicates that the Au particle is instantaneously saturated with Al as TMAI enters the reactor cell, consistent with the high diffusion rate of Al in Au [57]. When TMAI is switched off and GaAs
growth continues, a certain amount of Al will remain in the Au. The Al concentration in the Au particle slowly decreases as growth continues. For each monolayer grown the concentration decreases by a factor $b$ which is the ratio between the amount of group III material incorporated in one monolayer at the growth front and the total amount of group III material stored in the Au. The Al concentration, $C_{Al}$, at the $L$th monolayer grown after the switch is thus

$$C_{Al}(L) = a(1-b)^L \quad (4.1)$$

where $a$ is the Al concentration of the last monolayer grown before TMAI was turned off ($L = 0$).

**Figure 4.2:** (a) cross-sectional STM image of an AlGaAs segment on a GaAs nanowire, the sides of the embedded nanowire is marked with a dotted line. An Al containing tail is grown even after TMAI is switched off as a consequence of Al stored in the Au particle. The dark diagonal lines in the image are steps on the cleaved surface. (b) Schematic illustration of the embedded GaAs-AlGaAs heterostructure used for the XSTM measurements, image (a) is marked in the schematic. (c) The Al concentration profile of the tail.
In Figure 4.2(c) equation (4.1) has been fitted to the experimental data using $a=0.096$ and $b=0.05$. The segment thus contains 10% Al and 5% of the group III material in the particle is consumed for each monolayer grown. The fraction of the stored material that is consumed is dependent on the size of the Au particle and will increase with decreasing size as the ratio between the growth interface and the particle volume increases. It should therefore be expected that smaller wires have sharper interfaces.

Furthermore, it is expected that well defined heterostructures are more easily grown by switching the group V material which has a low solubility in Au [54,60]. Accordingly, they will not cause diffuse interfaces as a consequence of stored material in the Au particle. The equilibrium group III composition of the seed particle however depends on the group V surrounding [35] which can cause transient effects in the growth rate. Fröberg et al. recently found that the In content of the seed particle is higher in PH$_3$ ambient than in AsH$_3$ ambient and that this results in an initial increase of the growth rate of an InAs segment in an InP nanowire as the excess In stored in the Au particle during InP growth is expelled [58]. In this work Fröberg studied InAs-InP heterostructures grown by chemical beam epitaxy (CBE) and determined the In content in the Au to be 44% and 34% in PH$_3$ and AsH$_3$ ambient respectively. As CBE is a process close to equilibrium these values can be considered to be close to the equilibrium compositions. This furthermore means that short InAs segments can be grown from In stored in the Au only, with just AsH$_3$ and no TMI entering the reactor cell. By switching from a TMI-PH$_3$ ambient to AsH$_3$ ambient for a few seconds the excess In is expelled, forming an InAs QD with well defined height. Figure 4.3 shows a high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image from Paper II of a nanowire with diameter $d=16$ nm. Five InAs$_{0.85}$P$_{0.15}$-InP QDs are marked with arrows. The QD closest to the top is grown from stored In only by switching on AsH$_3$ for 5 s and the rest are grown with 5 s AsH$_3$ and an additional 1, 2, 5 and 10 s period of both AsH$_3$ and TMI respectively. As the volume of excess In stored in the Au is proportional to the volume of the seed particle ($\sim d^3$) and the growth interface area is defined by the base of the hemispherical seed particle ($\sim d^2$) the length of the InAs segment grown from stored In scales linearly with its diameter ($\sim d$). For the QD studied with varying $d$, this resulted in a QD height, $h$:

$$h = C \cdot d + R(d) \cdot t_{\text{TMI}}$$  \hspace{1cm} (4.2)

where $C$ is a constant related to the difference in the In content of the seed particle in TMI-PH$_3$ and AsH$_3$ ambient respectively, $t_{\text{TMI}}$ is the growth time when both TMI and AsH$_3$ is on, and $R(d)$ is the size dependent growth rate. At the growth conditions used in this study it was determined that $C = 0.35$. The growth rate after the initial In expulsion from the Au particle was less than 1 nm/s making it possible to control the height accurately. Thus well defined QDs with a height of 0.35$d$ and higher can be produced.
It should however be noted that although memory effects of group V material stored in the Au particle is not expected, memory effects in the reactor cell itself need to be considered. In Paper II the QDs were not pure InAs but InAs$_{0.85}$P$_{0.15}$ and an As rich tail was observed after the QDs. This means that both P and As remain in the reactor cell after the respective precursor has been switched off. This effect, called carry-over, is known from layer-by-layer MOVPE growth. It is known that excess As adsorbed on the substrate surface, the reactor walls and susceptor [59] remain stable for a long time after AsH$_3$ is switched off and contribute to a diffuse heterostructure interface. It has been observed by Borgström et al. [60] that the timescale for As carry-over in nanowire heterostructures is substantially longer than for MOVPE planar growth which is consistent with the lower growth temperature. Borgström however also showed that the carry-over effect can be minimized by carefully tuning the switching sequence.

**Figure 4.3:** HAADF-STEM image of five InAs$_{0.85}$P$_{0.15}$ QDs, marked with arrows, in an InP nanowire. The QD closest to the top (to the left in the image) is grown with In stored in the Au particle only and the others are grown with an additional 1, 2, 5 and 10 s of TMI (from left to right). The tip of the nanowire is resting on a carbon film giving rise a bright signal which is not associated with any compositional change in the nanowire.

### 4.2 Radial Heterostructures: Core-Shell Nanowires

Nanowires are very sensitive to their surroundings due to the large surface-to-volume ratio. Although this is something that is utilized in sensor applications [18, 19], surfaces are generally considered a bad thing in semiconductor electronics and -optics. Every semiconductor surface has surface states. They are caused either by the dangling bonds or whatever impurity that terminates this bond, generally oxygen as a result of oxidation. Surface states often result in energy levels within the band gap and pin the Fermi energy there. The charge carriers then rearrange themselves until the Fermi level coincides with the surface states. If the surface states are deep into the band gap this will create a depletion layer a couple of tens nm deep at the nanowire surface. For a thin nanowire this is enough to deplete it entirely and make it non-conducting. Furthermore deep surface states often act as non-radiative recombination centers reducing the emission efficiency [61]. Although all semiconductor surfaces have surface states they can be more or less severe. Among the III-V materials InAs stands out as the Fermi level is pinned in the conduction band [62], creating an accumulation layer of electrons rather than a depletion layer. GaAs on the other hand has the poorest surface properties of the
III-V materials with surface states forming deep into the band gap [63]. Pure GaAs nanowires are therefore not very useful neither for electronic nor optical applications. The solution to the problem is to passivate the surface states chemically by terminating the dangling bonds with atoms that do not create deep states, e.g. S [64], or to simply move the surface states away from the charge carriers confined in the core by growing a large band gap shell around the nanowire. The latter approach is advantageous mainly since the effect is not degrading over time as with the chemical passivation methods. However, other advantages also exist.

Nanowires are generally too thin to serve as a good optical waveguide. This is because they are significantly thinner than the wavelength of the light they are emitting. A practical lower limit for a nanowire to function as a single mode optical waveguide is when

\[
\frac{\pi D}{\lambda}(n_1^2 - n_0^2)^{1/2} \approx 1
\]

where \(D\) is the nanowire diameter, \(\lambda\) is the wavelength, and \(n_1\) and \(n_0\) are the refractive indices of the nanowire and the surrounding medium, respectively. For a GaAs nanowire at 300 K (\(\lambda \approx 870\) nm, \(n_1 \approx 3.6\)) the minimum diameter is 80 nm. This limitation is of course undesirable if one wants to utilize the confinement effects of a thin nanowire while at the same time upholding a good optical cavity for lasing or single photon generation. When a shell is used the core diameter can be chosen arbitrarily small while the overall diameter is kept larger to optimize the waveguiding of the light. Choi et al. [66] studied lasing GaN nanowires and reported that an AlGaN shell improved the photonic confinement and made it possible to achieve lasing from nanowires with smaller diameters.

Another advantage with a shell is that it can be grown lattice mismatched to the core to induce pseudomorphic strain. The core adopts the lattice constant of the shell material and thereby also changes its band gap. This offers flexibility in designed band structure engineering where the band gap and charge carrier effective masses of the core can be tuned [67].

All the core-shell nanowires used for the optical studies in this work have a GaAs core, the III-V material most susceptible to surface states. In order to avoid strain and dislocations lattice matched or only slightly mismatched shell materials should be used. No binary material is perfectly matched to GaAs but three different ternary materials are possible. The obvious choice would perhaps be Al\(_x\)Ga\(_{1-x}\)As which is practically lattice matched to GaAs for all compositions (within 0.15%). In our experiments the GaAs core however generally displayed quite broad luminescence when Al\(_x\)Ga\(_{1-x}\)As shells were used whereas samples with Ga\(_x\)In\(_{1-x}\)P and Al\(_x\)In\(_{1-x}\)P shells had better optical properties. Therefore Ga\(_{0.5}\)In\(_{0.5}\)P and Al\(_{0.5}\)In\(_{0.5}\)P shells, which are the compositions that are lattice matched to GaAs, were used for the optical studies in Paper III and IV. Strain effects of lattice mismatched Ga\(_x\)In\(_{1-x}\)P shells were also studied in Paper III.
4.2 Radial Heterostructures: Core-Shell Nanowires

4.2.1 Morphology and Crystal Structure

Since $<$1,1,1>-B is the favored growth direction of III-V nanowires, the low index sidefacets of ZB nanowires are $\{-1,1,0\}$, $\{-2,1,1\}$ or a mixture of the two [68, 69, 70]. In the cross-sectional TEM studies on GaAs-AlInP core-shell nanowires presented in Paper IV and V we showed that in fact all three side facet variations can be present in a single wire as a consequence of tapering. Cross-sections from the top of the nanowire displayed $\{-1,1,0\}$ facets for the core, while cross-sections from the bottom part displayed $\{-2,1,1\}$ facets and a mixture of the two facets was seen in the middle section of the GaAs core. The AlInP shell displayed $\{-1,1,0\}$ side facets from bottom to top. A schematic model of the nanowire is seen in Figure 4.4.

We concluded that $\{-1,1,0\}$ side facets are formed directly underneath the Au but due to side facet growth at low temperature (core growth conditions) the core tapers and forms $\{-2,1,1\}$ side facets at the bottom part of the nanowire. At higher temperatures, above 600 ºC, (shell growth conditions) $\{-1,1,0\}$ facets are again formed. It appears as if there is a surface reconstruction changing the surface energies somewhere between 450 and 600 ºC. A similar temperature dependence has indeed been observed by Nötzel et al. [71] in reflection high-energy electron diffraction (RHEED) studies of molecular-beam epitaxy on planar GaAs substrates. They observed a reversible onset of the formation of $\{1,1,0\}$ facets on a (1,1,2) surface in the temperature range of 550-590ºC.

Figure 4.4: Schematic illustration of the core-shell morphology. The core has $\{-1,1,0\}$ side facets at the top, $\{-2,1,1\}$ side facets at the bottom and a mixture of the two in between. The shell displays $\{-1,1,0\}$ side facets from top to bottom.
Figure 4.5: (a) TEM image of a GaAs-AlInP core-shell nanowire, the red square marks the location of image (b). (b) TEM image of the shell, red arrows mark twin planes initiated in the nanowire core that have propagated out into the shell during growth, black arrows mark twin segments formed during growth on the \(\{1,1,1\}\) microfacets of the shell. The nanowire axis is marked by an arrow in the lower left corner. (c) Shell thickness as a function of growth time.

Figure 4.6: (a) STM image of an embedded GaAs nanowire with AlGaAs shell. The image shows two twin segments marked with red arrows and the corresponding \(\{1,1,1\}\) microfacetted pockets filled up with AlGaAs illustrating the rapid nucleation at these sites. (b) Model of the AlGaAs shell formation as observed in the STM images. The AlGaAs fills up the corrugations formed on the nanowire side facets at the twin boundaries.

The nanowires generally display a high density of twins and Johansson et. al. [72] showed that the twins cause \(\{1,1,1\}\)A and B microfacets, resulting in a corrugated surface. As the shell grows epitaxially it will adopt the crystal structure of the GaAs core, including its imperfections. Figure 4.5(a) shows a TEM image of...
4.2 Radial Heterostructures: Core-Shell Nanowires

a GaAs-AllnP core-shell nanowire where the core can be seen as a dark shadow. Figure 4.5(b) is a high magnification image of the outer part of the shell and shows that twin segments and stacking faults originating in the core propagate out into the shell during lateral growth. The arrow in the lower left corner marks the nanowire axis. Twin boundaries perpendicular to the growth axis originate in the core, these are marked with red arrows. Furthermore, Figure 4.5(b) shows a corrugation with its deepest point at the twin boundary marked with the left red arrow. It can also be seen that new twins form during growth on the \{1,1,1\} micro-facets of the corrugated nanowire surface, these are marked with black arrows. A defect free shell therefore requires a defect free core with no \{1,1,1\} micro-facets.

The growth rate of the shell is initially very rapid as the corrugated surface offers a vast amount of nucleation sites for shell growth. Figure 4.5(c) shows the shell thickness of an AllnP shell for different growth times in the <-1,1,0> and <-2,1,1> directions respectively. The figure shows an initial high growth rate that after a few seconds decreases when the corrugations have been filled up to some extent. In the cross-sectional STM experiments reported in Paper VII it was also observed that the growth rate in the \{1,1,1\} faceted pockets is higher than for the rest of the shell. Figure 4.6(a) shows such a cross-sectional STM image of a GaAs nanowire with AlGaAs shell embedded in GaAs. Two twin segments can be seen as well as two corrugations with \{1,1,1\} side facets. The deepest point of the pocket coincides with a twin boundary. Although only a monolayer thin AlGaAs shell has been grown on the non corrugated side facets the pockets are already filled up. Figure 4.6(b) schematically illustrates how the AlGaAs fills up the corrugations. The red square marks the position of Figure 4.6(a).

4.2.2 Phase Segregation

During shell growth the nanowire core acts as the substrate. It is however a substrate that is far from planar with its hexagonal shape and micro-faceted surface and therefore capillarity effects need to be considered. Ternary materials generally segregate when they are grown on non planar surfaces. As mentioned in chapter 2.3 the chemical potential of a surface depends both on the crystal orientation of the facets (the density of the dangling bonds) and the surface curvature as well as on surface stress and entropy of mixing of the epitaxial layer. For a non planar substrate, \(\mu\) varies over the surface. Since variations in \(\mu\) is the driving force in epitaxy, gradients in \(\mu\) will induce surface diffusion fluxes towards regions with lower \(\mu\). The adatom flux \(j\) is described by the Nernst-Einstein relation

\[
\dot{j} = -\frac{nD_s \nabla \mu}{kT}
\]

where \(n\) is the surface density of adatoms, \(D_s\) is the surface diffusion coefficient, \(k\) is Boltzmann’s constant and \(T\) is the temperature. Phase segregation can be caused
by differences in diffusion lengths between the growth species. Species with long diffusion lengths will more easily move to the low µ regions and aggregate there. This phenomenon was described by Biasiol and Kapon who studied self-ordered growth of AlGaAs vertical quantum wells in V-grooves (etched V-shaped trenches) on planar substrates [73]. Since Ga has a longer diffusion length than Al it aggregates at the bottom of the V-groove where µ is low and forms a Ga rich vertical quantum well. Figure 4.7(a) shows a schematic illustration of the chemical potential and the surface diffusion as presented in the model by Biasiol and Kapon.

In the cross-sectional TEM studies on GaAs-AlInP core-shell nanowires presented in Paper IV and V, similar phase segregation effects were observed. Figure 4.8 shows dark field images of cross-sectional slices from the top (a), center (b) and bottom (c) part of a nanowire. As Al is a lighter element than In, Al rich domains are seen as dark areas in the dark field images. These Al rich domains can be seen as dark lines in the <-2,1,1> directions where two {-1,1,0} shell facets meet during growth. An intentional AlP spacer that prevents interdiffusion over the core-shell interface can also be seen as a shadow around the core.

![Figure 4.7](image)

**Figure 4.7:** (a) Schematic of a non planar surface profile with corresponding profile of the chemical potential and surface diffusion flux. (b) Schematic of the surface diffusion on the shell side facets causing phase segregation observed in Figure 4.7.

At the bottom part of the nanowire the core side facets are {-2,1,1} while the shell equilibrium shape consists of {-1,1,0} facets. According to Wulff’s rule the equilibrium shape represents the low specific surface energy facets [74], or in other words $\mu_{\{-1,1,0\}} < \mu_{\{-2,1,1\}}$ during shell growth. Hence there will be a surface diffusion flux towards the {-1,1,0} facets, and since the growth species have different diffusion coefficients phase segregation will take place. During shell growth non equilibrium facets with high surface energy, the {-2,1,1} facets, grows
faster than the equilibrium ones, the \{-1,1,0\} facets, and eventually vanishes. As the profile sharpens, the chemical potential at the top of the \{-2,1,1\} apex increase as does the surface diffusion away from the apex. In the end the \{-2,1,1\} apex reaches a self-limited size. Growth species with long diffusion lengths (In in this case) effectively move away from the convex surface leaving growth species with short diffusion lengths (Al in this case) to accumulate there. This should be seen in contrast to a concave surface where species with long diffusion lengths accumulates. Thus Al rich domains with self-limited widths of 5 nm form in the \<-2,1,1> directions as illustrated in Figure 4.7(b). The exact size and composition of the self-limited profile depends on the interplay between capillarity, surface stress and entropy of mixing as the capillarity effect will be counterbalanced by surface stress and a decrease in entropy in the phase segregated domain as described by equation 2.5. On a smaller scale the \{1,1,1\} microfacets on the sidewalls of the nanowires are also expected to cause segregation effects with In rich domains forming at the bottom of the concave pockets. As the TEM signal is an average over the thickness of the cross-section such domains could not be observed. In the images there are however also weak periodic oscillations of the contrast in the shell displaying regular concentric hexagonal patterns. These fluctuations could not be confirmed within the accuracy of the X-ray energy dispersive spectrometry (± 2%). The origin of this contrast oscillation is not yet understood but one possible explanation could be fluctuations in the precursor flow during growth.

**Figure 4.8:** Cross-sectional HAADF-STEM images of GaAs-AlInP core shell wires. (a) Approximately 50 nm from the top of the nanowire. (b) Approximately 1.2 μm from the top of the nanowire. (c) Approximately 2.1 μm from the top of the nanowire. Al rich domains have darker contrast. Scale and orientation, as indicated in (a), are the same for all images. The scale bar is 50 nm. Images by J. B. Wagner.
Chapter 5

5. Optical Spectroscopy of Nanowires

Semiconductor luminescence is the result of a radiative recombination of an electron and a hole. Optical spectroscopy is therefore a useful tool to investigate the electronic structure of the semiconductor. The spectroscopic method used in this work is photoluminescence (PL) spectroscopy where the charge carriers are created by light absorption. Laser light with energy greater than the band gap excites electrons to the conduction band, leaving holes behind in the valence band. The charge carriers thermalize to the corresponding band edges and after a finite lifetime the electron-hole pairs will recombine, either radiatively by emitting a photon or non-radiatively via deep levels caused by, e.g. surface states. The emitted photons will have a wavelength corresponding to the energy of the transition and the spectrum therefore reveals information about the energy structure. In order to remove effects of thermal broadening of the spectral lines the measurements are normally performed at liquid He temperatures.

5.1 Photoluminescence Measurements

The setup used for the PL measurements is shown in Figure 5.1. In order to study the wires individually and to avoid the substrate background luminescence, the wires were transferred to a patterned SiO$_2$ or Au surface. This was done simply by gently scraping the wires off the substrate using a piece of clean room paper which was then brushed over the Au surface. The samples were placed in a liquid He cooled cold-finger cryostat mounted on a translation stage. Laser light hitting the sample at an angle was used to excite the nanowires and emission was collected by an optical microscope. The luminescence signal was filtered to remove scattered laser light, passed through a spectrometer and detected with an array detector. Using the grating as a mirror in the zeroth order to image the sample, single nanowires could be located and isolated (using the entrance slit of the spectrometer) for spectroscopy. For steady state measurements a continuous wave laser was used as excitation source and the luminescence was detected using a liquid N$_2$ cooled charge coupled device (CCD) or a HgCdTe detector for signals above and below 1.2 eV respectively. For time-resolved measurements a pulsed laser was used for excitation and a streak camera was used for detection.
5.2 Quantum Dots in Nanowires

The energy spectrum of a QD is given by the solutions to the Schrödinger equation. In chapter 1 the single particle Hamiltonian was discussed and the particle-in-a-box solution was given. A QD in a nanowire can be approximated as a cylindrical box where the confining potential has a diameter $d$ and height $H$. For a hard wall potential (infinite potential barriers) the solution to the single particle Hamiltonian

$$H_0 \Psi(r) = \left[ -\frac{\hbar^2}{2m^*} \nabla^2 + V(r) \right] \Psi(r) = E \Psi(r)$$  \hspace{1cm} (5.1)$$

is

$$E_{m,s,n} = \frac{\hbar^2}{2m^*} \left[ \frac{4\chi_{m,s}^2}{d^2} + \left( \frac{m \chi_{m,s}}{H} \right)^2 \right] \quad m \geq 0, \quad s \geq 1, \quad n \geq 1$$  \hspace{1cm} (5.2)$$

where $\chi_{m,s}$ are the zeros of the Bessel function of the first kind [75]. The ground state of such a dot is $|m, s, n\rangle = |0,1,1\rangle$. The quantum numbers $m$ and $s$ correspond to lateral confinement while $n$ corresponds to confinement along the nanowire axis.
All the dots studied in Paper II had a disc-like shape with a height substantially smaller than the diameter. Therefore confinement is largest in the height direction and \( n = 1 \) for both the ground state and the first excited state, the first excited state is therefore \( |1,1,1\rangle \). The splitting between the ground state and the first excited state is thus only related to lateral confinement. Although the QDs lack spherical symmetry the shells can be named in analogy with atomic orbitals for simplicity. Thus the ground states are called the s-shell, the first excited states are called the p-shell and so forth.

For a real QD the potential barriers are not infinite and the effective mass is different for electrons and holes. As the effective mass is larger for holes than for electrons and the potential well in the valence band generally is shallower than in the conduction band, the confinement mainly affects the electron states. Level splittings are therefore smaller for the hole levels than the electron levels. Heterostructures are furthermore generally subjected to strain given by the lattice mismatch, the elastic properties of the materials and the geometry of the structure. Compressive strain reduces the bond lengths of the material and increases the band gap while tensile strain reduces the band gap. These effects can be accounted for in a strain dependent \( k \cdot p \) model \([76]\). In such a model the strain is computed from the linear deformation potential theory by minimizing the free energy of the structure using the finite difference method and the calculated strain tensor elements are then used as input to a strain dependent Hamiltonian.

To fully describe the energy spectrum few particle interactions also need to be considered, in particular the Coulomb interactions between the particles, which are described by the following Hamiltonian:

\[
H_{\text{Coulomb}} = \frac{1}{2} \sum_{i \neq j}^{n} \frac{q_i q_j}{4 \pi \varepsilon r_{ij}} \tag{5.3}
\]

where \( q_i \) and \( q_j \) are the charges of particle \( i \) and \( j \), \( r_{ij} \) is the distance between them and \( \varepsilon \) is the dielectric constant. Due to their opposite charges electrons and holes attract to form bound pairs called excitons. The exciton binding energy lowers the energy levels slightly as compared to single particle values. A second exciton puts the QD in a biexciton state. Depending on if attractive electron-hole interactions or repulsive electron-electron/hole-hole interactions dominate the binding energy can be either positive or negative. For large QDs the biexciton has a lower energy than the exciton, i.e. a positive binding energy. This is reasonable since in the quantum well limit biexcitons would not form if it was not energetically favorable. For smaller QDs the charge distributions and Coulomb interactions depend sensitively on the size and shape of the dot. A sign inversion of the binding energy can occur resulting in a biexciton with higher energy than the single exciton if repulsive electron-electron, hole-hole Coulomb interactions dominate over attractive electron-hole interactions. A third exciton, a triexciton, has yet another energy state. Figure 5.2 schematically shows the exciton, biexciton and triexciton states of
5.2 Quantum Dots in Nanowires

A QD and the possible recombination paths. The electron ground state can accommodate two electrons with opposite spins due to the Pauli exclusion principle and the third electron ends up in the first excited state. The hole configuration is described in a corresponding way.

Figure 5.2: Schematic illustration of excitonic states in a QD, spin configurations are marked with small arrows (↑↓) and possible recombination paths are marked with large arrows. (a) The exciton (X) is formed by one electron-hole pair. (b) The biexciton consists of two electron-hole pairs and, (c), three electron-hole pairs form a triexciton.

The exciton state (X) has four different spin configurations resulting in a fourfold degeneracy [77]. For a non-symmetrical QD this degeneracy is lifted due to exchange interactions resulting in a fine structure. Only two of these states are optically active due to selection rules resulting in a doublet exciton line in the PL spectrum which however often is unresolved. The biexciton state (X₂) has only one spin configuration due to the Pauli exclusion principle but in the PL spectrum the biexciton to exciton recombination can again happen in four different ways out of which two are optically active resulting in a doublet biexciton line. The triexciton emission is more complicated than the two first excitons as a significant number of recombination paths are possible. Two types of recombination events are possible illustrated in Figure 5.2(c). The X₃ recombination between the electron and hole ground states, |0,1,1⟩ (s-shell), results in lines in the vicinity of the X and X₂ lines while the X₃* recombination between the first excited states, |1,1,1⟩ (p-shell), results in lines at substantially higher energies. Cross recombination between e.g. an electron |0,1,1⟩ state and a hole |1,1,1⟩ are forbidden due to selection rules. Transition probabilities are only high between levels of the same principal quantum numbers.
Chapter 5. Optical Spectroscopy of Nanowires

5.2.1 The Quantum Dot Spectrum

In Paper II the PL spectra of InP nanowires with InAs$_{0.85}$P$_{0.15}$ QD heterostructures were studied. TEM studies showed that the wires had a WZ crystal structure and only a few ZB segments were observed but typically no more than a few nm long. Since the WZ polytype of InAs and InP only has been observed in nanowires the material properties are not well known. The PL spectrum of two InP nanowires with and without a QD can be seen in Figure 5.3. Pure InP nanowires exhibited broad luminescence between 1.4 and 1.5 eV. ZB InP has a band gap of 1.42 eV [78] while the band gap of WZ InP has been reported to be 1.50 eV [79, 80], the luminescence in this range is therefore expected to come mainly from charge carriers confined in the ZB segments.

Nanowires with a single QD showed discrete lines between 0.94 and 1.1 eV with a state filling behaviour and size dependence indicative of QDs. They furthermore showed a broad complex set of lines from 1.2 eV all the way up to the InP signal. This indicates that InAs$_x$P$_{1-x}$ domains in the wires give rise to localized states other than those of the dot. An As rich tail after the dots due to As carry-over was observed in the TEM measurements but it is also possible that As-P exchange occur on the nanowire side facets and either of these effects could be the cause of the InAs$_x$P$_{1-x}$ domains.

![Figure 5.3:](image)

Figure 5.3: The blue trace shows the PL spectrum of a pure InP nanowire with no QD. The red trace shows the spectrum of a nanowire with a single InAs$_{0.85}$P$_{0.15}$ QD. Except for the QD luminescence there is a complex set of lines above 1.2 eV corresponding to InAs$_x$P$_{1-x}$ domains formed due to As carry-over or As-P exchange on the nanowire side facets.

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The simplest way to assign the QD peaks is to study the power dependence of the QD PL spectrum and follow the successive state filling. Such power dependence from one of the QDs is seen in Figure 5.4(a). At a low excitation power density the dot is filled with only one exciton at a time and only a single peak is visible. As the excitation power density is increased a biexciton peak appears and when it reaches a point where the dot on the average is filled with two excitons the single exciton peak starts to diminish. The dot is constantly replenished with new charge carriers and a situation with only one exciton in the dot rarely occurs. At even higher excitation power density the p-shell starts to fill and the $X_3$ and $X_3^*$ lines appear and rise together with increased excitation power density. It has here been assumed that the QD is neutral, i.e. that there is no excess of either electron or holes in the dot. Charged excitons would give rise to multiple lines due to the larger number of spin configurations. The few discrete peaks in the spectra indicate that the QDs generally are neutral.

Figure 5.4: (a) Excitation power dependence for a single QD showing the $X$, $X_2$, $X_3$ peaks in the s-shell as well as the p-shell. (b) Size dependence of the QD spectrum for three dots with diameters 11, 16 and 22 nm at three different excitation powers. $P = 800 \text{ W/cm}^2$. 
5.2.2 Size Dependence of the Quantum Dot Spectrum

The size dependence of the QD spectrum was studied by varying the diameter, \( d \), of the dots from 9 to 22 nm. The dots were grown using only In stored in the Au particle, as described in chapter 4.1.2, so that the QD height, \( h \), scaled with the diameter as \( h = 0.35d \). To reduce surface effects a 14 nm shell was grown around the dots using only the InP tapering. As the shell thickness was constant for all samples the ratio between the shell thickness and the dot diameter decreased with increasing diameter. Thus the strain induced by the shell on the dot was smaller for large dots. Figure 5.4(b) shows the normalized PL spectra for three different dots with diameters 11, 16 and 22 nm. For each dot the spectrum at three different excitation power densities is presented, the bottom trace shows the single X line, the middle trace shows both the X and X2 lines while the top trace shows the excited states. As can be seen in the spectrum of the QD with 22 nm diameter emits at 1300 nm, the important telecommunication window where fiber optics losses are minimized. The spectra blue shift towards higher energies and the level splittings increase with decreasing dot size as a consequence of stronger confinement. The X2 peak generally appears on the high energy side of the X peak, i.e. the biexciton binding energy is negative indicating that repulsive electron-electron, hole-hole Coulomb interactions dominate over attractive electron-hole interactions. Such antibinding biexcitons do not occur in quantum wells but can form in a QD as they are stabilized due to the full confinement. Figure 5.4(b) shows the general trend where the small dots display negative X2 binding energies while a few of the larger dots displayed positive binding energies. Rodt et al. [81] has reported a similar antibinding to binding transition with increasing dot size for self-assembled InAs-GaAs QDs while the opposite behavior has been reported by Persson et al. [82] for self-assembled InP-GaInP QDs. The few particle interactions in the QDs are however very sensitive to the size and shape of the dot and it is difficult to compare different systems.

As mentioned earlier QDs are often modeled using the \( k\cdot p \) method. A model, no matter how sophisticated, is however never better than its inputs. As InAs and InP only exists in the WZ polytype when grown as nanowires there is a lack of material parameters for these structures. In Paper II we therefore fitted experimental data to a strain dependent \( k\cdot p \) model with ZB material parameters using the electron effective mass as a fitting parameter. The energy splitting between the ground and first excited state emission, \( \Delta E \), mainly depends on the level splitting between the electron states and only depends on confinement in the lateral direction. For a deep enough potential well the splitting can be described by (5.2) and \( \Delta E \) has the following diameter dependence:

\[
\Delta E = \frac{2\hbar^2}{m_e} \left( \chi_{1,1}^2 - \chi_{0,1}^2 \right) \frac{1}{d^2}
\]  

(5.4)
from which the electron effective mass, $m_e$, can be determined. In Paper II the full strain dependent \textbf{k.p} model was of course used to determine $m_e$, the above discussed simple model is only for illustrative purpose. The inset of Figure 5.5 shows the experimentally measured $\Delta E$ as a function of diameter together with the results of the \textbf{k.p} calculations using the electron effective mass of ZB InAs$_{0.85}$P$_{0.15}$, $m_e^{ZB}$, (dotted line). It was found that $m_e=2m_e^{ZB}$ gave the best fit to experimental data (solid line). The inset of Figure 5.5 shows the experimentally measured $\Delta E$ as a function of diameter together with the results of the \textbf{k.p} calculations using $m_e=2m_e^{ZB}$. It was found that the band gap of WZ InAs$_{0.85}$P$_{0.15}$ was determined from the offset between experimentally determined transition energies for the ground state and the results of the \textbf{k.p} calculations using $m_e=2m_e^{ZB}$. It was found that the band gap of WZ InAs$_{0.85}$P$_{0.15}$ is larger by 190 meV compared to the ZB polytype. Figure 5.5 shows the experimentally determined transition energies for the ground state and the calculated transition energies using $m_e=m_e^{ZB}$ (dotted line) and $m_e=2m_e^{ZB}$ (solid line), the calculated values are shifted 190 meV for clarity.

**Figure 5.5:** Ground state transition energy as a function of the QD diameter, $d$. The height, $h$, scales with diameter as $h=0.35d$. Inset: Energy splitting between the ground and first excited state, $\Delta E$, as a function of the diameter. Experimental data are plotted as points with error bars indicating the standard deviation. Lines represents calculated values using $m_e=m_e^{ZB}$ (dotted line) and $m_e=2m_e^{ZB}$ (solid line). The calculated values for the ground state transition energies are shifted 190 meV upwards in energy for clarity.

The increase in band gap is large considering that ZB InAs$_{0.85}$P$_{0.15}$ has a band gap of 560 meV when not strained [78], but it is in reasonable agreement with the existing studies. Trägårdh \textit{et al.} [83] and Zanolli \textit{et al.} [84] have reported a band gap increase of 150 and 120 meV respectively for WZ InAs nanowires compared to the ZB polytype. As Zanolli noted part of the increase could however be due to differences in the strain between the two polytypes. The increased electron
effective mass can be compared to the nitrides where material parameters exist for both the WZ and ZB polytype and the electron effective mass increases between 0 and 33 % for the WZ polytype compared to ZB (InN and GaN respectively) [85]. In this respect a 100 % increase is unexpectedly large. However, considering the large fractional difference in band gap between the polytypes a large change in effective mass is also motivated.

To fully describe the system a WZ strain dependent $k\cdot p$ model should be used and the material parameters for WZ InAs and InP need to be determined. The elastic constants and band structure parameters for the WZ polytype could then be determined by studying the effects on the PL spectrum when varying the size and shape of the QDs as well as the shell thickness.

### 5.3 Core-Shell Nanowires

Electrons and holes can recombine either radiatively or non-radiatively and although the former is preferred for optical devices the latter can never be reduced to zero. There is thus a competition between radiative and non-radiative recombination. If $\tau_r$ and $\tau_{nr}$ are the radiative and non-radiative lifetimes respectively the total recombination probability is the sum of the radiative and non-radiative probabilities:

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$$  \hspace{1cm} (5.5)

The internal quantum efficiency is then given by:

$$\eta_{int} = \frac{\tau_r^{-1}}{\tau_r^{-1} + \tau_{nr}^{-1}}$$  \hspace{1cm} (5.6)

This is however not necessarily the same as the external quantum efficiency as not all photons emitted internally may escape the semiconductor due to total internal reflection.

Non-radiative recombination is described by the Shockley-Read-Hall model where a localized energy state in the forbidden band gap acts as a stepping stone between the conduction- and valence band [86, 61]. In the recombination process the recombination center captures one electron from the conduction band and one hole from the valence band while the energy is dissipated as phonons. The capture rate of both an electron and a hole is the highest when the energy state is at middle of the band gap and thus defects that create such states are the most effective non-radiative recombination centers. Such defects are e. g. vacancies, interstitials, other dislocations and especially surface states.
5.3.1 Surface Passivation

Two different shell materials, GaInP and AlInP, were used to passivate GaAs nanowires in Paper III and IV. Typical spectra from the core and the shell of a GaAs-GaInP and a GaAs-AlInP wire are seen in Figure 5.6. For each wire a single PL peak from the core is observed around 1.52 eV, the band gap of GaAs at 0 K. No significant strain shift in the position of the peak was observed, indicating that the shells on the average are lattice matched to the core with a composition around Ga\(_{0.5}\)In\(_{0.5}\)P and Al\(_{0.5}\)In\(_{0.5}\)P respectively. The shell spectra on the other hand display multiple peaks indicating that the shells are not homogeneous. When lattice matched to GaAs, Ga\(_{0.5}\)In\(_{0.5}\)P has a direct band gap of 2.0 eV while Al\(_{0.5}\)In\(_{0.5}\)P has an indirect band gap of 2.35 eV [78], for both shell materials the peaks appear at lower energies. This means that In rich domains are formed during shell growth which create local band gap minima that collect the charge carriers and shift the spectrum towards lower energies. In the cross-sectional TEM discussed in chapter 3.2.2 only Al rich domains were found and In rich domains were not observed. However, if they form in the corrugations on the sides of the nanowires they could very well be so small that the signal averages out in the TEM signal.

![Figure 5.6: Typical spectra from GaAs-GaInP (purple trace) and GaAs-AlInP core-shell nanowires. Expected band gaps for lattice matched shells are marked with arrows. Measurement performed at 5 K.](image)
The effect of the shell on the emission efficiency of the GaAs core is illustrated in Figure 5.7(a) where a wire without shell is compared to a wire with a GaInP shell. As the shell not only removes the GaAs surface states but also increases the volume of the wire so that it can absorb more light the wires where excited below the band gap of the shell. This way only the GaAs core was excited and volume effects can be disregarded. The effect of the removal of the GaAs surface states was an enhancement of the emission efficiency by 2 to 3 orders of magnitude. These measurements were made on wires with a 60 nm GaAs core since luminescence from thinner wires without shell could not be detected with our setup. For thinner wires the emission enhancement could therefore be even greater.

![Figure 5.7](image)

**Figure 5.7:** (a) PL spectrum from GaAs nanowires with and without GaInP shell. The shell enhances the emission efficiency 2 to 3 orders of magnitude. Measurement performed at 5 K. (b) Time-resolved PL from a GaAs-GaInP wire. The luminescence decay of the core was on the order of 100 ps while the shell generally showed a slower decay. Measurement performed by J. Trägårdh.

Except for an enhancement of the emission efficiency the effect of the removal of the GaAs surface states should also be seen in the luminescence decay time. The decay time should increase as the non-radiative surface recombination rate decreases. Time-resolved PL measurements on lattice matched GaAs-GaInP core-shell nanowires gave a decay time of around 100 ps for the core, see Figure 5.7(b). This is comparable to the <80 ps decay time reported by Titova et al. [20] for GaAs-AlGaAs core-shell nanowires. Unfortunately a comparison to the decay of a pure GaAs nanowire could not be made as the luminescence signal from these was too weak for the streak camera. The decay time around 100 ps is low compared to high quality GaAs quantum well structures which have decay times that are at least one order of magnitude larger [87], this suggest that although the surface states are removed other non-radiative recombination centers exist. Such recombination centers could e. g. be interface states at the core-shell boundary or they could be
related to the twins. Joyce et al. [88] reported improved PL emission from twin free GaAs-AlGaAs core-shell nanowires. Whether it is the twin boundaries themselves that act as recombination centers or if these are associated with the corrugated GaAs-AlGaAs interface which is a consequence of the twins is not known. It however seems unlikely that rotational twins form deep energy levels in the band gap as they are not associated with any unsaturated bonds.

### 4.3.2 Strain in Core-Shell Nanowires

Strain effects on the band gap of the core were measured for GaAs-Ga$_x$In$_{1-x}$P core-shell wires with lattice mismatched shells and compared to strain dependent \( k \cdot p \) calculations in Paper III. Four different samples were studied with a shell composition of Ga$_{0.34}$In$_{0.66}$P, Ga$_{0.48}$In$_{0.52}$P, Ga$_{0.58}$In$_{0.42}$P and Ga$_{0.69}$In$_{0.31}$P respectively according to XEDS point measurements. Thus the lattice mismatch to the GaAs core ranged from -1.3\% to 1.3\%. The core diameter was 40 nm while the shell thickness varied between 70 and 100 nm. If no strain relaxation takes place in the shell it should be sufficiently thick to fully strain the core. The linear deformation potential theory calculations showed that the strain situation hardly changes when the shell reaches a thickness equal to the core diameter. Figure 5.8 shows the spectra of representative nanowires from the four different samples. The red trace represents a situation where the core is under tensile strain, the green trace represents almost lattice matching and the blue and the black trace represents the situation where the core is under compressive strain. The band gap of the core was tuned from 1.37 to 1.61 eV. A broadening in the PL peak from the core was observed for the compressively strained samples, possibly due to inhomogeneous strain from the shell.

In Figure 5.9 experimental values of the band gap of the core and the shell respectively are plotted as a function of the Ga content in the shell, and compared to strain dependent \( k \cdot p \) calculations. Experimental values are plotted as crosses while solid and dashed lines represent calculated values for the core and the shell respectively. For the shell the centroid of the multiple peaks was taken as the average band gap which leads to an underestimation as small band gap regions contribute more to the spectrum than the ones with large band gap.
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Figure 5.8: PL spectra of GaAs-Ga$_{x}$In$_{1-x}$P core-shell wires with different shell composition. The core diameter was 40 nm while the shell composition varied between 70 and 100 nm. By straining the core the band gap was tuned between 1.37 and 1.61 eV.

Figure 5.9: The band gap of the GaAs core and GaInP shell as a function of $x$, the Ga content in the shell. Experimental values are plotted as crosses while the red and blue lines represent calculated values for the core and shell respectively.
Chapter 6

6. Tubular Nanowires

Just as the micro- and nanofabricated components of the integrated circuit have reduced the space, time and cost needed for calculations it is believed that micro-and nanofluidic devices will enable fast and cheap chemical and biological analysis and processing [89]. In this field nanowire and nanotubular structures are interesting as they have dimensions smaller than biological cells and can be used to probe and manipulate biological processes within the cells.

Freestanding nanotubes can be produced either from a negative or positive template [90]. For negative templating a porous membrane is used and a conformal oxide coating is formed on the pore sidewalls using e.g. atomic layer deposition (ALD) after which the membrane is removed leaving freestanding nanotubes. Positive templating makes use of polymer nanorods or semiconductor nanowires which are oxidized or coated with an oxide layer using ALD, the nanorod/nanowire is subsequently removed leaving the freestanding shell as a nanotube. The use of nanowire templates to fabricate nanotubes for nanofluidic applications has largely been pioneered by the Yang group who has demonstrated both detection of single DNA molecules [91] and solution field effect transistors [92] using nanotubes prepared from a nanowire template, tubular nanowires.

6.1 Cell Injection

The delivery of cell membrane impermeable molecules, such as drugs, proteins and nucleic acids, to cell cultures is a challenging task in cell biology [93]. The use of viral vectors or vesicle fusion exploit normal cellular functions but are often applicable only to certain cell types and/or molecules. Alternatively the membrane can be chemically, electrically or mechanically disrupted to make it temporarily permeable, methods that however reduce the viability of the cells. Microinjection is frequently used for loading cells but as the cells are injected one at a time using a glass needle it is a very time consuming method. It has therefore been proposed that arrays of microneedles can be used to treat entire cell cultures at the same time [93]. Another method is to use arrays of non-hollow probes coated with the molecule of choice to spear the cells. With these methods the cells are deposited on top of the needles/probes which penetrate the cell membrane and the cells are then cultured on this bed of nails. As the cells are cultured for several days it is
imperative that the size of the needles/probes is sufficiently small to minimize the damage of the cell membrane. In light of this nanowires and tubular nanowires are ideal tools for cellular delivery. Hällström et al. and Kim et al. have shown that cell viability is excellent on nanowires [94, 95] but reduces when the nanowire diameter gets too large (≈ 400 nm) [95].

6.2 Tubular Nanowires for Cell Injection

In our approach to produce tubular nanowires for cell injection we initially converted GaAs-AlInP epitaxially grown core-shell nanowires into nanotubes by selectively etching out the core as described in Paper VIII. This material system was not totally bio-compatible and the method was later changed so that an Al₂O₃ shell, deposited by ALD, was used instead of the epitaxial AlInP shell to improve the cell viability. I will here only cover the latter method as the methods are very similar. Figure 6.1 shows a schematic illustration of the process. In the first step the GaAs (111)B substrate was mechanically dimpled from the back side. Using a rotating copper wheel covered with diamond paste a trench was created at the backside of the substrate leaving 50 μm to the substrate surface. This was done in order to facilitate the backside connection to the tubes at a later stage. Size selected aerosols were then deposited on the front side of the substrate and nanowires were grown (a). A 10 nm thick layer of Al₂O₃ was subsequently deposited using ALD, covering the nanowires as well as the substrate surface (b). The nanowires were partially embedded in a benzocyclobutene (BCB) film, a spin-on dielectric with good mechanical properties, and then again capped with a 55 nm thick Al₂O₃ layer (c). A second polymer film, photoresist S1813, was used to cover the wires leaving only the tips sticking out (d) which could then be scraped off using a piece of clean room paper, (e), to access the core for etching. The back side connection to the tubes was created using a focused ion beam and wet etching with a drop of H₂O₂:H₂SO₄:H₂O (8:1:1) solution placed at the bottom of the trench, thus freeing the membrane (f). In order not to expand the membrane as the tubes were etched out, this was done from the front side by placing a drop of either H₂O₂:H₂SO₄:H₂O (8:1:1) or the slower etchant H₂O:NH₃:H₂O₂ (140:3:1) over the membrane (g). Finally the S1813 was removed leaving freestanding Al₂O₃ nanotubes with average outer and inner diameters of 200 and 70 nm respectively suspended by a BCB membrane, with a diameter around 100 μm. The membrane is sandwiched between Al₂O₃ layers in order not to leak any poisonous substances to the cell cultures. A reservoir for the injecting solution was glued to the back side connection using silicone rubber. Figure 6.2(a) shows a top view of two tubular nanowires.
Figure 6.1: Schematic of nanotube fabrication. (a) Growth of nanowires on a dimpled substrate. (b) Al₂O₃ deposition. (c) The nanowires are partially embedded in a BCB film which is capped by a second Al₂O₃ layer. (d) The wires are embedded in S1813. (e) Tips are cut. (f) Backside connection is etched. (g) Tubes are etched. (h) S1813 is removed.

Figure 6.2: (a) SEM image of the tubular nanowires in top view. (b) Macrophage deposited on tubular nanowires.

Mouse macrophage cells expressing green fluorescent protein (GFP) were deposited on the tubular nanowires, Figure 6.2(b) and incubated for 24 hours before injection. The samples were placed with the cells facing down submerged in a cell culture medium with the reservoir sticking up. A solution of culture medium and 80 μM propidium iodide (PI), a nucleic acid stain which red fluorescent signal increases dramatically when it enters the cell and binds to DNA, was used for the
6.2 Tubular Nanowires for Cell Injection

cell injection. This molecule cannot enter cells with intact cell membranes. The cells were studied using a confocal microscope as the PI solution was applied in the reservoir and allowed to diffuse through the tubes into the cells. Figure 6.3(a) shows an overview of the sample after injection with the membrane edges marked by a yellow circle. Cells which are injected are red fluorescing while not injected cells are green only. The membrane can be slightly under etched as illustrated in Figure 6.1(h) and therefore cells in the vicinity of the membrane also express a PI signal since they too are connected to the PI reservoir. Figure 6.3(b) is a superposition high resolution image of a single cell (green) on the membrane (blue). The focus plane in the cell image is placed at the tips of the nanotubes and PI can be seen emerging as red spots within the cell. Figure 6.3(c) shows snapshots of a cell on the membrane as the PI solution diffuses through the tubes and into the cell.

As described in Paper VIII, macromolecules such as DNA can also be transported through the nanotubes. In its folded state a DNA strand is however too large to diffuse through the tubes and it has to be pulled through electrophoretically. In Paper VIII T4-phage DNA 170 kbp (55 μm) long were stained with TOTO-1 intercalating dye and applied to the back side of the membrane while the front side was monitored in a microscope. No cells were used in these experiments, they were only designed to check whether DNA transport was at all possible. When a bias of 5 V was applied DNA emerged from the tips of the nanowires. Figure 6.4 shows a time series of images where a DNA strand emerges at t=0 and then moves to the right, the DNA is marked by a green arrow. Each image is a superposition of a white light image of the membrane, color coded blue, and the fluorescence image, color coded red. The tips of the tubes are seen as dark circles as an effect of diffraction. The large electric fields required (1 V/μm for a 5 μm long tube!) and the fact that many of the DNA strands stuck inside the tubes however indicates that the surface charge of the inner walls needs to be modified for transport to be efficient. An immobile DNA strand stuck in a nanotube is marked by a yellow arrow in the first frame. It is therefore clear that smaller molecules such as PI can be delivered to cell cultures as they easily diffuse through the tubes but macromolecules cannot be delivered at this point.
Figure 6.3: Injection of PI in macrophages. (a) Overview of the cell culture, the membrane edge is marked with a yellow circle. Cells that are not injected are green fluorescing while injected cells are red fluorescing. (b) Zoom in of a single cell on the membrane, PI can be seen emerging from the nanotube tips as red spots. (c) Time series showing the uptake of PI in a cell.

Figure 6.4: Time series of images where a DNA strand emerges from a nanotube at t=0, marked with a green arrow. A yellow arrow in the first frame marks an immobile DNA strand.
Appendix

Characterization Techniques

1. Electron Microscopy of Nanowires

Due to the small size of the nanowires the spatial resolution of optical microscopes is not enough to study them in detail. The nanowires are only larger than the wavelength of visible light in the axial direction. Thus an illumination source with a smaller wavelength must be used. In electron microscopy a high energy electron beam where the electrons have a de Broglie wavelength in the pm regime is used as illumination source for imaging.

1.1 Scanning Electron Microscopy

In scanning electron microscopy (SEM) an electron beam is focused to a small spot size. The beam is deflected and scanned over the sample surface using the electromagnetic field of the scan coils. Some of the electrons are backscattered from the sample while others are absorbed. The energy transferred to the sample by the absorbed electrons is enough to generate new electrons, secondary electrons, which can escape the sample if generated close to the surface. Detectors register the signal of the secondary and backscattered electrons as the beam scans over the sample and a topological image of the sample can be produced. The resolution of SEM is limited by the spot size and is generally around 10 nm.

SEM characterization was done routinely on all nanowires after growth. Diameter and side facet morphology was checked in top view projections and the length was measured in side view with the sample tilted from the e-beam.
1.2 Transmission Electron Microscopy

In transmission electron microscopy (TEM) the image is generated by electrons transmitted through the sample which therefore must be very thin. Generally the beam is not focused but collimated and the sample is tilted in so that one crystal direction is parallel to the beam. The resolution limit is around 0.1 nm giving atomic resolution. However, to be precise all information that is extracted is an average of the whole atomic column along the beam direction. The electrons can either be transmitted straight through or scattered at specific angles. Imaging using transmitted or scattered electrons is called bright-field and dark-field imaging respectively in analogy to optical microscopy. A hybrid between SEM and TEM is scanning transmission electron microscopy (STEM) where the beam is focused to a small spot size and scanned over the sample (although still parallel to the optical axis). STEM improves the point resolution slightly compared to TEM and gives the possibility of elemental analysis with e.g. X-ray energy dispersive spectrometry (XEDS).

In this work high-angle annular dark field scanning TEM (HAADF-STEM) was used for imaging. This is a technique where only the electrons scattered at high angles are used to produce the image giving a strong atomic number contrast. The nanowires were normally studied in side view projection but cross-sectional studies were also performed to investigate the morphology and composition of the core-shell nanowires radially. For these studies the wires were embedded in an epoxy resin as they were standing on the substrate and 30 nm thin slabs were cut using an ultramicrotome with a diamond knife, see Figure A.1. The cut was made at a 2° angle giving wire cross-sections from different heights of the wires. The slabs were then placed on a Cu-grid and the cross-sections were imaged along the [1,1,1] axis.

**Figure A.1:** Schematic illustration of the microtomy. (a) 30 nm thin slabs were cut at an angle giving wire cross-sections from different heights of the wires. (b) Top view of the cross-sections within an epoxy slab.
1.3 X-ray Energy Dispersive Spectrometry

X-ray energy dispersive spectrometry (XEDS) is a tool for elemental analysis. It can be used together with either SEM or STEM. An electron beam is focused on the sample and excites electrons in the inner shells of the atoms. As these inner shells are filled by electrons from outer shells characteristic X-rays are emitted. The spectrum of these X-rays is a fingerprint of the atoms and can be used for elemental analysis.

2. Scanning Tunneling Microscopy

For surface studies with atomic resolution scanning tunneling microscopy (STM) is the ideal tool. A sharp conducting tip is brought in proximity of the sample and a voltage is applied between them. As the tip gets close enough electrons can tunnel across the vacuum barrier between the tip and the sample. The tunneling current is exponentially dependent on the width of the vacuum barrier or in other words the distance between the tip and the sample. This strong dependence gives the possibility of topological imaging of a surface with atomic resolution. However the current is also directly proportional to the surface local density of states giving elemental contrast to the images. It is therefore important to remember that the images are a combination of geometry and electronic structure. Imaging can be performed either at negative or positive bias. Negative bias means tunneling electrons from the sample to the tip and mapping out filled states or in other words imaging the group V material. Positive bias means tunneling electrons from the tip to the sample and mapping out empty states or in other words imaging the group III material. Imaging is normally done in a constant current mode where the tip is scanned over the surface while keeping the current at a fixed value. For each measuring point an advanced feedback system adjusts the tip-sample distance using piezoelectrical height adjustment with a sub-Ångström precision, it is these height adjustments that are displayed as the image.

To study defects, impurities and heterostructure interfaces within a nanowire using STM, the wire has to be cleaved so that an atomically flat cross-section is exposed. For STM studies free standing wires cannot be used but they have to be embedded. For this work the wires were grown on (0,0,1) GaAs substrates instead of (1,1,1)B. The wires were embedded in AlGaAs as this material easily is lattice matched to GaAs. The embedding was done by extended shell growth, in principle the shells were grown so thick that they merged and embedded the wires completely. Cleaving and imaging was done in the {1,1,0} plane. Figure A.2 illustrates the principle of the cross-sectional STM studies on embedded nanowires.
Figure A.2: Schematic illustration of the STM principle on embedded nanowires.
References


[18] Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M.; *Science* **2001**, *293*, 1289-1292


[28] Herman, M. A.; Richter, W.; Sitter, H. *Epitaxy*, Springer-Verlag, **2004**
References


References


References


[74] Wulff, G. Z. Kristallogr. 1901, 34, 449


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References


