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Abstract

Wurtzite phase InGaP nanowires are grown and characterized for research into 3D LEDs with increased emission efficiency in the green and amber range. GaP nanowire cores are grown with a Vapor-Liquid-Solid growth process with the aid of gold nanoparticles. InGaP shells are then grown around these cores, after which another GaP layer is grown, creating a quantum well structure. The nanowires are characterized through scanning electron microscopy, transmission electron microscopy and photoluminescence spectroscopy. A buffer layer, gradually increasing in In concentration in the radial direction, is grown before growing the InGaP shell, and the influence of this layer on the physical and optical characteristics of the nanowires is examined. While the buffer layer aids in growing straight nanowires, it also induces undesirable effects in the photoluminescence emission, broadening and weakening the spectrum considerably. Multishell nanowires are grown by alternating GaP and InGaP layers, resulting in multiple quantum wells inside a single nanowire. These nanowires exhibit increased emission intensity compared to single quantum well nanowires, implying that increasing the number of quantum wells in a nanowire is beneficial to the emission. The emission strength of all nanowires grown here decreases significantly with increasing temperature, resulting in very weak emission in a very broad range at room temperature. More research is still to be done into increasing photoluminescence efficiency of these nanowires at normal operating temperatures for LEDs before a device can be developed. In general, there is still more research to be done into optimization of the growth process and improving the optical properties of these wurtzite InGaP nanowires, but the initial results are promising.
1 Introduction

A long-standing problem in Solid-state lighting (SSL) is the lack of efficient emitting materials in the green and amber range of the visible light spectrum. This problem is commonly known as the green gap.
Currently the workaround for this problem is to coat InGaN LEDs, which emit in the UV or blue range, with phosphors. This coating absorbs the emission and re-emits light at a higher wavelength.
However, for reasons such as the cost of phosphor and a need for more narrow wavelengths of emission, it is desirable to develop a direct material emitting in this range.

Concurrently, non-planar LEDs are a growing topic of interest in the SSL industry, as some of these device structures allow for higher efficiencies and novel properties.
Nanowires are of particular interest in the field of LEDs. These 3D, wire-like nanostructures allow for the use of certain alloys or growth of crystallographic structures that are not possible to realize in bulk material.

For this project, the wurtzite phase AlInGaP nanowire LED is studied for insight into 3D LED structures and a possible way to solve the green gap problem.
It is possible to create semiconductor heterostructures in nanowires, such as a core-multishell structure, which exhibit quantum well-like behavior.
Before venturing into AlInGaP nanowire LEDs, the InGaP variant has to be researched and understood. This is the focus of this particular thesis.

The growth process of core-multishell wurtzite InGaP nanowires is described, and the physical properties of these nanowires are characterized.
The main objective in this thesis is to characterize the optical behavior of these nanowires through photoluminescence spectroscopy.

Wurtzite InGaP structures are grown with various properties and are then optically characterized.
The aim is to optimize the wurtzite InGaP nanowire growth through iteration and characterization, in preparation for research into wurtzite AlInGaP nanowire LEDs.
2 Background

2.1 Semiconductors

Semiconductors are a material group of which the conductivities are between the values of metals and of insulators [1]. A possible classification of semiconductors is the distinction between compound and elementary semiconductors. Compound semiconductors consist of either group III and V elements (III-V) or group II and IV elements (II-IV) [2]. Elementary semiconductors are composed only of group IV elements [1].

\[
\begin{array}{ccc}
\text{III} & \text{IV} & \text{V} \\
B & C & P \\
Al & Si & As \\
Ga & Ge & Sb \\
In & & \\
\end{array}
\]

Figure 2.1: Table of semiconductor materials and their respective groups.

2.1.1 Band gap

All solids have their own characteristic energy band structure. The difference between semiconductors, metals, and isolators can be explained using the band structure, as can be seen in figure 2.2.

\[
\text{Metal} \quad \text{p-type} \quad \text{Intrinsic} \quad \text{n-type} \quad \text{Insulator}
\]

Figure 2.2: Diagram of band structures of different types of materials, filled electron states are indicated in gray.

The band gap is defined as the energy difference between the bottom of the conduction band and the top of the valence band. An insulator is a material with a large band gap, which thermally excited electrons cannot cross. In contrast, a semiconductor has a band gap small enough that thermally excited electrons can cross it at temperatures below the melting point of the material. Finally, conductors have a band structure so that there is no band gap, as the conduction and valence band overlap in these materials.
The band gap energy of a semiconductor is dependent on a multitude of factors, such as material composition, temperature, strain, and (crystalline) structure.

2.1.2 Doping

An important property of semiconductors is that their electrical properties can be modified by introducing impurities. This process is known as doping. Two types of doping can be distinguished.

In **n-type** doping an atom in the semiconductor crystal is replaced by an atom that has one valence electron more than the original material, this atom is then called a **donor** [2]. This electron is free to move through the material and acts as a charge carrier. It requires less energy to be excited into the conduction band than the electrons of the original material. In this case the electrons are the majority charge carriers, hence the term n-type.

An example of n-type doping is doping silicon with phosphorus. Silicon has 4 valence electrons (4-valent) while phosphorous is 5-valent (Figure 2.1).

In contrast, **p-type** doping is done with a dopant that has one valence electron less than the original material. These impurity atoms are called **acceptors**, as they accept electrons from the valence band, leaving holes in this band [2] In case the holes are the majority charge carriers and dominate the conductivity, the material is p-type.

Again taking the example of silicon, in this case boron (3-valent) could be used for p-type doping (Figure 2.1).

2.1.3 Band structure

In a solid state, the outermost electrons, which are loosely bound, detach from their atoms and move throughout the material. The existence of band structure is a result of these electrons moving in a periodic potential. A derivation of this behavior with a simplified periodic potential, the Dirac Comb, is given by [3]. This derivation is summarized as follows;

The roaming electrons are affected by the nuclei, which are evenly spaced. This potential is represented by a Dirac Comb, a series of evenly spaced delta function spikes.

Bloch’s theorem states that in a periodic potential repeating itself after a distance \(a\) the wavefunctions satisfying the Schrödinger equation can be taken to satisfy

\[
\psi(x + a) = e^{iKa} \psi(x)
\]  

(2.1)

We can use this theorem to generate the complete solution after solving the Schrödinger equation in a single cell. The Dirac Comb is represented by

\[
V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)
\]  

(2.2)

connecting the x-axis back to itself after \(N\) (Avogadro’s Number) periods.
In the region $0 < x < a$ the Schrödinger equation can be written as

$$\frac{d^2 \psi}{dx^2} = -k^2 \psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (2.3)$$

This results in the general solution

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad (2.4)$$

in this region.

In the cell to the left of the origin, Bloch’s theorem states that the wave function is

$$\psi(x) = e^{-ika} [A \sin(k(x+a)) + B \cos(k(x+a))] \quad (2.5)$$

on the interval $-a < x < 0$. Continuity of the wavefunction at $x=0$ and a discontinuity in the derivative proportional to the strength of the delta function results (see [3] for details) in a condition for the possible values of $k$ of

$$\cos(Ka) = \cos(ka) + \frac{ma}{\hbar^2 k} \sin(ka) \quad (2.6)$$

Plotting the right side of this equation as

$$f(z) \equiv \cos(z) + \frac{\beta \sin(z)}{z} \quad (2.7)$$

gives the following graph.

![Graph of f(z) (Equation 2.7) for $\beta=10$ [3].](image)

In this figure the "allowed" values of $f(z)$ lie between -1 and 1, since $f(z) = \cos(Ka)$. To put it differently, there are allowed bands of $k$ separated by forbidden gaps. In reality the potential is not as simple as a Dirac Comb, but the band structure arises from any periodic potential used to approximate nuclei separated by fixed distances.

A material where a band is entirely filled acts as an insulator, since a large energy will be needed for an electron to jump across the forbidden gap. If a band is partially filled it takes a small amount of energy to excite an electron, creating a conductor.

In a semiconductor a band is almost completely filled, but due to the small band gap electrons are thermally excited into the next band, leaving holes in the band which also act as charge carriers.
In reality the band structure of a semiconductor is more complex than this. An important property of electrons and holes in the semiconductor material is their effective mass, which is derived from the energy-wavevector relation to be [2]

\[ \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 \epsilon}{dk^2} \] (2.8)

It is important to note that this is not the actual mass \( m \) of a charge carrier, but rather the mass that the carrier seems to have when responding to forces. As such, the effective mass may be very different from the actual mass, and may even be negative.

In certain semiconductors there may be a degeneracy in the energy bands. This means that there are different bands with the same energy at the point where the band gap is smallest. For example the so-called heavy hole and light hole bands, so called because their curvature or effective masses differ significantly.

### 2.1.4 Strain

Strain can have great effects on the properties of a semiconductor crystal. It can for instance lift the degeneracy of the light and heavy hole bands. This can result in a multitude of different effects, such as amplifying or stifling the optical emission depending on the type of strain applied.

Strain can also change the band gap size, with compressive stress typically widening and tensile stress diminishing the band gap [4].

In general it is found that hydrostatic strain, i.e. a strain that is uniform in all directions, does not lift the degeneracy of energy bands, because it does not change the crystal structure. Shear strain, in contrast, does affect symmetry and thus changes the crystal structure. This usually means that different energy bands are affected differently, and thus this can result in a degeneracy being lifted [4].

Strain can arise from lattice mismatches (common in heterostructures), doping, coating and many other processes crucial in producing devices [5].

Since strain is an inevitable consequence of producing heterostructures [5], figuring out how to mitigate it or even use it in a constructive manner is an important consideration for this project.
2.1.5 Heterostructures

Different semiconductor materials or materials with different dopant types can be joined with one common crystal structure to produce a heterostructure. The inequality in band gaps between these materials lead to interesting properties and a wide range of applications.

One such heterostructure is a p-n junction. It is created by doping a single semiconductor crystal in two separate regions, where one region is n-type and the other is p-type doped. The holes on the p side desire to diffuse to the n side to fill the entire crystal, as would the electrons the other way around. This diffusion creates an excess negative charge on the n side and a positive charge on the p side, thus creating an electric field. At some point this electric field is strong enough to inhibit further diffusion, causing an equilibrium.

![Diagram of a p-n junction](image)

**Figure 2.4: Diagram of a p-n junction**

Because of the jump in potential in the joining region, a p-n junction can function as a diode, allowing a large current to flow when a voltage is applied in one direction, and only a small current when the voltage is applied in the opposite direction.

If light is shone on a p-n junction, an incident photon that is absorbed creates an electron and a hole. These carriers diffuse to the junction, where the electric field separates them, producing a voltage across the barrier. This is called the photovoltaic effect, and it allows p-n junctions to be used as solar cells or photodetectors.
Another heterostructure that is more of interest for this particular project is the **quantum well**. This type of structure can be created when a material with a smaller band gap is wedged between two regions of a material with a higher band gap (barriers). The charge carriers are confined in this potential well in the direction of the structure, but are free to move perpendicular to the structure.

![Diagram of a semiconductor quantum well](image)

**Figure 2.5:** Diagram of a semiconductor quantum well

The system only behaves as a quantum well when the size of the "well" layer is small enough (typically up to 10 nm) so that the system is quantized [6]. Depending on the different semiconductor materials used, there may be a significant lattice mismatch between the well layer and the barrier layers, and the growth might not be epitaxial. It is however, up to a certain critical thickness, possible to grow layers with different lattice constants. These layers will be strained, but, due to their size, are able to adopt the local lattice constant, retaining epitaxial crystal structure [6].
2.2 Nanowires

Nanowires are nearly one-dimensional nanostructures with a typical length to width ratio greater than 10 and a width of less than some tens of nanometers [7]. This morphology leads to their physical properties being vastly different than bulk, 3-D structures. The wire-like structure and small radius give rise to different mobility behavior of charge carriers.

There are two approaches to growing nanowires, these being the bottom-up and the top-down approach.

The top-down approach is mainly done by lithographic methods, such as electron beam or X-ray lithography. The problem with these methods is that the resolutions needed to construct nanowires are hard to achieve, and methods that can achieve such resolutions are usually very slow compared to bulk production [7]. Etching processes are especially undesirable for semiconductor nanowires, as these processes invariably introduce surface defects and impurities, which influence the behavior of structures at nanoscale a great deal [8].

For these reasons the bottom-up approach, especially self-organized growth, where nanowires grow naturally without external techniques, is the more desirable approach for most applications. Several growth techniques have been developed for this approach. These include chemical vapor deposition, molecular beam epitaxy and vapor-liquid-solid (VLS) growth [8]. VLS growth is the technique that is used in this project.

Figure 2.6: Scanning Electron Microscope images of two different nanowire samples
3 Experimental Setup

3.1 Growth

The growth method used in this project is free-standing Metalorganic Vapour Phase Epitaxy or MOVPE (also known as MOCVD). This is a bottom-up growth method using gold particles to nucleate a nanowire on a substrate. The process is schematically represented in figure 3.1.

![Figure 3.1: Schematic illustration of the MOVPE growth process.](image)

(a) Gold nanoparticles are imprinted onto the GaP wafer. (b) Vapour phase reactants are injected, creating an alloy of the nanoparticle with group III elements. (c) Nucleation of the nanowire starts at the interface of the alloy particle and the wafer. (d) Growth proceeds perpendicularly to the wafer, material nucleates at the nanowire - nanoparticle interface. Figure from [9].

Gold particles are deposited onto a substrate. Precursors are then introduced in vapour phase, forming a liquid alloy with the gold particle. Introducing more precursors causes the gold-alloy particle to be supersaturated, which causes the precursors to precipitate at the particle-substrate interface, forming a solid wire [9].

The growth happens in the form of a wire and not in a random structure because of the anisotropy of growth rates. The growth direction perpendicular to the substrate grows fastest, and the slower growth rates of the other directions constrain the growth into a nanowire shape. In this project first a core of GaP is grown. Then the gold particle on top of the nanowire is etched away. After this the growth is started again, this time including Indium, so a radial shell of InGaP is grown around the wire. Another GaP layer is then grown around this shell. This process can be repeated several times to form multiple InGaP quantum wells wedged between GaP buffers. During this process HCl is supplied as an etching gas, etching away undesirable growth artifacts.

The advantage of growing a shell epitaxially around a GaP (wurtzite) core is that the shell takes on the crystal structure of the core. This is done because it is speculated to be impossible to directly grow wurtzite InGaP, and if it were possible it would entail re-optimizing the entire growth process, which is impractical.

Several parameters are attempted to be optimized during the course of these project. These include V/III ratio, growth time and HCl concentration.
3.2 Characterization

There are several ways to characterize nanowires, and a few will be discussed here. Scanning electron microscopy is used to check the length and width of nanowires, and gives insight into growth defects. Tunneling electron microscopy is used to determine the composition of a nanowire across its cross-section. Finally photoluminescence spectroscopy, the main focus of this thesis, is used to characterize the emission of the nanowires, which in turn can be used to make some statements about properties such as band-gap energy, internal and/or external quantum efficiency and defect emission.

3.2.1 SEM

A way of characterizing the growth of the nanowires on a somewhat superficial level is through scanning electron microscopy (SEM). SEM works by scanning the sample with a focused beam of electrons, which interact with atoms in the sample and produce signals that can be converted into an image. As can be seen in figure 3.2 SEM imaging can be useful for determining characteristics of the nanowires, both qualitatively and quantitatively. The SEM can be used to measure the thickness and length of the wires, and the images can be analyzed to see how uniform the sample is and how defective the growth is. The resolution that the SEM can achieve can be up to 1 nm.

![Figure 3.2: SEM images of wurtzite InGaP core-(multi)shell nanowires.](image)

determism
3.2.2 TEM

Transmission electron microscopy or TEM provides a more in-depth view of the composition and crystalline phase of the nanowires. In TEM, electrons are sent through the sample, interact with it, and are detected on the other side. Two imaging modes of the TEM are used, being High-resolution TEM (HRTEM) and Energy-dispersive X-ray spectroscopy (EDX).

![HRTEM image of a wurtzite core-shell nanowire.](image1)
![EDX graph of a wurtzite core-shell nanowire.](image2)

**Figure 3.3:** HRTEM and EDX images of a wurtzite core-shell nanowire. Courtesy of Dr. Marcel Verheijen.

HRTEM produces a high resolution image which is reconstructed from the electron beam that is detected after passing through the sample. This electron beam is ideally a plane wave, and its phase and amplitude are modulated by interaction with the atoms in the sample. Thus, the detected wave contains information about the sample’s structure. Since this technique has a resolution of around 1 Å, individual atoms can be resolved. HRTEM produces images such as figure 3.3a, from which a trained eye can determine the crystallographic phase. This technique is useful in determining whether the nanowires are growing without defects in the desired phase.

EDX graphs are produced by exciting a sample with a high-energy electron beam, which causes the atoms in the sample to emit x-rays. Because each element’s atomic structure is different, the x-ray energies can be mapped to elements. This can be used to produce graphs such as figure 3.3b, which show the concentration of the semiconductor materials in a cross-section of a nanowire. This is useful in determining whether the growth parameters such as III/V ratio have the desired effect.
3.3 Photoluminescence

An important tool in characterizing the semiconductor nanowires is photoluminescence spectroscopy. This technique provides useful information about the nanowires, such as band gap energy and the effect of defects.

Photoluminescence measurements can be done in several ways, starting with measuring the wires still on the wafer (as grown measurement). Doing spectroscopy this way gives insight into the behavior of an ensemble of nanowires as they would exist in a device, thus characterizing in a way the emission of said device. A small downside of this method is that the wafer might also exhibit photoluminescence, possibly leading to an inaccurate spectrum if the intention is to characterize only the wires. In a device the wafer would be replaced, so for this purpose it is also useful to be able to see the behavior of the sample without the wafer. It is however useful to see the behavior of a large ensemble of nanowires (macro-PL) as this is how they would behave in device. Most defects, unless they are structural, are averaged out (even though it is always desirable to have no defects).

Measuring the nanowires as grown in this setup entails measuring the emission of up to a few hundred nanowires at once. This means that any variance on a wire-by-wire basis is usually averaged out, which might not be desirable in order to understand the physical properties of individual wires.
It is possible to transfer the nanowires on a different, non-emitting substrate, such as SiOx. This can be done by rubbing the sample on a SiOx substrate or by transferring the wires with tweezers.

![Image of nanowires transferred onto a SiOx substrate. Captured with a camera magnified by an objective.]

As can be seen in figure 3.4 this process deposits the nanowires on the substrate in random orientations and the amount of wires in an area varies massively. This results in bunches of nanowires in some places, and single wires which are quite well isolated in others. Both of these features are interesting for photoluminescence measurements. Measuring the emission of the bunches gives the behavior of an ensemble of nanowires, as on the wafer, without the emission of the wafer interfering with the measurement. The more important part of this method of measurement (micro-PL) is that the behavior of a single nanowire or a small group of nanowires can be determined. This can give insight into the uniformity of a nanowire or the effect of defects on the emission of a single wire. Since most wires are oriented horizontally along the surface, it is possible to scan the laser spot along the length of a single nanowire, showing the degree of uniformity of a wire.
3.3.1 Setup

The setup used to determine the photoluminescence spectrum of the nanowires is as follows. Two different lasers are used, the first being a Cobolt 405nm diode laser, which delivers a continuous signal. The other laser is a 420nm pulsed laser. This laser delivers a 10ps pulse of laser light in selectable intervals ranging from 1 to 16 MHz. The pulsed laser can be useful in avoiding overheating the wires, which is speculated to occur at high powers when using the continuous laser.

![Figure 3.5: Part of the photoluminescence setup, showing the fiber containing the laser light (1) and the filter wheel (2).](image)

The light from either of these lasers is guided through a fiber optics cable (1) to the optical table. There it is reflected into a filter wheel (2) which is used to vary the intensity with which the samples are excited without having to manually place filters for each measurement. It is possible to filter the laser light further if even lower excitation powers are desired.
After passing through the filter wheel (2) the laser light passes through some additional filters (3) and is guided into a beamsplitter cube (4). This is a 90:10 beamsplitter, set up so that 10% of the laser power is directed to the power meter (5) in order to determine the power with which the wires are excited. The remaining power (90%) goes into an objective (6) which focuses the laser into a relatively small spot on a region of a sample inside the cryostat (7). The cryostat is connected to a vessel with liquid Helium, which can be used to obtain a temperature inside the cryostat in the range of 4 to 293K.

The photoluminescence emission together with a portion of the laser light that is reflected emerges from the objective again (represented in orange) and is guided by the beamsplitter through a low-pass filter (8) eliminating the laser light from this signal. This is done so as not to damage the CCD array inside the monochromator, since the reflected laser power is many times more powerful than the emission. This filtered signal is then guided towards the monochromator (9) where the spectrum is determined.
The monochromator is equipped with different gratings, which determine the resolution and the range with which the spectrum is displayed. This is a tradeoff, in the sense that a finer grating gives a higher resolution, but a smaller range. The least fine, or "coarse", grating gives a resolution of approximately 0.5 nm and a range of about 570 nm. One step finer, the "fine" grating gives a much better resolution of approximately 0.05 nm, but has a range of only 60 nm.

This highlights the potential uses of both of these gratings; the coarse grating can give a wider view of the spectrum, which can be useful particularly if there are multiple emission peaks or the peaks are particularly wide. Contrarily, the fine grating can be used to resolve features that are too small for the coarse grating to resolve. Sharp peaks with a width of less than 0.5 nm are averaged out by the coarse grating, whereas the fine grating shows these peaks clearly (up to a minimum width of 0.05 nm). The tradeoff is that part of the peak may fall outside of the range.

This is illustrated in figure 3.7. The coarse grating has a larger range (actually from 315 to 880 nm in this instance) but fails to resolve several smaller peaks that can only be identified by the fine grating. An additional downside of the fine grating is that it captures significantly fewer photons than the coarse grating, requiring longer integration times in order to give a decent spectrum without too much noise.

Lastly there is the "ultra-fine" grating with a resolution of around 0.015 nm and a range of around 16 nm. For the purposes of this project this grating turns out to not be very useful, as it is practically impossible to explain the origin of every miniscule peak that becomes visible when using it.
The laser spot needs to be focused to be as small as possible for accurate measurements. For this purpose, the setup is changed to be as follows.

**Figure 3.8:** Setup for focusing the laser spot, showing the white light coming out of a fiber (1), beamsplitter (2), objective (3), cryostat with sample (4) and camera (5)

In order to actually see the laser spot and focus it, white light is generated and guided to the optical table through a fiber (1). There it is combined with the laser light and guided through the beamsplitter (2) into the objective (3) and onto the sample (4). The sample reflects a portion of the white light and laser light, which are guided through the beamsplitter into a camera. This setup is also used in doing measurements on transferred nanowires in order to find suitable bunches or single wires.

In general, the "best" focus should occur when the laser spot is smallest. However, in practice this does not always result in the highest photoluminescence intensity. Therefore, in order to fine-tune the focus, the spectrum is measured and displayed continually whilst the focus is moved, allowing for the optimal focus to be found. It is crucial to not change the focus too much, since a change of 1-2 micron (greater than the NW length) means that the focus is no longer on the nanowires, but light from a reflection is being gathered, which is not desirable. In this context, it is not unusual for the optimal focus to be subjective (up to a certain small range of focus), and it is up to choice where exactly to focus, as different focal points might result the same intensity but different spectra.
4 Results and discussion

4.1 GaP Cores

In order to characterize the influence that growing shells has on the optical and physical properties of the nanowires, the behavior of the GaP cores is characterized. The growth of pure wurtzite, defect-free GaP nanowires has been successfully developed by the PSN group, resulting in nanowires as seen in figure 4.1.

![SEM image of GaP nanowires](image)

**Figure 4.1:** SEM image of GaP nanowires

The photoluminescence spectra of the GaP Cores show some broad peaks, along with several sharp peaks, as can be seen in the following figure.

![Photoluminescence spectra of GaP cores for different excitation powers](image)

**Figure 4.2:** Photoluminescence spectra of GaP cores for different excitation powers.

Some of the sharp peaks corresponding to excitons have previously been identified and characterized further. The three sharp peaks correspond to the A, B, and C excitons and the broad peak is due to donor-acceptor-pair emission. The emission at room temperature is fairly weak, and only visible at relatively high excitation powers. The band gap transition of this material is proven to be direct, but has a small matrix element.
4.2 Growing a single InGaP shell around GaP cores

After etching the gold droplet from the top of the GaP cores, an InGaP shell was grown around the cores. The resulting core-shell nanowires were analyzed by TEM.

![Figure 4.3](image1.png)

**Figure 4.3:** Left: Bright field TEM image of a InGaP shell, GaP core nanowire. Right: Raw EDX counts of same nanowire. Courtesy of Dr. Marcel Verheijen.

Figure 4.3 shows a confirmation of the growth of a pure wurtzite InGaP shell, with no additional defects introduced by the growing of the shell. The EDX graph also shows the shell, with an In concentration of around 20%, approximately what was intended for this particular sample.

The top of the wire has a blob of In-rich material, which was determined by TEM to have a zincblende crystal structure.

The photoluminescence emission spectra of these nanowires are determined at different laser excitation powers and temperatures.

![Figure 4.4](image2.png)

**Figure 4.4:** Photoluminescence spectra of wurtzite GaP/InGaP/GaP core-shell nanowires. Left: Spectra at different excitation powers at 4K. Right: Spectra at different temperatures.

The material shows emission at 4K for relatively low excitation powers, and emits at room temperature. It might be possible to determine an approximate indium concentration from the PL spectra, since the emissions for wurtzite GaP (around 600nm) and wurtzite InP (around 850nm [10]) are known. In practice this proves to be difficult if not impossible, producing dubious results. This is probably the result of many effects factoring in to the location of a peak, such as strain, and a possible non-linearity in the emission of the ternary.

These results prove the optical activity of the material, making it possible to proceed with further optimization.
4.3 Single quantum well GaP/InGaP/GaP nanowires

Several GaP core/InGaP shell/GaP shell samples have been grown and characterized, and the growth parameters have been adjusted for subsequent growths based on the characterization results.

4.3.1 Graded shell buffer layer

Single quantum well nanowires have been grown by first growing what is called a graded shell buffer layer around the core. This layer is grown by gradually decreasing the Ga concentration whilst increasing the In concentration. In theory this layer should reduce strain between the cores and the quantum well [11]. After this layer the InGaP shell is grown, which will act as a quantum well, and this layer is then capped by another GaP shell.

![Image](a) SEM image of the sample

![Graph](b) Graph of the molar flow fractions during growth of the sample

**Figure 4.5:** SEM image and graph of the molar flow fractions of a graded shell single QW NW sample.

The SEM image in figure 4.5a shows that the wires are relatively uniform and straight. Some defects are visible, such as slight tapering towards the top, and a blob of material on the top which is known to have a zincblende crystal structure (see section 4.2.

The molar fraction graph in figure 4.5b first shows the molar flows during growth of the graded shell, then for the InGaP quantum well, and finally for the GaP outer shell.
The photoluminescence emission spectra of these wires have been determined at various powers. These measurements were done on the wires "as grown", on the wafer.

![Graded Shell WZ InGaP single QW NW](image)

**Figure 4.6:** PL spectra at various powers of a graded shell single QW NW sample.

These nanowires exhibit a broad emission (FWHM of 157nm), with a sharp peak at around 610nm combined with a broad peak which spreads out over a massive range. This emission is undesirable, as one of the objectives is to get as narrow an emission spectrum as possible. Considering that this spectrum extends all the way from the emission of pure wurtzite GaP (600nm) to pure wurtzite InP (850nm) it is possible that the indium composition in this sample varies significantly, perhaps as a result of the graded buffer, creating emission in every region between the two pure compositions. Some of this emission might also be attributed to defects, as seen in poor quality GaP.

Normalizing these curves can give information on the behavior of the shape of the spectrum as a function of the excitation power. This is shown in the following figure.

![Graded Shell WZ InGaP single QW NW](image)

**Figure 4.7:** Normalized PL spectra at various powers of a graded shell single QW NW sample.
The relative intensity of the broad peak compared to the sharp peak diminishes with increasing excitation power. Possibly the quantum well is emitting at around 610nm, whereas the rest of the nanowire or especially the graded buffer emitting up to 850nm. In this case the QW emission becomes disproportionately stronger with increasing power.

Even though the wires physically look straight and relatively defect-free, the PL spectra leave much to be desired.

### 4.3.2 Single QW nanowires without buffer layer

It is suspected that the graded buffer layer might degrade the PL emission of the wires. Therefore, new wires are grown without a buffer layer.

![SEM image of the sample](image1)

![Graph of the molar flow fractions during growth of the sample](image2)

**Figure 4.8:** SEM image and graph of the molar flow fractions of a single QW NW sample without a graded buffer layer.

As can be seen in figure 4.8a, these wires are less uniform than the wires with a buffer layer. There is more bending and some defects are visible. This indicates that the buffer layer does aid in reducing strain, thus reducing bending and defects. This is not too surprising, since the buffer layer allows the lattice to gradually relax from the GaP to the InGaP lattice constant, whereas removing it introduces an abrupt change in the lattice constant, inducing strain in the wires.

The molar fraction graph (figure 4.8b) shows that the InGaP layer is grown directly around the GaP cores.
The photoluminescence emission spectra of this sample are determined at several laser excitation powers.

![PL spectra at various powers of a single QW NW sample without buffer layer.](image)

**Figure 4.9:** PL spectra at various powers of a single QW NW sample without buffer layer.

The emission spectra of this sample are significantly less broad, with a FWHM of 11nm, a massive improvement over the sample with the buffer layer. The peak intensity is also considerably higher (almost an order of magnitude greater) than that of the spectra of the sample with the buffer layer. It is possible that including a buffer layer allows some carriers to escape from the quantum well into the buffer layer, where they recombine and emit at a higher wavelength.

It is unfortunate that the buffer layer has this effect on the emission, as it was effective in producing more uniform and straight nanowires.

![Normalized PL spectra at various powers of a single QW NW sample without buffer layer.](image)

**Figure 4.10:** Normalized PL spectra at various powers of a single QW NW sample without buffer layer.

From the normalized spectra it can be seen that the shape of these spectra stays roughly the same with increasing power.
4.3.3 Temperature dependence of PL spectra in single QW NWs

The photoluminescence spectra were determined for a graded shell nanowire sample at several temperatures up to room temperature.

![Normalized PL spectra at various temperatures of a graded shell single QW NW sample](image)

**Figure 4.11:** Normalized PL spectra at various temperatures of a graded shell single QW NW sample

The location of the peak seen at 4K shifts to a higher wavelength as the temperature is raised. Also, starting at around 20K, a broad peak emerges centered around 750nm, growing stronger respectively as the temperature is raised and eventually dominating the "original" peak, which almost completely disappears at room temperature.

Not pictured here is that the peak intensity falls dramatically when the temperature is raised, and a very high excitation power and long integration times are needed to capture any decent spectrum at all at room temperature.
4.4 Multiple quantum well nanowires

Several nanowire samples with multiple quantum wells have been grown and will be discussed in this section.

4.4.1 Triple quantum well nanowires

Nanowires with three quantum wells were grown, both with and without a buffer layer. First the nanowires without a buffer layer are discussed.

Figure 4.12: SEM image and graph of the molar flow fractions of a 3QW NW sample without a graded buffer layer.

These nanowires are not considerably thicker than their single quantum well counterparts, which means that if the emission increases strongly, it is likely attributable to the extra quantum wells, and not to the thickness of the wires. These nanowires are straight and uniform, but have some sort of small pedestal at the base, although this is not suspected to result in significant emission.

The molar flow graph shows the three InGaP quantum wells and the three GaP barriers. This recipe is basically the recipe from figure 4.8b repeated three times.
Photoluminescence emission spectra have again been determined for these nanowires at several excitation powers.

![Figure 4.13](image-url)

**Figure 4.13**: PL spectra at various powers of a 3QW NW sample without buffer layer.

This sample has a quite sharp spectrum and a strong peak emission. It is important to note that these spectra were measured with the fine grating, and the samples were excited with a different laser. Since less light is gathered with the fine grating, and the excitation powers of the different lasers are not the same, this means that the peak intensities cannot directly be compared with the previous results.

Accounting for this and comparing to the single QW nanowires, the emission is considerably stronger.

Considering these wires are not a lot thicker, this emission is probably attributable to the two additional quantum wells emitting strongly instead of an increase in surface area.

Looking at figure 4.13, the shape of the spectra is consistent with increasing power. This indicates that there is no major emission arising from effects that are strongly power-dependent.
Triple quantum well nanowires have been grown with a buffer layer, to examine whether this layer might have a different effect on the emission in multiple QW nanowires.

These nanowires are considerably more bent than their buffer-less counterparts. It is not clear whether this is a result of the added buffer layer, or whether there is a different cause. It has been found that growths with the same recipe at different points during a growth cycle can look considerably different, due to for instance material accumulating on the susceptor.

The bending in these wires is severe enough that at some point wires bending towards each other begin to touch, and a blob of material is formed at the meeting point. These blobs might have a zincblende crystal structure, as they look similar to the blobs seen in section 4.2.

In the following the photoluminescence spectra at various excitation powers and temperatures shall be discussed, with measurements having been done on the sample as grown, as well as on bunches of nanowires and single nanowires transferred onto SiOx.
The emission of this sample has a reasonably sharp peak (FWHM 15nm) and a decently strong peak emission. The peak of this emission is more narrow than the peak for the sample without a buffer layer.

This might not necessarily be the effect the buffer layer itself, but may be due to unknown variables in the growth process changing.

Some small peaks at higher wavelengths can be seen in these spectra. These peaks are possibly the result of alloy fluctuations and well width fluctuations modifying the band structure of the material. This would result in carrier localization, giving emission in very specific wavelengths instead of cooling down towards the lowest band gap.

It is also possible that some of the emission is the result of the touching tips of some nanowires. This is plausible if these blobs are actually in zincblende and (relatively) In-rich, as the blobs in section 4.2, since more In should result in a higher emission wavelength.

The shape of the spectra remains relatively constant with power, however some of the small peaks that modulate the large peak at low powers seem to disappear at higher powers. At low powers there is localized emission due to well width fluctuations. An increase in optical pumping power creates a greater number of carriers, which spill over and fill the entire quantum well structure, instead of being localized, resulting in emission over many wavelengths and a smoother spectrum.
The temperature dependence of the photoluminescence emission of this sample has been determined and is shown in the following figure.

**Figure 4.17:** Normalized PL spectra at various temperatures of a graded shell 3QW NW sample

This sample exhibits roughly the same behavior as in section 4.3.3, although the broad peak appearing at higher temperatures is located at a higher wavelength.

In this measurement series, the location and shape of the original peak seemed to depend strongly on the focal point, especially at higher temperatures. A shifting of the focal point of a few tens of nm resulted in a shifting of the location of the peak or a change in its shape. It is not clear what causes this phenomenon.

Some nanowires from this particular sample have been transferred onto SiOx, and PL emission spectra have been determined of several bunches of nanowires and single wires.
The PL emission from different bunches of nanowires is examined.

**Figure 4.18:** PL spectra at various excitation powers of a bunch of graded shell 3QW nanowires.

The location of the peak seen here is the same as the peak seen when determining the spectrum as grown, namely between 580-600 nm. Some smaller peaks appear at either side of the major peak. It is possible that these peaks are the result of one or a few nanowires emitting differently, and that the effects of these wires are averaged out when looking at the as grown sample. This is plausible since although bunches are still a collection of nanowires, the total number is lower than is sampled when the nanowires are measured as grown. The photoluminescence emission of a different bunch of nanowires of the same sample is examined at 50K.

**Figure 4.19:** PL spectra at various excitation powers of a bunch of graded shell 3QW nanowires at 50K.
The phenomenon observed here is speculated to be band filling, with first the lowest energy bands (highest wavelength) being filled, indicated by the peak at 592nm getting stronger. When increasing the excitation power, the extra energy goes into filling higher energy bands, which can be seen in the spectra by the emergence of emission at wavelengths lower than the primary peak wavelength.

When increasing power, a new peak arises at around 584nm, which eventually dominates the original peak. This corroborates the existence of band filling, as this peak corresponds to a new band transition at a higher energy. This peak eventually dominates the original peak. At this point, increasing the power further does not change the relative intensity of the two peaks, but a third peak starts to emerge at around 578nm, indicating yet another transition with a higher band gap energy.

The emission of the same bunch of nanowires is examined at various temperatures up to room temperature.

**Figure 4.20:** PL spectra at various temperatures of a bunch of graded shell 3QW nanowires at 50K.

At 4K the spectrum has a dominant peak modulated by a large amount of smaller peaks. If the temperature is raised, these small peaks appear to be smoothed out and disappear. This behavior can probably be linked to well width fluctuations as well. At low temperatures the carriers are confined in very specific locations, causing emission with specific band gap energies. When raising the temperature, the carriers are able to diffuse more easily across the quantum well, filling all of the local wells and barriers regardless of local composition. This then results in the disappearance of the small peaks in favor of emission over a larger number of specific wavelengths, which average out into the smoother spectra seen at higher temperatures.

At temperatures closer to room temperature the same behavior is seen as was seen previously, with emission over a wide range of wavelengths.

In figure 4.20b the effect of the low-pass filter used in the setup can be seen, cutting off (nearly) all emission with a wavelength lower than 450nm.
Some emission spectra from some single nanowires are also determined and compared.

**Figure 4.21:** PL spectra of two different single graded shell 3QW nanowires.

It can be seen that the emission from two different nanowires is in general quite similar, with respect to the location and FWHM of the peak. However, looking at the smaller peaks modulating the large peaks, practically no wavelengths of peaks seen in one nanowire correspond to those seen in another. This indicates that these peaks are due to inhomogeneities, and a general difference in physical characteristics. The difference with the spectra determined from the as grown sample indicates that these defects are indeed averaged out when considering a large ensemble of nanowires.
The camera can be used to view some single nanowires and compare them based on their appearance.

(a) Camera picture of two single nanowires.

(b) Spectra of two different single graded shell 3QW nanowires at 100K

\textbf{Figure 4.22:} Comparison of two different single graded shell 3QW nanowires

It can be seen that the bent nanowire exhibits a considerably lower peak emission than the straight wire. The bending of the wire probably induces a lot of strain, negatively effecting the emission.
The locations of the peaks are also different between these two nanowires. This behavior is most likely again induced by the bending of one of the nanowires.
This result indicates the importance in growing straight nanowires. In this particular result, a straight nanowire exhibits a 10x stronger peak emission than a bent nanowire.
Moving the cryostat so that the laser spot moves along the length of a nanowire allows for a consideration of the uniformity of one single wire.

Figure 4.23: PL spectra when scanning a single nanowire along its length.

In this instance a single nanowire is not at all uniform along its axis. Emission at some points completely disappears in favor of other peaks. This particular spectrum could also be explained by the spot moving towards or away from the defect-rich top of the nanowire, which should have a different emission spectrum.

Because of the results seen in this section, it is safe to say that it is not (yet) sensible to try and identify any particular peaks that are seen, since the spectra of the wires changes so dramatically based on spot on the sample/wire, excitation power, etc.
4.4.2 Five quantum well nanowires

A sample with five quantum wells without a graded buffer layer is examined.

These wires are very thick (upwards of 250nm), which is to be expected from the long growth times.
The wires are also strongly tapered, and show a large amount of facets or defects along the sidewalls.

**Figure 4.24:** SEM image and graph of the molar flow fractions of a 5QW NW sample without a graded buffer layer.

This sample emits the strongest of any sample that was examined, with emission of an order of magnitude greater than the previous sample, the best up until then.
The peak is decently sharp with little influence from other, smaller peaks.

**Figure 4.25:** PL spectra at various powers of a 5QW NW sample without a buffer layer.
Comparing the emission of this sample with that of the previously considered 3QW sample (with graded buffer) results in the following figure.

![Figure 4.26: Comparison of the PL spectra of the no buffer 5QW sample (Black) and a 3QW graded buffer sample (red).](image_url)

Here the increase in emission is evident, along with the location of the peak shifting to the right for the 5QW sample. This shift might be the result of the "extra" quantum wells emitting more towards higher wavelengths, indicating a higher indium concentration in the outer wells.

Conversely, the shift might also be attributed to the lack of a graded buffer, perhaps resulting in increased strain and a shift of the emission.

The increase in emission strength seems to be the result of the larger number of quantum wells, but it is also plausible that it is just a result of there being more material in general that can emit.

Comparing the diameters of the 3QW (200nm) and 5QW (250nm) wires, it seems that this large increase cannot solely be attributed to an increase in material, which leads to believe that the additional quantum wells are indeed emitting more. This leads to the conclusion that the emission from the outer quantum wells is stronger than that of the inner wells.
5 Conclusion

It seems clear that multiple quantum well nanowires optically perform significantly better than single quantum well nanowires. The emission of multiple quantum well nanowires is in general less broad (smaller FWHM) and the peak emission intensity is greater. Whether this is completely due to extra quantum wells emitting or whether the increase in diameter plays a large role is yet to be determined. TEM feedback is needed to confirm or deny the existence and quantify the thickness and composition of the quantum wells.

Given that growing nanowires with the same recipe does not always result in nanowires that are physically comparable and perform the same optically, more work needs to be done in optimizing the growth process in order to increase reproducibility and predictability of the growth.

In single quantum well nanowires the addition of a graded buffer layer appears to be disastrous for the emission, resulting in a spectrum with a massive range. The growth of the nanowires does seem to benefit from the buffer layer, as the nanowires with this layer are in general more straight than their counterparts with no buffer. While this indicates that there might be less strain, since there is less bending, the worse emission means that this buffer layer has to be reconsidered or modified in the future.

Meanwhile the spectrum of the photoluminescence emission is still quite inhomogeneous, with effects such as well width fluctuations inducing many small peaks at varying wavelengths. This is not desirable for a device, where the aim is to have one single reasonably sharp peak. There is still more research to be done into the growth of quantum wells in these nanowires, especially into reducing alloy and well width fluctuations.

The optical performance of the nanowires decreases substantially with increasing temperature, culminating in a very weak and very broad emission spectrum at room temperature for all samples. This behavior is very undesirable for the operation of a device, and further research needs to be done into increasing the efficiency at higher temperatures.

Concluding, there is plenty more research to be done on wurtzite InGaP nanowires for optical devices and considerable challenges to be overcome. The current results are promising for the relatively early stages and inspire confidence to proceed with further development.
References


