Growth and Characterization of Heterostructure Nanowires

Master thesis by Peter Krogstrup

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Preface & Acknowledgement

This thesis is concerned with the growth of III-V nanowires using a solid source Molecular Beam Epitaxy (MBE) system located at the Nano-Science Center, Niels Bohr Institute, University of Copenhagen, and the following characterization of the these structures. Right from the beginning of the work presented here, main focus was directed towards growth of Au-catalysed axial heterostructure nanowires, using the group III elements indium and gallium and the group V element arsenic. After a detailed and exciting process and a lot of gained knowledge, new and interesting structures are achieved, and I am therefore pleased to present the results here. Many interesting growth related results are also presented, and a new model for Au-catalyzed nanowire growth is proposed, as it is explained how the adatoms are transferred to the incorporation site at the growth interface via two different routes: 1) Interface diffusion and 2) Volume diffusion through the catalyst particle. Many different results presented throughout this thesis are obvious objects for further investigation as new interesting areas for MBE growth have opened up investigations which I hope somebody, if not myself, get the opportunity to do. All nanowires analyzed are characterized with electron probe techniques, such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM), High Angle Annular Dark Field (HAADF)-STEM and Energy Dispersive X-ray analysis (EDX).

The outcome of this thesis would not have been possible without help from a team of highly qualified people, so I will now let the ‘thank you’ show begin. First of all I would like to thank my supervisors Erik Johnson, Claus B. Sørensen and Jesper Nygård for making me part of the nanowire team at the Niels Bohr Institute and for supporting me and taking time to discuss data and theory and helping me to get a better understanding of the field in general. Erik Johnson for patiently helping me with the characterization part with the TEM related techniques which plays a significant role in this work, but also for theoretical discussions, ranging from thermodynamical theory to kinetical properties. Claus B. Sørensen for helping me with the growth of nanowires, without his experience on MBE grown nanowires, high quality nanowires would not have been possible within the time frame of this work. I am also grateful for the many discussions

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I have had with him on growth related mechanisms. Jesper Nygård for keeping a great overview on the whole project, and at the same time giving me the opportunity to go in the directions I found interesting. I owe a special thanks to Martin Aagesen for helping me, especially with the experimental work but also for theoretical discussions on NW growth in general. I should also thank Jun Yamasaki from Nagoya, Japan, for his excellent EDX data and high resolution HAADF-STEM work on the heterostructure nanowires. Based promary on his work a new NW growth model is proposed. Thank you to Jakob B. Wagner and Robert Pennington, CEN, DTU, for lots of good EDX data on many different heterostructures, and a thank you to Magni Glyvradal for helping on writing a fantastic matlab program which determine diameters of NWs from SEM images. At last thank you to all the other people who was somehow involved in this thesis and to all at the electron transport group for the help and support I have received whenever I had a problem or question.

All the raw EDX data and HAADF images which are used for presenting this work are obtained by either J.Yamasaki, Nagoya University, Japan, Jakob B. Wagner or Robert Pennington, CEN, DTU, Denmark (sometimes in collaboration with me in the two latter cases). All use of the MBE system was done with help from Claus B. Sørensen.

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Notation

A list of the most used abbreviations in this work are given here.

- NW: Nanowire
- MBE: Molecular Beam Epitaxy
- TEM: Transmission Electron Microscopy
- SEM: Scanning Electron Microscopy
- HAADF: High Angle Annular Dark Field
- STEM: Scanning Transmission Electron Microscopy
- EDX: Energy dispersive X-ray analysis
- ZB: Zinc Blende
- WZ: Wurtzite
- DP: Diffraction Pattern
- CL: Cliff Lorimer
- VLS: Vapor-Liquid-Solid
- VSS: Vapor-Solid-Solid (or Volume diffusion)
- IFD: Interface Diffusion

- The NW axial heterostructure notation A/B indicates that material B is on top of A.
1 Introduction

Semiconductor nanowires are quasi one-dimensional crystalline structures with sizes of typically $\sim 1-10 \, \mu m$ in length and only $\sim 10-150 \, nm$ in diameter (see Figure 1), which is interesting for electrical measurements since they give strong confinement for the conducting electrons in width but not in length. These structures have already made an impact in applications as diverse as mass sensors, single-electron transistors and photon sources, and will probably find new areas for applications as the field develops. Interesting and promising results have motivated ongoing efforts to grow nanowires from various materials and to understand the underlying growth mechanisms in detail. This is not only to get better insight in the fundamental nature of the NW structures but also to obtain a better insight of potential and new possibilities in the field.

![Image of InAs NWs with an in-built Ga$_x$In$_{1-x}$As segment.](image)

Figure 1: A SEM image of InAs NWs with an in-built Ga$_x$In$_{1-x}$As segment. This heterostructure is not observable in SEM images, but in section 2.2 and 2.3, STEM-based techniques which can be used to measure the composition will be discussed.

The field of NWs has received increasing attention in recent years and NWs are
today grown with many different materials by many different growth techniques. However semiconductor nanowires which are probably the most analyzed and promising wires for future applications all consist of either group IV or group III and V elements, initiated by metal seed nano-particles typically of gold. This thesis will be concerned with the growth and characterization of MBE grown semiconductor NWs consisting of the group III materials In and Ga and group V material As. These kind of wires has been reported and studied intensively during the last decade or so [2],[3],[5],[13],[19], studies which have given us new insight into the growth mechanisms and possibilities for potential applications in a hopefully near future. Many characteristics are already known and are controllable, such as the structure, possible heterostructures and NW dimensions. There has also been much interest in developing a growth model which describes the NW growth more detailed than the traditionally and well known Vapour-Liquid-Solid (VLS) model. The VLS model was developed over 40 years ago on Au-assisted Si wires with diameters on the micrometer scale, but the recent intense study on particle assisted NWs have shown failure of this model. New models are proposed for specific NW systems but still fundamental insight into the actual growth mechanisms is missing before a general model or framework for all NW growths can be proposed. In order to gain knowledge on this subject a very important part is the characterization process. Besides this introduction and the conclusions, this thesis has been split up into three different parts. The first part, 'Characterization of Nanowires' is mainly a theoretical chapter describing possible III-V nanowire structures and relevant characterization techniques which can be used with a TEM. Interpretation of the data gained from electron probe measurements is not always straightforward and therefore a relatively careful discussion on NW structure and how to interpret data from the measurements will be the starting point. The second part 'Nanowire growth', is concerned with the physics behind the epitaxial growth of wires. The basic ideas behind NW growth as well as a more detailed thermodynamical and kinetical view on the growth are discussed. A section on how to control the wire diameter is presented. The third part, Nanowire Heterostructure Growth, is concerned with growth of axial heterostructures. The results and interpretation of the characterization data will be presented and discussed using the framework developed in the first two parts.
2 Characterization Of Nanowires

Transmission Electron Microscopy (TEM) constitutes arguably the most efficient tool for the characterization of micro/nano-meter size materials like NW’s. In a TEM, electrons are accelerated by an electrostatic potential to energies of typically 100 to 300 KeV, causing electron-wavelengths in the picometer regime. Spatial resolution at this level would be desirable, but since we cannot make perfect electron lenses without spherical aberration, we are nowhere near building TEMs that approach this limit. Nevertheless, the best TEMs today are corrected to a large extent for aberration effects, achieving a sub-0.1nm spatial resolution which is smaller than the size of an atom. There exist a wide variety of different characterization techniques incorporated into a modern TEM instrument, and many of these can be used to characterize the NW structure and composition. To characterize a given crystal structure though, typically the conventional TEM techniques such as image mode or diffraction mode is used.

Figure 2: A ray diagram showing the basic principle of the diffraction and imaging process in a TEM. Conventional TEM techniques such as images and diffraction patterns are obtained in the image and back focal plane respectively.

While the image plane gives us an image of the NWs in real space, the back focal

\footnote{A focusing lens suffers from spherical aberration since it does not produce a perfect focal point. The reason is that it focuses rays more tightly if they enter it far from the axis than if they enter closer to the axis.}

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plane gives us an image in reciprocal space (diffraction pattern) which can tell us a great deal about the crystal structure (see figure 2).

2.1 Determining the crystal structure

Determining the crystal structure often requires an analysis of the corresponding diffraction pattern, but before analyzing the pattern, we will start to discuss the two possible structures, Zinc Blende (ZB) and Wurtzite (WZ), one may find in III-V NWs. As mentioned in the previous section, the substrates used in this project have mainly been (111) InAs wafers (ZB) with a 'B' terminated surface plane\(^2\). The growth direction of the wires is perpendicular to the surface, that is in the [111] crystal direction. While the ZB crystal structure consists of two interpenetrating fcc lattices of respectively group III and group V materials, shifted \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), the WZ structure consist of two interpenetrating hcp lattices shifted \((0, 0, \frac{3}{8})\). The ZB and WZ structure in the growth direction can be described via two different close packed modes, only differing by their stacking sequence, see Figure 3. When the stacking sequence is ABCABC the crystal structure becomes ZB which has a unit cell of 8 atoms, and when the stacking sequence is ABAB it becomes WZ structure with a unit cell of 4 atoms. For both structures we will use the 3-index notation \((hkl)\) to derive the structure factor and its selection rules, but for the WZ structure we will use 4-index notation \((hkil)\), where \(i = -(h+k)\), to index the lattice planes and reflections in the DPs.

When the NWs are examined in a TEM, we use the wave properties of electrons to determine which type of crystal structure it originates from. Like all waves in a crystalline lattice they scatter only in certain directions given by Bragg’s law. In the case of TEM imaging we use Bragg’s law for small angle scattering \(\lambda = 2d\theta\), because the wavelengths of the electrons \(\lambda\) are in the pico-meter regime and the spacing between the lattice planes \(d\) are in the Ångström regime and we hence have small angles \(\theta << 1\). When analyzing a crystal, the diffracted beams in diffraction mode terminate on the imaging apparatus, generating a diffraction pattern which consists of a series of spots. Each spot corresponds to a given set

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\(^2\)The surface plane \((111)B\), are the plane perpendicular to the vector with miller indices \(hkl=(111)\), and the 'B' tell us that it is a group V terminated surface

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Figure 3: The figure shows two crystals of the possible structures in crystalline III-V nanowires, ZB and WZ. A close packed pattern appears for both structures, when looking along the growth direction. The two growth modes differs by their stacking sequence.

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of crystal planes and the ordering of these spots is a fingerprint of the crystal structure.

The structure factor $F_{\vec{G}}$ of a crystals unit cell is a measure of how the monocystal scatters incident electrons (or other incident radiation in general). Compared to X-rays, the electron scattering power is $\approx 10^4$ times larger because of the Coulomb interactions between the incident electrons and the charges in the sample [7], and therefore also multiple scattering effects appear in the electron diffraction patterns (DP). As a start we will focus on single scattering using the kinematical approximation, which assumes that every atom in the sample sees the same undisturbed incident electron beam. The scattered amplitude of a given spot in a DP depends on the unit cell structure factor of the corresponding crystal plane (hk1) and on the atomic form factor $f_j$, which is a measure of the amplitude of a wave scattered from an isolated atom j. $|F_{\vec{G}}|^2$ and $|f_j|^2$ are proportional to the scattered intensity of the unit cell and a single atom, respectively. $f_j$ depends on the angle between the incident and scattered electron beam, while $F_{\vec{G}}$ is given as

$$F_{\vec{G}} = \sum_j f_j e^{i\vec{G} \cdot \vec{r}_j} \quad (1)$$

Here $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is the reciprocal lattice vector and $\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3$ is the positions of the atoms in the unit cell relative to some reference point, typically $\vec{r} = (0, 0, 0)$. The primitive vectors $\vec{b}_i$ of the reciprocal lattice are constructed in such a way that they have the property

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij} \quad (2)$$

and the structure factor becomes

$$F_{\vec{G}} = \sum_j f_j e^{i\vec{G} \cdot \vec{r}_j} = \sum_j f_j e^{i(hx_j + ky_j + lz_j)} \quad (3)$$

The structure factor for a given structure can be used to find the selection rules which determine how $F_{\vec{G}}$ depends on the miller indices h,k and l of the scattering planes. There are basically two ways to form a DP in a TEM. Either we focus the beam on a small area of the NW forming a convergent beam electron diffraction pattern (CBED), or spreading it into an almost parallel beam and selecting
an area by using an aperture, Selected Area Diffraction (SAD) (figure 5). The direction [UVW][UVTW] \(^3\) of the incident beam relative to the crystal orientation is called the zone axis. All spots of a given DP originates from a plane with a normal vector perpendicular to the zone axis, i.e. \(hU + kV + lW = 0\) \((hU + kV + iT + lW = 0)\) where hkl (hkil) refers to the diffraction spot from a specific plane in a cubic (hexagonal) crystal with miller indices hkl (hkil). The distance \(R\) between the central spot (the undiffracted beam) and a diffraction spot is given by \(\tan(\theta) = \frac{R}{L}\), where \(L\) is the camera length and \(\theta\) the scattering angle. Using this and Braggs law for small angles together with the lattice spacing, \(R\) becomes

\[
R = \frac{L\lambda}{a} \sqrt{h^2 + k^2 + l^2}, \quad \text{cubic basis} \tag{4}
\]

or

\[
R = \frac{\lambda L}{2a} \sqrt{\frac{4}{3} (h^2 + hk + k^2) + \frac{3}{8} l^2}, \quad \text{hexagonal basis} \tag{5}
\]

Since the distance \(d\) between the lattice planes in the hexagonal basis is given by

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right) \tag{7}
\]

where \(c\) is the length of the 3rd basis vector (the two others have same length \(a\)). The connection between \(a\) and \(c\) are \(c = \sqrt{\frac{8}{3} a}\) and therefore \(\frac{1}{2d} = \frac{1}{2a} \sqrt{\frac{4}{3} (h^2 + hk + k^2) + \frac{3}{8} l^2}\).

Since \(\frac{L\lambda}{a}\) is a constant for a given DP, the ratio of the spot spacings of two reflections \(h_1k_1l_1\) and \(h_2k_2l_2\) is then easily calculated, and is here given together with the angle between reflection 1 and 2,

\[
\frac{R_1}{R_2} = \sqrt{\frac{h_1^2 + k_1^2 + l_1^2}{h_2^2 + k_2^2 + l_2^2}}, \quad \text{ZB} \tag{6}
\]

\[
\theta_{12} = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}, \quad \text{ZB} \tag{7}
\]

or

\[
\frac{R_1}{R_2} = \sqrt{\frac{4}{3} (h_1^2 + h_1k_1 + k_1^2) + \frac{3}{8} l_1^2} \tag{8}
\]

\[
\theta_{12} = \cos^{-1} \left( \frac{h_1h_2 + k_1k_2 + \frac{1}{2} (h_1k_2 + h_2k_1) + \frac{9}{32} l_1l_2}{\sqrt{(h_1^2 + k_1^2 + h_1k_1 + \frac{9}{32} l_1^2)(h_2^2 + k_2^2 + h_2k_2 + \frac{9}{32} l_2^2)}} \right), \quad \text{WZ} \tag{9}
\]

\(^3\)We will use the notation ZB(WZ) to distinguish between the properties of ZB and WZ respectively.
Now we have the means to identify a given ZB or WZ DP. I will here propose an overall procedure to identify a DP from an arbitrary NW with a known growth direction.

**DP analysis procedure for III-V NWs** The procedure in indexing a DP depends on what is known a priori. When dealing with III-V NWs we know its ZB(WZ) structure and that the beam direction \([UVW]([UVTW])\) is perpendicular to the known growth direction of the NW. It is important to note that this require that the NW lie horizontally on the copper grid introduced in the TEM. If not, tilting of the sample has to be done until the electron beam is perpendicular to the NW growth direction. With this knowledge a possible procedure would be

- Measure three different distances \(R_i\) for the reflections closest to the origin and find the ratios \(\frac{R_1}{R_2}\) and \(\frac{R_2}{R_3}\). Measure the angles between them and put them in the ‘measured’ column together with the ratios in a table like Table 1

<table>
<thead>
<tr>
<th>(\vec{B} = [?])</th>
<th>(\phi_{12})</th>
<th>(\phi_{23})</th>
<th>(\frac{R_1}{R_2})</th>
<th>(\frac{R_2}{R_3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([UVW]_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([UVW]_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([UVW]_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([UVW]_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Example of a table to fill out for comparison of diffraction spot distance ratios and their intermediate angles.

- List a set of possible beam directions \([UVW]([UVTW])\), provided that they are perpendicular to the axial growth direction \([h'k'l']([h'k'i'l'])\) of the NW, i.e. \([UVW] \cdot [h'k'l'] = 0\). \([UVTW] \cdot [h'k'i'l'] = 0\). The possible beam directions are filled in the \([UVW]_x\) column in a table like Table 1.

4 A ruler tool in a graphics editing program (ex. Photoshop or Gimp) or equivalent measuring pixel and angles is recommendable.
• Because the group of reflections hkl comes from planes (zone planes) parallel to the beam direction, we can use the restriction \[ [U \ V \ W] \cdot (h \ k \ l) = 0 \]
(or \[ [U \ V \ T \ W] \cdot (h \ k \ i \ l) = 0 \]), eq. (4) (or (5)) and selection rules to find the three shortest allowed distances \( R_{hkl} \) to the center spot. Use eq. (6) and (7) (or eq. (8) and (9)) to fill out the columns. To save time with the calculations use the IDL program in Appendix A, which gives all the possible beam directions and corresponding reflections, and calculates the angles and spot ratios of a chosen set of reflections. Choose the zone axis with the best fit between the measured and calculated values.

• Indexing the DP should be easy when three reflections are known since reflections with -(hkl) are mirrored in the central spot. If there are reflections in other directions, it is easiest to see what the indexing should be from symmetry in the DP. Use the knowledge that the cross product eq. (10) between to adjacent reflections (counterclockwise) should give the zone axis, to double check correct indexing.

\[
U = k_1 l_2 - l_1 k_2 \\
V = l_1 h_2 - h_1 l_2 \\
W = h_1 k_2 - k_1 h_2 \quad (10)
\]

The advantage of this procedure is that it does not require any knowledge of the camera length or wavelength and its associated uncertainties. All NWs involved in this thesis are as mentioned previously, grown on (111)B substrates which is also the direction the NWs prefer to grow. The spot spacing ratios and intermediate angles of the three closest spots of typical zone axes of (111) NW DPs are given in Table 2.
As we have seen there are basically two possible structures in III-V NWs, ZB and WZ, and an example of a DP-analysis of each structure is done below.

### 2.1.1 Zinc blende diffraction pattern analysis

**The structure factor and selection rules** - The kinematical approximation  
As mentioned the ZB structure is two interpenetrating fcc lattices shifted \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), in our case one containing group III material and the other containing group V. The atomic positions of the unit cell are (in units of the lattice constant \(a_{zb}\)),

<table>
<thead>
<tr>
<th>Atom</th>
<th>Positions (r_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group III</td>
<td>((\frac{1}{4} \frac{1}{4} \frac{1}{4}), (\frac{3}{4} \frac{3}{4} \frac{3}{4}), (\frac{3}{4} \frac{1}{4} \frac{3}{4}), (\frac{1}{4} \frac{3}{4} \frac{3}{4}))</td>
</tr>
<tr>
<td>Group V</td>
<td>((000), (\frac{1}{2} \frac{1}{2} \frac{1}{2}), (\frac{1}{2} 0 \frac{1}{2}), (0 \frac{1}{2} \frac{1}{2}))</td>
</tr>
</tbody>
</table>

Using that the electronic form factor \(f_j\) takes on the values \(f_V\) for group V and \(f_{III}\) for group III, the structure factor becomes
Characterization Of Nanowires

\[ F_{\vec{G}} = \sum_{V} f_{V} e^{2\pi i(hx_{j}+ky_{j}+lz_{j})} + \sum_{III} f_{III} e^{2\pi i(hx_{j}+ky_{j}+lz_{j})} \]

\[ = f_{V} \left( e^{2\pi i0} + e^{2\pi i(\frac{1}{2} + \frac{1}{2})} + e^{2\pi i(\frac{1}{2} + \frac{1}{2})} + e^{2\pi i(\frac{1}{2} + \frac{1}{2})} \right) \]

\[ + f_{III} \left( e^{2\pi i(\frac{1}{4} + \frac{1}{4} + \frac{1}{4})} + e^{2\pi i(\frac{1}{4} + \frac{1}{4} + \frac{1}{4})} + e^{2\pi i(\frac{1}{4} + \frac{1}{4} + \frac{1}{4})} + e^{2\pi i(\frac{1}{4} + \frac{1}{4} + \frac{1}{4})} \right) \]

\[ = f_{V} \left( 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)} \right) \]

\[ + f_{III} e^{\frac{i\pi}{2}(h+k+l)} \left( 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)} \right) \]

(11)

The selection rules come from analyzing the structure factor with the different combinations possible for hkl:

\[ F_{\vec{G}} = \begin{cases} 
4(f_{V} \pm if_{III}) & \text{if } h, k, l \text{ are all odd} \\
4(f_{V} - f_{III}) & \text{if } h, k, l \text{ are all even and } h + k + l = 2(2n + 1) \\
4(f_{V} + f_{III}) & \text{if } h, k, l \text{ are all even and } h + k + l = 2(2n) \\
0 & \text{if } h, k, l \text{ are mixed even and odd} 
\end{cases} \]

(12)

where n is an integer. When \( F_{\vec{G}} = 0 \) we call it the kinematically forbidden reflections.

The atomic scattering factor The atomic scattering factors \( f_{j} \) can be found exactly only if one knows the exact wave function of the atom. The way to find the scattering factor is as follows: Schrödinger Equation (SE) → the wavefunction → the total charge density → the atomic potential → the atomic scattering factor. But since the wave function can be found exactly only for the hydrogen atom, all other factors must be evaluated using approximations. If we assume the atom to have a spherical electron distribution we obtain the Born approximation for the

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atomic scattering factor

\[
f_B^j(\theta) = \frac{8\pi^2 me}{\hbar^2} \int_0^\infty \phi(r) \frac{\sin (2k \sin(\theta) r)}{2k \sin(\theta) r} r^2 dr
\]

where \( \phi(r) \) is the potential difference between the nucleus and the electron shell. Eq.(13) has been solved numerically for certain angles (by using Poisson’s equation) and are listed in tables for crystallography\(^5\) [6]. The calculated values are plotted for Indium, Gallium and Arsenic with a 3-order polynomial fit to get approximated values at the relevant diffracted angles, see figure 4.

![Atomic form factor for electron scattering](image)

**Figure 4:** The scattering amplitude as function of \( \frac{\sin \theta}{\lambda} = \frac{1}{2d_{hkl}} \), where \( d \) is the lattice spacing between the planes with miller indices \((hkl)\). The original listed values are multiplied with a relativistic gamma factor of: \( E_{\text{kin}} = E_{\text{tot}} - E_{\text{rest}} = \gamma m_0 c^2 - m_0 c^2 \Leftrightarrow \gamma - 1 = \frac{E}{m_0 c^2} \Leftrightarrow \gamma = 1.39 \), corresponding to electron kinetic energies of 200 KeV.

In the figure \( f_B^j(\theta) \) is plotted as function of the scattering angle \( \frac{\sin \theta}{\lambda} = \frac{1}{2d_{hkl}} \) and since the lattice spacing for a cubic basis is \( d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \) we get \( \frac{1}{2d} = \frac{a}{\sqrt{h^2+k^2+l^2}} \). The lattice constants \( a \) for InAs are 6.06Å and for GaAs 5.45Å, so the scattering angles for InAs are smaller than corresponding angles in the GaAs case, and this

\(^5\)Values used in this thesis are taking from the International Tables for Crystallography, Vol. III
give rise to a difference in the scattered intensity. Below the most relevant angles are listed for the two cases of interest, and a measure for the relative intensities of single scattering is tabulated as well.

| InAs | \( \frac{1}{2d} = \sqrt{h^2+k^2+l^2} \) | \( f_{In} \) | \( f_{As} \) | \( |F_{hkl}|^2(\propto I) \) |
|------|-----------------|---------|---------|----------------|
| 200  | 0.165 Å\(^{-1}\) | 9.13    | 7.07    | 67.24          |
| 111  | 0.143 Å\(^{-1}\) | 10.01   | 7.72    | 2557           |
| 220  | 0.233 Å\(^{-1}\) | 7.20    | 5.45    | 2560           |

Table 3: InAs and GaAs form factor values for different scattering angles in ZB structure

**Example of DP analysis, ZB** Figure 5 shows a diffraction pattern of an [100] axially grown nanoflake\(^6\). Using the DP analysis procedure outlined above, we start to measure the R-ratios and angles between the three nearest reflections, and put in the table (4). Four possible beam directions could be \([UVW] \cdot [100] = 0 \rightarrow [01\overline{1}], [010], [01\overline{2}], [011]\). It is only necessary with four different low order zone axes because of the symmetry in hkl. To each zone axis the three shortest matching planes are found with the restriction \([UVW] \cdot \{hkl\} = 0\). The best fit between the measured values and the calculated values from eq.(6) and (7) reveals a [011] beam direction, see table 4. (The 'shortest' reflections in the [011] zone are \{hkl\} = (1\overline{1}1), (200), (02\overline{2}), and are obtained from the restriction [011] \cdot hkl = 0 and the selection rules). The indexing is hereafter straightforward.

In figure 5 it is easy to see that the intensity ratio of spot (200) and (1\overline{1}1) is no way near the expected ratio \( \approx \frac{67}{2557} \) according to the kinematical approximation

\(^6\) A nanoflake is like a NW grown epitaxially and catalyzed by a gold particle. A flake grows in two dimensions rather than one like wires, the reasons are not fully understood but until now it has only been possible to grow them on substrates with a (100) surface.
Table 4: The calculated and measured values which turn out to make the best fit, reveals a ZB structure and a $\vec{B} = [011]$ beam direction.

<table>
<thead>
<tr>
<th>$\vec{B} = [011]$</th>
<th>$\phi_{(111)-(200)}$</th>
<th>$\phi_{(022)-(200)}$</th>
<th>$R_{(200)}$ ( \frac{R_{(111)}}{R_{(200)}} )</th>
<th>$R_{(200)}$ ( \frac{R_{(022)}}{R_{(200)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>54.9°</td>
<td>35.4°</td>
<td>$\frac{381}{333} = 1.14$</td>
<td>$\frac{381}{548} = 0.70$</td>
</tr>
<tr>
<td>Calculated</td>
<td>54.74°</td>
<td>35.26°</td>
<td>$\frac{2}{\sqrt{3}} = 1.155$</td>
<td>$\frac{2}{\sqrt{3}} = 0.707$</td>
</tr>
</tbody>
</table>

Figure 5: **A** SAD and **B** CBED diffraction pattern of ZB structure in the same orientation. The DPs are taking with the 200keV TEM at HCØ and the patterns originates from the same part of a InAs nanoflake with an axial [100] direction. (Both DP images are inverted)
and table 3. The reason is that when the beam is diffracted once it will easily be rediffracted. This repeated diffraction is called dynamical diffraction. In some directions this effect is strong as in the (200) direction. Unlike the kinematic theory of diffraction which only describes the position and an approximate intensity of Bragg or Laue diffraction peaks in reciprocal space, dynamical theory corrects for refraction, shape and width of the peaks, extinction and interference effects. However, we will only consider the kinematical analysis, since it is almost impossible to make a usable quantitative analysis on a given structure using dynamical theory.

2.1.2 Wurtzite diffraction pattern analysis

The structure factor and extension rules - The kinematical approximation  The WZ structure is two interpenetrating hcp lattices shifted \([0, 0, \frac{2}{3}]\) of group III and V respectively. To gain most symmetry in hkl and therefore getting a structure factor which is easier to interpret, we use the freedom to shift the coordinate system by \(-[\frac{2}{3}, \frac{1}{3}, 0]\). The atomic positions of the unit cell are then (in units of the WZ lattice constants a and c.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>The positions (r_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group III</td>
<td>((\frac{2}{3}, \frac{1}{3}, \frac{3}{8}), (\frac{1}{3}, \frac{1}{3}, \frac{7}{8}))</td>
</tr>
<tr>
<td>Group V</td>
<td>((\frac{2}{3}, 0), (\frac{1}{3}, \frac{1}{2}))</td>
</tr>
</tbody>
</table>

yielding a structure factor:
\[
\begin{align*}
F_{G} &= \sum_{V} f_{V} e^{i(hu + kv + lw)} + \sum_{III} f_{III} e^{i(hu + kv + lw)} \\
    &= f_{V} \left( e^{i\pi \left( \frac{2}{3}h + \frac{2}{3}k \right)} + e^{i\pi \left( \frac{2}{3}h + \frac{2}{3}k + l \right)} \right) + f_{III} \left( e^{i\pi \left( \frac{2}{3}h + \frac{2}{3}k + \frac{1}{3}l \right)} + e^{i\pi \left( \frac{2}{3}h + \frac{2}{3}k + \frac{2}{3}l \right)} \right) \\
    &= f_{V} \left( e^{i\pi \left( 4h + 2k \right)} + e^{i\pi \left( 2h + 4k + 3l \right)} \right) + f_{III} \left( e^{i\pi \left( 4h + 2k + \frac{1}{3}l \right)} + e^{i\pi \left( 2h + 4k + \frac{1}{3}l \right)} \right)
\end{align*}
\]

(14)

The extinction rules are not as obvious as in the ZB case, but when writing \( F_{G} \) as in the last line of eq.(14) it is easy to see that \( F_{G} \) is non-chancing when \( h \) and \( k \) are increased by a multiple of 3. So the different combinations for \( h \) and \( k \) can be put into a 3x3 matrix as

\[
\begin{array}{c|c|c|c}
 h \downarrow & k \rightarrow & 3i & 3i+1 & 3i+2 \\
 \hline
 3j & \alpha_{1} & \alpha_{2} & \alpha_{3} \\
 3j+1 & \beta_{1} & \beta_{2} & \beta_{3} \\
 3j+2 & \gamma_{1} & \gamma_{2} & \gamma_{3} \\
\end{array}
\]

Here \( i \) and \( j \) are integers. If we look at \(|F_{G}|\) instead of \( F_{G} \) it turns out that we can divide the 9 combinations into only 2 groups, the diagonal and off-diagonal elements, and the extinction rules becomes:

For the diagonal elements (\( \alpha_{1}, \beta_{2}, \) and \( \gamma_{3} \)):

\[
|F_{G}| = \begin{cases} 
2(f_{III} \pm f_{V}) & \text{if } l = 4n, (+) n: \text{even(odd)} \\
2\sqrt{f_{III}^{2} + f_{V}^{2}} & \text{if } l = 4n - 2 \\
0 & \text{if } l = 2n + 1 
\end{cases}
\]

(15)

and for the off diagonal elements

---

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Characterization Of Nanowires

\[ |F_G| = \begin{cases} 
(\pm)f_{III} + f_V & \text{if } l = 4n, (+(-) n: \text{even(odd)} \\
\sqrt{f_{III}^2 + f_V^2} & \text{if } l = 4n - 2 \\
\sqrt{3(f_{III}^2 + f_V^2 + \sqrt{2}f_{III}f_V)} & \text{if } l = 2n + 1, \text{ and } n=-3,-2,1,2,5,6,.. \\
\sqrt{3(f_{III}^2 + f_V^2 - \sqrt{2}f_{III}f_V)} & \text{if } l = 2n + 1, \text{ and } n=-1,0,3,4,7,8,.. 
\end{cases} \] 

(16)

n being an integer.

The atomic scattering factor In the WZ structure the lattice constants are \( a_{wz}(InAs) = 4.27 \) \([9]\) and \( a_{wz}(GaAs) = 4.0 \). Erik Johnson found the latter value on a GaAs NW using the ZB lattice parameters for magnification calibration in HRTEM images \([44]\). As for the ZB structure, we use the selection rules to find the atomic form factor values at the relevant scattering angles from the polynomium fit in figure (4). Because of the symmetry in h and k, we only show the planes which have different lattice spacing in table (2.1.2), e.g. the planes (100), (010), (110), and (110) have the same lattice spacing because of the \( \sqrt{\frac{4}{3}(h^2 + hk + k^2)} \) term in eq.(5).
**Characterization Of Nanowires**

InAs

| hkl | $\frac{1}{2d} = \frac{1}{2a_{wz}} \sqrt{\frac{4}{3} (h^2 + hk + k^2) + \frac{3}{8} l^2}$ | $f_{\text{In}}$ | $f_{\text{As}}$ | $|F_{hkl}|^2 (\propto I_{hkl})$ |
|-----|--------------------------------------------------|----------------|-------------|-----------------------------|
| 100 | 0.135 Å$^{-1}$                                   | 10.35         | 8.10        | 340.4                      |
| 101 | 0.153 Å$^{-1}$                                   | 9.70          | 7.40        | 142.0                      |
| 102 | 0.169 Å$^{-1}$                                   | 9.00          | 7.00        | 130.0                      |
| 110 | 0.234 Å$^{-1}$                                   | 7.20          | 5.50        | 645.2                      |

GaAs

| hkl | $\frac{1}{2d} = \frac{1}{2a_{wz}} \sqrt{\frac{4}{3} (h^2 + hk + k^2) + \frac{3}{8} l^2}$ | $f_{\text{Ga}}$ | $f_{\text{As}}$ | $|F_{hkl}|^2 (\propto I_{hkl})$ |
|-----|--------------------------------------------------|----------------|-------------|-----------------------------|
| 100 | 0.144 Å$^{-1}$                                   | 7.30          | 7.65        | 223.5                      |
| 101 | 0.163 Å$^{-1}$                                   | 7.00          | 7.30        | 90.07                      |
| 102 | 0.180 Å$^{-1}$                                   | 6.45          | 6.75        | 87.17                      |
| 110 | 0.250 Å$^{-1}$                                   | 4.80          | 5.05        | 388.1                      |

**Table 5:** InAs and GaAs form factor values for different scattering angles in WZ structure

**Example of DP analysis, WZ** As we have seen the WZ structure is a bit more complicated than the ZB structure, but the principles in the DP analysis procedure are the same. Figure 6 shows a DP of a [0001] WZ (or a [111] if ZB) axial NW. Now following the procedure outlined at the start of the section, we measure the spot ratios and the intermediate angles for the 3 nearest reflections and put them in table (6). Trying WZ structure and using 4 index notation, the restriction $[0001] \cdot [UVIW] = 0$ gives us 4 different first order possibilities for the zone axis (Remembering the symmetry in $h$ and $k$), $[2\bar{1}00], [1\bar{1}20], [10\bar{1}0], [1\bar{1}00]$. It turns out that the $[1\bar{1}00]$ direction gives the best result when comparing with the measured ones in table (6). The 3 allowed reflections with the smallest $R$, (002), (110), (112) are easily found using the selection rules and the restriction $[1\bar{1}00] \cdot (hkl) = 0$. So now using eq.(8) and (9) the calculated values are inserted in the table, and miller indexing the spots in the DP can be done.

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Table 6: The comparison shows a good agreement between the measured and calculated values when having a $\vec{B} = [1\overline{1}00]$ zone axis.

<table>
<thead>
<tr>
<th>$\vec{B} = [1\overline{1}00]$</th>
<th>$\phi_{12}$</th>
<th>$\phi_{23}$</th>
<th>$R_1/R_2$</th>
<th>$R_2/R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>90°</td>
<td>31.2°</td>
<td>0.59</td>
<td>1.16</td>
</tr>
<tr>
<td>Calculated</td>
<td>90°</td>
<td>31.5°</td>
<td>0.61</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Figure 6: $[1\overline{1}00]$ zone axis DP for the WZ structure. The DP stems from a InAs region on a InAs/GaAs nanowire of $\approx 80\text{nm}$ in diameter.
2.2 Elemental composition analysis using EDX

Energy dispersive x-ray analysis (EDX) is a technique which is incorporated in many modern electron microscopes and is used to analyze the elemental composition of an area on a sample. The electron beam is focused on the area of interest, and although we so far only have considered elastic scattering, a small fraction of the electrons from the beam interacts inelastically with the electrons in the sample, causing them to be knocked out of their orbits. When electrons from an inner orbital is kicked out, less bounded electrons fall into the empty states created, releasing the excess energy as either a photon in the x-ray regime or as an auger electron.

![Diagram of electron transitions](image)

**Figure 7:** The x-ray transitions used for EDX analysis on NWs consisting of gallium, indium and arsenic. The splitting of lines due to spin are shown, although the splitting is not detectable in a EDX spectra. So for the two $K\alpha$ values, the $K\alpha_1$ value is typically chosen as center peak value, since this is the peak with the highest intensity. (Values are taking from [43].)

For incoming electrons with energies in the typical TEM regime we can roughly
say that, the lighter the atoms are the lower their contribution to the x-ray intensity becomes. Primary reasons for this are that the collision cross section is larger for heavier atoms and that the lighter atoms have a smaller binding energy, and therefore are more likely to emit auger electrons than characteristic x-rays. Detecting and analyzing the emitted x-ray spectrum, the characteristic wavelengths are identified. The size of the characteristic peaks can then be approximated to be proportional to the amount of the corresponding element present. EDX linescan is a very important tool when analyzing heterostructure NWs, since it can tell you the composition variation along a line, with a lateral resolution of few nm’s. To make a good and reliable analysis many issues have to be taking into account. A procedure of a quanti

2.2.1 Discussion on quantification of EDX data

To make a reliable and a fairly precise EDX analysis, a detailed process has to be followed. Various software programs commonly used for EDX analysis are only approximative and can primarily be used for quick analysis of somewhat limited accuracy. The reason for this is that the analysis is highly dependent on both the microscope used and the specimen analyzed. That is why a procedure of how to quantify raw EDX data from NWs is developed and presented here, but before outlining the procedure I will discuss the physics behind leading to the method used.

Background contributions: Bremsstrahlung and tail overlapping. Two different phenomena may cause what we call a background yield, either 'bremsstrahlung' or contributions from overlapping tails of adjacent peaks in the spectrum. Tail overlapping from adjacent peaks is not what we normally call background, but since we are only interested in what we have to remove to get the pure contribution of a given element it will be referred to as background. Bremsstrahlung occurs when an electron from the beam interact inelastically with the nucleus, creating an x-ray with a energy corresponding to the deceleration of the electron
from the beam. For a given material the likelihood of bremsstrahlung depends on the nuclear cross section, which again depends on the average atomic number of \( Z \). For x-ray energies above \( \approx 2 - 3 \text{keV} \) the bremsstrahlung is very well modeled by Kramers expression

\[
N(E) = KZE_0 - E
\]

where \( N \) is the number of bremsstrahlung photons within the energy range of \( E \) and small derivation \( \Delta E \) from \( E \). \( E_0 \) is the energy of the electron before the interaction and \( K \) is the Kramers constant, which takes account of numerous parameters in the system and specimen, but what matters for this purpose is that for a given measurement it is constant. So when analyzing the bremsstrahlung background intensity from an EDX linescan dataset, it can be useful to employ the ratio for the bremsstrahlung backgrounds as,

\[
\frac{N_A(E_A)}{N_B(E_B)} = \frac{Z_1 E_0 - E_A}{E_A \bar{Z}} \frac{Z_2 E_0 - E_B}{E_B \bar{Z}} \quad (18)
\]

where element A is in region 1 and element B in region 2. This method requires at least one spectrum of each region on the heterostructure NW, since it needs a background reference. This can be found within an area in the spectrum with no peaks to disturb the pure bremsstrahlung yield. As an example - if we know region 1 contains pure GaAs, the indium yield in the same region must be pure background, and so if \( N_{In} \) is known, \( N_{Ga} \) or \( N_{As} \) is known according to eq.(18). Also the more simple and obvious consideration, more atoms scatter more, must be taken into account if the wire thickness changes from one region to another. It is normal that the software package following the EDX system, includes a routine for background removal, but since the software does not have any prior knowledge of the specimen or microscope it can be necessary to make the background removal yourself to get meaningful results. The bremsstrahlung background contributions at the characteristic lines used are typically small when analyzing typical NW materials, and can therefore in most cases be ignored. The EDX data we obtained from the NWs had a high peak to background ratio (P/B) and in these cases bremsstrahlung can be ignored. Removal of contributions from tails of adjacent peaks is a little more tricky. If

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the characteristic x-ray lines of the NW material are clearly separated from other characteristic lines, then the tail contributions can be ignored. If two materials are close to each other in the periodic table their electron binding energies are almost equal. Therefore adjacent peaks are unavoidable as all their characteristic lines are separated by small amounts. Since the characteristic x-ray lines of Ga and As are close to each other (see Figure 7), the tails from the adjacent peaks are overlapping. This is the most important background contribution to correct for, in the case of NWs containing Ga and As.

The Cliff-Lorimer ratio technique - The thin foil criterion  Once the background intensity is subtracted it is relatively easy to make the quantitative x-ray analysis, relying on the “thin foil criterion” (TFC) assumption [8],[11]. TFC implies that the specimen is thin enough to ignore any absorption or fluorescence effects during the passage out of the specimen[11]. In the case of NWs, TFC should be a safe approximation, and lead to a simple quantitative analysis of the spectrum using what is called the Cliff-Lorimers ratio technique,

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]  (19)

Here \(C_x\) is the percentage content of element x in the analyzed volume and \(I_x\) the intensity of characteristic x-rays from element x. The Cliff Lorimer (CL) factor \(k_{AB}\) is a proportionality factor which varies from microscope to microscope, and can be determined experimentally using a sample containing a known fraction of the materials A and B. Having three or more elements in the analyzed region, requires two or more equations like (19). If there are N different elements in the region the quantification is achieved using

\[
C_A + C_B + \ldots + C_N = 100\%
\]  (20)
2.2.2 Procedure for quantification of EDX linescan data of heterostructure nanowires containing ternary segments.

In the following, bremsstrahlung is neglected due to the high P/B ratio we have in our EDX data. However, if the bremsstrahlung contribution is large, one should either choose the characteristic K-lines which have higher P/B ratio, or correct for it using Kramers formula, as described above. As this thesis is concerned with the elements In, Ga and As, these will be the referred elements, but because this procedure is held on a general level other elements can be used as well. The procedure will be divided into three parts:

1: Background removal Choose the characteristic lines which are free (or most free) of tails from adjacent peaks. Plot the raw linescan data of the relevant elements to get an idea of the concentration profile. In the case of $\text{InAs}/\text{Ga}_x\text{In}_{1-x}\text{As}/\text{InAs}$ NWs we see a rise in the As K counts at the $\text{Ga}_x\text{In}_{1-x}\text{As}$ segment, see Figure 8. This is due to the contribution from the tail of the Ga K-line in this region. As we know that As is the only material which can occupy group V sites, it should remain constant if the interaction volume is not increased. As clearly seen in Figure 8, this contribution can be significant and should be corrected for. This is easily done with an approximating method by subtracting the average excess value from the data in this region. The Ga signal is also affected by the tail of the As peak, but this is just the average value of Ga in the pure InAs region, and this value is subtracted from the whole Ga data set.

2: C-L factor determination After background removal, the ratios of the C-L factors have to be found using wires of the same structure and with dimensions that are similar to the wires of interest but with known compositions. This would be GaAs and InAs wires if analyzing $\text{GaInAs}$ segments. The CL factors are then

---

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Figure 8: Raw EDX data of Ga and As K-lines from a linescan on a InAs/GaInAs/InAs NW. Background from adjacent peaks can be, as seen on the profiles, important to correct for. Here in the case of Ga and As as they have characteristic lines very closely spaced. The In counts are left out, since they do not play a role here. The rise in the Ga content on the left side of the $Ga_xIn_{1-x}As$ segment is due to shell(GaInAs) structure which is developed during the $Ga_xIn_{1-x}As$ growth.

Easily found by tuning $\alpha = \frac{K_{Ga}}{K_{As}}$ (where $K_A$ is the CL factor for element A) by an iterative process to get the atomic fraction ratios $\left< \frac{C_{Ga}}{C_{As}} \right> = 1$ and $\beta = \frac{K_{In}}{K_{As}}$ to get $\left< \frac{C_{In}}{C_{As}} \right> = 1$, using eq.19 for every point in the linescan. In appendix A2 the IDL program ’alpha beta determination.pro’ can be used for this purpose.

3: Final quantification  Now we have what it takes to make a reliable analysis. Using the C-L ratio technique for ternary materials, we get the atomic compositions:

$$C_{as} = \frac{1}{\alpha \frac{I_{Ga}}{I_{as}} + \beta \frac{I_{In}}{I_{as}}} C_{In} = \beta \frac{I_{In}}{I_{as}} C_{as}, C_{Ga} = \alpha \frac{I_{Ga}}{I_{as}} C_{as}$$ (21)
In appendix A3 the program 'edx quantification.pro' can be used for this purpose. The final data are plotted and written to a text file. A Ga mole fraction x is also calculated from a given region of interest. Figure 9 shows an example of an analysis on a InAs/Ga_xIn_{1-x}As/InAs′ NW, where the InAs region under the gold particle is assumed to be pure InAs and the InAs region under the Ga_xIn_{1-x}As core segment is a core shell structure containing a pure InAs core with a GaInAs shell.

Figure 9: A) TEM image of a InAs NW with a Ga_xIn_{1-x}As core segment. B) A close up HAADF-STEM image on the barrier region, the red line indicates the trace of the EDX line scan. C) Raw EDX data are quantified with the Clift-Lorimer ratio technique. D) Background removed and quantified EDX data.

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Figure 9 B indicates the region and line on the wire where the scan was performed, and figure C the quantified raw EDX data. It is clear that the raw data do not match the expected values. In the pure InAs region we have a relatively large background yield of gallium, and its average value will be our background reference. The Ga content in the shell of the core-shell structure is expected to be much higher than in the $Ga_xIn_{1-x}As$ core segment. This is due to the short diffusion length of Ga relative to In on the sidewalls of the NW. We will treat this subject in section 3.3.

2.3 High resolution High-Angle Annular Dark-Field imaging

One of the weaknesses of the EDX analysis is the spacial resolution due to the probe size and the interaction volume, which makes it impossible to quantify the elemental composition on a scale below some few nanometers (section 2.2.1). However, it is possible to make a qualitative elemental composition analysis with an atomic spacial resolution with a method called 'Z-contrast imaging' or 'High Angle Annular Dark-Field (HAADF) imaging', images which are acquired in STEM mode. At high scattering angles (above $\sim 50$ mrad) the incoming electrons scatters of the atoms in the specimen like Rutherford scattering, which scales with the atomic number approximately like $Z^2$. This Z-dependence on the intensity in the images is also most pronounced at high scattering angles because it is free of interference effects between different lattice planes which will blur the elemental mapping. If the probe size is smaller than the spacing between the lattice planes parallel to the beam, the electrons can be considered as being confined to one atomic column [45], as the atomic columns is scanned sequentially across the specimen. This electron channeling along the atomic columns therefore suppress coherent interference effects between the different atomic columns. As the intensity of each atomic column depends on the average atomic number, a HR-HAADF image provides a compositional map with atomic resolution, see Figure 10.
Figure 10: A high resolution HAADF image of a $Ga_xIn_{1-x}As$ segment on a $InAs/Ga_xIn_{1-x}As/InAs$ heterostructure NW, which will be presented in section 4.3, where both WZ and ZB structure is present. The GaAs mole fraction $x$ in this region is only $\sim 0.1$, so the group III sites in the HAADF image represents almost only indium atoms which are brighter due to the higher atomic number $Z$. The atomic columns are clearly separated. The two crystal structure illustrations at the left are taking from Figure 3. Image taking by J.Yamasaki, Japan.

The possibility of getting a spacial resolution on the atomic level require a alignment of the sample and very good focusing of the beam. For NWs this method can be very useful if one for example wish to estimate the sharpness of a transition between two segments of different composition on a heterostructure nanowire, and we will use this method in section 4.3.
3 Nanowire Growth

3.1 Introduction

One of the major tasks in the science of NWs and their associated heterostructures is to understand and to control the growth mechanisms. All NWs presented in this thesis are Au-assisted III-V NWs grown by solid source Molecular Beam Epitaxy (MBE) in a Varian GEN II MBE machine. It is a technique where ultrapure elements are heated in separate cells so that they slowly begin to evaporate, creating a flux out through a narrow hole in the cell, which is directed into a high vacuum chamber creating a molecular beam with a large mean free path. The beam terminates and condenses at a wafer, typically a GaAs or InAs wafer, located at a rotating sample holder in the center of the growth chamber and the epitaxial (layer by layer) growth begins.

Figure 11: The basics involved in MBE growth. Within the work of this thesis only 4 elements are used: Au, As, In and Ga.
The general procedure which was common for the majority of all the NW growths performed in this thesis will be outlined here. The substrates used were InAs wafers with a (111)B surface orientation. After thorough degassing in a separate buffer chamber, the substrates were transferred to the growth chamber and heated to 530°C in a flux of As$_2$ to desorb the surface oxide. The As$_2$ Beam Equivalent Pressure (BEP) used was $1.5 \cdot 10^{-5}$ torr. After oxide removal the substrate temperature was lowered to 490°C and the Au was then either deposited in-situ directly on the oxide free surface and left to anneal in the As$_2$ flux for 4 min, or deposited before growth in an e-gun evaporation chamber getting arrays of Au-particles using a E-beam lithography technique, see section 3.4. For the in-situ deposition, the deposition time of the Au determines the size of the catalyst particles and thus the resulting nanowire diameters. I have not performed a calibration of the Au deposition rate but a deposition time of 30 sec at a source temperature of 1350°C results in wire diameters of $80(\pm10)$ nm. Following the annealing step, the substrate temperature was lowered to the growth temperature typically of 423°C. RHEED intensity oscillation data, which were recorded as part of the calibration on a separate (100) calibration piece prior to growth, give a measure of the bulk InAs(GaAs) growth rate as function of the temperature in the In(Ga) cell. All the nanowires grown have been InAs-based with a bulk growth rate of 1.5 $\mu$m/hr, while for the $Ga_xIn_{1-x}As$ segments different Ga growth rates were used, see section 4.

NW’s were conventionally assumed to grow via the Vapor-Liquid-Solid (VLS) process, a theory which was developed over 40 years ago for Au-assisted Si NW’s with diameters on the micrometer scale. It is a process where the molecular beam (the vapour phase) is incorporated into growing NW’s (the solid phase) via diffusion through already deposited catalyst particles, often Au droplets (the liquid phase). The materials are transferred to the catalyst/NW growth interface, where the enhanced growth rate at the interface compared to the bulk growth rate is the reason for freestanding NWs, Figure 12. Today we know that for most materials the growth process is not that simple, and further understanding of particle-assisted NW growth is needed. Since the detailed growth process is material dependent, the discussion of NW growth will focus on the wires involved in this thesis, namely NWs containing In, Ga and As catalyzed by Au droplets. Studies of InAs and GaAs NW growth [1],[19] have shown that while In and Ga
alloys readily with Au, the solubility of As in Au is under the detectability limit and it is therefore expected to alloy only weakly with Au. This assumption is supported by various studies on material interactions in bulk alloys [18],[20] and on binary alloy phase diagrams [17]. The primary route to the incorporation site of As is therefore expected to come from the sidewalls or from the Au surface near the growth interface. In the case of GaAs and InAs growth we know from standard binary alloy phase diagrams that Ga and In alloys with Au with a eutectic melting temperature of $349^\circ C$ and $455^\circ C$ respectively.

Our InAs based NWs have as mentioned above, been grown at temperatures around $420^\circ C$, and therefore a solid Au-In catalyst is expected. Bearing in mind, small particles which have a large surface to volume ratio has a lower melting point than the bulk material, due to the Gibbs-Thomson effect, see section 3.2. But the size of the 80 nm Au-In droplets should not be effected significantly. Generally we know that successful growth of NW’s has also been achieved for temperatures way below the eutectic melting point of the III-Au bulk alloys ([1],[5],[12]), so under these conditions it is expected that the group III materials are incorporated via the Vapour-Solid-Solid (VSS) process [19], which is the same process as the VLS although with a solid catalyst. In the VSS process the route to the incorporation site of group III materials is expected to come from the catalyst via solid phase diffusion, and it is today the general interpretation of GaAs and InAs NW growth. Based on a detailed characterization of some of the heterostructure NWs grown in the thesis, we are not convinced of the VSS diffusion theory, so an alternative interpretation will be given in section 4.

Figure 12: The basic principle of III-V NW growth in a MBE chamber

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3.2 Thermodynamics of nanowire growth

A full understanding of the physics behind nanowire growth requires besides a thermodynamical study also an atomistic view on the wire and its kinetic processes involving surface diffusion[1]-[3],[9]-[10]. As a start we will consider thermodynamics to get an idea of how the basic parameters such as pressure and temperature affect crystal growth at solid-vapor interfaces without a catalyst. Like all thermodynamic processes the system will strive to minimize the free energy, and since we in this case are looking at a system at a given temperature and pressure, the expression of Gibbs free energy \( G = U + PV - T\sigma \) will be used to describe when the crystallization is energetically possible. The important parameter here is the chemical potential, defined as \( \mu = \frac{\delta G}{\delta n_{P,T}} \), where \( n \) is the number of particles in the system.

Neglecting surface effects, epitaxial growth in regions with no catalyst particle involves phase transitions between two distinct phases, the vapor and the solid phase. To obtain equilibrium between these two phases their chemical potentials must be equal

\[
\mu_{\text{vapor}} = \mu_{\text{solid}} \tag{22}
\]

If the pressure or temperature is changed so that eq.(22) is not fulfilled, the phase with the lowest chemical potential becomes stable. This implies that if the difference of the chemical potentials \( \Delta \mu = \mu_{\text{vapor}} - \mu_{\text{crystal}} \) is positive (negative), crystal growth (etching) occurs. Treating the vapor as an ideal gas, it can be shown using eq.(22) as a reference, that at a given interface temperature \( T \) the difference in the chemical potentials can be written as ([15],[16])

---

8U: The system's internal energy, \( P \): pressure, \( V \): Volume, \( T \): Temperature, \( \sigma \): Entropy

9The lower the temperature the higher the thermodynamic driving force toward solidification. Because of the high melting points for the semiconductor materials used, the system during MBE growth is always undercooled.

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\[ \Delta \mu = kT \ln \left( \frac{P}{P_0} \right) \]  

(23)

where \( P \) and \( P_0 \) are the vapor pressure and equilibrium vapor pressure respectively. For sufficiently (or infinitely) large phases, or in other words, for flat phase boundaries, the crystal pressure and the vapor pressure are equal. However, for small particles the large surface to volume ratio effects the crystal pressure since the surface atoms are attracted inwards. Using Laplace equation [16] to estimate the pressure of the Au particle,

\[ P_{\text{Au-part.}} - P_{\text{vapor}} = \frac{4\sigma}{d} \]  

(24)

where \( \sigma = 1,175 \text{N/m} \) [34] is the surface tension of Au and \( d \) the diameter of the Au particle. Neglecting the vapor pressure we see that the pressure inside 80 nm Au particles is \( \approx 600 \text{ atm} \). So for NW growth eq.23 should be used with caution since it is difficult to say how \( \Delta \mu \) drives the system with small crystal dimensions and catalyst particles involved. Nevertheless eq.23 is the driving force for epitaxial crystal growth at the substrate, and for MBE growth this is believed to be very high [15] which is the same as saying that the growth is a 'highly non-equilibrium' process. Under these conditions we might not expect the growth rate to be controlled completely by the thermodynamic driving force, but also by the kinetics of the reactive species. This is because the kinetics involving surface reaction rates and diffusion are not rapid enough to allow equilibrium to be established. However, the thermodynamic driving force may still control much of the growth process because of near equilibrium conditions near the solid/vapor interface [15], so eq.23 will only be used conceptually. The temperature dependence of \( \Delta \mu \) is given by [16]

\[ \Delta \mu = \Delta s_m (T_m - T) \]  

(25)

where \( T_m \) is the melting temperature and \( \Delta s_m \) is the entropy of melting. \( T_m \) is known for almost all kinds of alloys, but \( \Delta s_m \) is typically only known for single component materials. For multicomponent systems the chemical potentials of the different elements are just added up to give the total chemical potential. So for vapor phases containing for example In and As\(_2\), we have \( \Delta \mu = (\mu_{\text{In}} + 1/2\mu_{\text{As}_2})_{\text{vapor}} - \text{InAs}_{\text{solid}} \) and eq.(23) becomes
\[ \Delta \mu = kT \ln \left( \frac{P_{In}P_{As}^{1/2}}{P_0(\text{In})P_0(\text{As})^{1/2}} \right) \]  

(26)

Here \( P_i \) is the partial pressure of element \( i \). Eq. 23 can be used conceptually to describe the pressure dependence on growth on the substrate and to some extent on the side facets of the wire. We have to note that the reaction rate toward solidification is dependent on both materials, so it is primarily only the pressure of the material which is in lack that will change the rate, the other pressure can be treated as a constant.

In order to describe the enhanced growth rate at the growth interface between the catalyst particle and the crystal we must consider the corresponding interfacial energy. Interfacial energy is the sum of Gibbs free energy of all the atoms present at the interface, and at this interface it is a highly non-equilibrium region with a very high thermodynamic driving force. In this case the growth rate is not limited by the magnitude of the huge driving force but by the amount of materials available for incorporation, which depends not only on the amount of materials evaporated into the growth chamber, but also on the surface-related kinetics of the various elements [21]. To evaluate if the Thomson-Gibbs effect play a significant role or not on a particle’s melting point, one must use the surface energy \( \sigma \) and the entropy of melting \( \Delta s \) of the given material. The equation of Thomson-Gibbs which yields \( \mu \) as a function of the size of the particle, is given by

\[ \mu = \frac{4\sigma v_c}{d} \]  

(27)

Here \( v_c \) is the volume per atom. Combining eq. 25 and eq. 27 we get the following expression for the melting point of a particle with diameter \( d \),

\[ T = T_m - \frac{4\sigma v_c}{\Delta \sigma d} \]  

(28)

Since it has not been possible to find the values of \( \sigma \) and \( \Delta s \) for Au-In alloys, we will settle for pure Au and see how it affects a Au particle with a diameter of 80 nm. The result yields \( T_m - T \approx 12^9 K \), where \( \Delta s_{Au} \) [35] is determined to be 57.6 J/mol K. This is a deviation less than 1%. If the same deviation would apply for a corresponding 80 nm particle consisting of a Au-In alloy, the melting point

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would deviate less than $5^0K$. But since we do not know the values of $\sigma_{Au-In}$ and $\Delta s_{Au-In}$ we can only use it to get a feeling of the melting point for these sizes of particles. In any case it does not seem probable that the Au-In catalyst would be liquid under the growth temperatures used.

### 3.3 Kinetics involving surface diffusion

There are basically four elementary processes occurring at the surface during crystal growth [15],[16],[22],[23]:

- **Adsorption** The first step in crystal growth is to absorb the growth material onto the crystal surface. The ratio of the adsorbed material to the incoming material is defined by what is called the sticking coefficient, which depends on the type of material and on the substrate. The atoms that are adsorbed on the crystal surface but not yet incorporated or desorbed are called adatoms.

- **Desorption** Adatoms will always have a probability of getting desorbed from the surface again, a process which is temperature dependent since they need a certain amount of energy to escape (or desorb). This energy is called the *activation energy of desorption*, and is dependent on the surface structure and type of adatom. At relative low growth temperatures desorption can be neglected, and is usually done in MBE growth.

- **Surface diffusion** Once the atoms are absorbed at the surface they will diffuse around on the surface boundary until they either desorb from the surface or get incorporated in the crystal. In normal diffusion, a net transport of atoms takes place from a region of higher concentration to one of lower concentration induced by a concentration gradient. The adatom concentration is so low that the probability of collisions is typically neglected in models describing mass transport by surface diffusion [27],[28],[29],[46],[47]. In processes like Au-assisted NW growth, the growth rate at the growth interface is to some extent determined by the mean path length (or time)
at which the adatoms diffuse on the surface before incorporation or desorption, and this is called the *diffusion length*. The effective mean distance at which the adatoms travel in a certain direction will in this thesis be called the *migration length*. Both lengths are of course related and are highly temperature dependent and can vary significantly from element to element. For NW growth the migration length is typically divided into two groups, substrate migration length $\lambda_s$ and NW sidewall migration length $\lambda_w$, see fig.13.

![Diagram of Nanowire Growth](image)

**Figure 13:** *Two migration lengths of adatoms are used in the description of NW growth.*

$\lambda_s$ is somewhat more complex to analyze than $\lambda_w$ because of its 2 dimensional surface dependence. Assuming that the incoming material is distributed homogeneously on the surface substrate, two situations have to be evaluated. First, the probability of finding an In atom a distance away from the site of adsorption can be approximated to have a Gaussian distribution, and therefore the fraction of available In adatoms collected for NW growth a distance away from the NW will also follow a Gaussian distribution [27].

- **Incorporation** The incorporation of adatoms on crystal surfaces may occur in two distinct processes, first a two dimensional (2-D) nucleation process, and second, incorporation by single adatoms at kinks and steps created by

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the first process. Incorporation on atomically flat surfaces usually requires a 2-D nucleation process because a single atom that has only one bonding face is normally at a not stable site and will therefore diffuse to the next site. In the 2-D nucleation process several adatoms combine forming a small nucleus of only one atomic layer on the surface. The nuclei tend to dissolve if they fail to reach a certain critical nucleus radius $r_c$. However, if the nucleus radius exceeds $r_c$ it will become stable, and since the step between the flat surface and nucleus has two bonding faces the incorporation of adatoms will have an increased probability. The stability of multi-bonding sites is why incorporation of adatoms at kinks and steps plays a dominating role in crystal growth.

It is important to understand the surface diffusion of group III species in order to control the NW growth. Because the As flux is $\approx 10$ times larger than the flux of group III elements, it is not expected to be the limiting factor of the growth rate in spite of the shorter diffusion length[25]. The diffusion lengths of Ga and In, on the other hand, are shown to have an important role on au-assisted GaAs and InAs NW growth[24],[29]. From SEM images of positioned InAs NW arrays, see Figure 14, it is possible to see that the topography of the substrate in the vicinity of the NWs differs from the areas without wires. This could be an indication that the material around the NWs is either used for NW growth or incorporated at the root of the NWs. In both cases it may be a measure of $\lambda_w$ of In adatoms. The longest wires are up to $6\mu m$ long and show no sign of tapering. This indicates a large $\lambda_w$ of the In adatoms on the wire sidewalls, since we may assume that all material which comes from the substrate or NW sidewalls is transferred all the way to the catalyst [26].

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So from fig.14 it seems reasonable to assume that $\lambda_w > \lambda_s$. There can be several reasons for this. The $<111>$-B substrate has a polarized As terminated close packed surface having many possible group III sites open pr. unit area, whereas the NW site facets $\{11\bar{2}\}$ and $\{1\bar{1}0\}$\textsuperscript{10} are non-polarized meaning that there are equal numbers of group III and group V sites. Another possibility is that if collisions between the adatoms plays a role on the NW sidewalls, the net diffusion toward the sink (growth interface) would be enhanced. As an analog explanation for this, one can imagine a fluid transported through a bottleneck where the opening is analog to the the growth interface, the fluid velocity at the narrow regions is larger than at the wide regions due to collisions. In the microscopic diffusion regime this means that the meantime spent by atoms in a given region on the

\textsuperscript{10}Claus B. Sørensen showed that both site facets $\{11\bar{2}\}$ and $\{1\bar{1}0\}$ are possible by analyzing SEM images. (No reference possible)
sidewall of higher adatom concentration is shorter than on the substrate of lower adatom concentration, and again giving lesser probability of getting incorporated or desorbed. This would of course require a high adatom surface density. Due to the unknown mechanisms underlying the movements of the atoms, it is difficult to estimate this density although it will be discussed below.

The diffusion models used for describing NW growth today more or less all [27],[28],[29],[46],[47] assumes steady state fickian diffusion with a diffusivity $D$ and adatom density $n$ described by,

$$ D \Delta^2 n - n/\tau + R = 0 \quad (29) $$

with the additions $n/\tau$ and $R$ which take account of the incorporation and effective impingement rate of adatoms respectively. Two equations like equation (29) are required, one for the substrate and one for the NW sidewalls. The NW length as function of the NW diameter can be extracted from the solutions to the equations, and they seem to fit relatively nice. However, if the diffusion length is much longer than the migration length because the adatoms move in many different directions before incorporation, and if the adatoms at the same time do not interact, it does not make sense to use a concentration gradient as in fickian diffusion. If we imagine that the atoms are moved by a concentration gradient towards the growth interface with some mean velocity, we can estimate a density of adatoms on the NW sidewalls from the known growth rate: The incorporation rate is $\nu = \frac{\text{atoms incorporated}}{\text{time}}$ and so the flux of adatoms in the z-direction on the wire sidewalls would be $\Phi = \frac{\nu}{2\pi r}$ where $r$ is the radius of the wire, if impingement of adatoms on the sidewalls is negligible. Using the fact that the typical MBE growth rate for 80 nm InAs NWs under the growth conditions described above is $\approx \frac{5\text{nm}}{s}$, the adatom current on the NW sidewalls towards the catalyst will be equal to the adatom incorporation rate at the growth interface which is $\nu \approx 7,5 \cdot 10^5 \frac{\text{atoms}}{s}$. If we as a rough approximation say that the adatoms have a thermal velocity corresponding to the substrate temperature, the indium adatom velocity is $v_{\text{adatom}} \sim \sqrt{\frac{ekT}{m}} \approx 500 \frac{m}{s}$. The density pr. unit length on the NW sidewalls is then $n = \frac{\nu}{v_{\text{adatom}}} = 0.0015 \frac{\text{adatom}}{\mu m}$. Here the attractive potential from the substrate is neglected which is of course not reasonable. It has not been possible to find the mobility of In adatoms on any surface, but if the mean velocity is only say 1/100 of the thermal velocity which is just a wild guess, the adatom density is still very low ($\sim 1 \frac{\text{adatom}}{\mu m}$). These considerations may act as an inspiration to try to describe adatoms diffusion with for example random walk

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theory instead of normal diffusion induced by a concentration gradient.

3.4 Controlling NW dimensions

To control the NW diameter one must be able to control the size of the Au particle. To do this an e-beam lithographic process was developed to position size defined Au-droplets, a process which has not been reported before for MBE growth of III-V NWs. NW arrays (Figure 14) have been made with a wide variety of techniques ranging from top-down etching to e-beam lithographic processes as the one used. One of the advantages of MBE growth is the ultra pure crystal growth due to a ultra high vacuum chamber, so to avoid any form of contamination the substrates have to be ultra clean before introducing it to the growth chamber. The recipe for producing these arrays of Au particles is found in appendix B, and have been done in collaboration with Martin Aagesen, SunFlake A/S, NBI. To find a relationship between the amount of applied Au in the evaporation chamber and the resulting NW diameter, we assume that the Au particle can be described as a cylinder after resist lift off, and as a result of free surface area minimization after heating in the MBE chamber prior to growth, the particle will attend a form of a solid half sphere of volume 

\[ V = \frac{1}{12} \pi d^3 \]

see Figure 15.
During the annealing step prior to growth, the substrate is heated up to 550°C, which will make the Au caps alloy with In from the substrate and form liquid droplets. The volume of the droplet will therefore be bigger than the volume of the cylinder because of the incorporated In, but we ignore this since we only use volume ratios in the further modeling. If two or more Au caps are within a given critical distance of each other, they will combine and form a larger droplet. So when making a pattern with dots in the software program which follows the e-beam writer, different nanowire diameters are possible by placing one, two or more dots next to each other. The droplet shape is a result of free surface area minimization due to free energy minimization.

The volume of the cylinder is $V = a(Q)h$ where $h$ is the height and $a(Q)$ is the area of the top face which depends on the amount of charge $Q$ exposed into the dot during the E-beam lithographic process. Other factors may also affect the size of the area, such as how good the electron beam is focused and variation in the thickness of the electron resist, but we assume that these factors play a negligible role within a single lithographic process. $h$ will always be known to a high accuracy.
Figure 16: SEM images of single and double dot patterns before NW growth. The height of the dots are \( h = 60 \) nm and the lower inset show NWs grown from a double dot pattern corresponding to an applied amount of gold of \( h = 2 \cdot 60 = 120 \) nm.

Although the Au particle alloys with In during the heating process which will increase the volume of the half sphere to some extent, we will estimate the volume of the cylinder and the half sphere to be equal,

\[
a(Q) h = \frac{1}{12} \pi d
\]

Measuring the diameter \( d_1 \) for a given growth of NWs, the diameter \( d \) of the NW will be given by,

\[
d = \left( \frac{a(Q) h}{a_1(Q) h_1} \right)^{\frac{1}{2}} d_1
\]

Here the only unknown factors are the \( a(Q) \)’s. \( a(Q) \) is the only parameter which

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is difficult to reproduce from growth to growth since it depends not only on the amount of charge $Q$ which is difficult to control exactly, but also on how good the beam is focused. But within a single lithographic process, exposing with the same amount of charge in all dots we get $a = a_1$ and therefore,

$$d(h) = \left( \frac{h}{h_1} \right)^{\frac{1}{3}} d_1$$

(32)

To determine the NW diameters, a Matlab program was developed in collaboration with Magni Glyvradal, master student at the Nano-Science Center, NBI. This program reads the intensity in every pixel of a SEM image which makes it possible to extract the NWs dimensions with a reliable and consistent method, see figure 17.
Figure 17: (a) A SEM image of an area of positioned NWs. The inset figures show how the threshold value for the NW boundaries is determined in a Matlab program designed to extract the NW dimensions. (b) A view of the graphic interface of the program, where the threshold value for the intensity is applied. Values over the threshold value are white while values under is black. (c) After the NW boundaries are determined, an area (the red square in (b)) is selected and an image of this area pops up showing the average diameter of each wire. (d) The NW diameter distribution is then fitted with a Gaussian function, which gives the average NW diameter of the whole area. In this case we have used $Q=120\text{fC}$ and $h=120\text{ nm}$ ($2\cdot60\text{nm}$), resulting in an average diameter of $105.5\text{ nm}$.

From this program it is easy to extract an average diameter of a collection of wires in an image.

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To demonstrate whether eq. (32) is applicable or not, a wire array was produced with lines of different thickness, see Figure 18, using different number of dots for each line. The gold thickness \( h \) applied in the e-gun chamber was 15 nm. To get the best contrast difference between the wires and the substrate in the SEM images, the horizontal sample holder was used. Since the Matlab program need NWs which are separated from each other in the images, it was only possible to tilt the sample holder in the SEM 15 degrees to ensure that the NWs did not overlap in the image.

Figure 18: \textit{SEM images from positioned wires with different diameters arranged into rows. Arrows are pointing from the row to the corresponding number of Au caps times the thickness \( h = 15 \text{ nm} \) of the applied gold. The number below the arrows is the mean diameter of the wires in that row. The images are tilted 15° from vertical.}

Using equation 32 with \( h = 30 \text{ nm} \) \( (d_1 = 93 \text{ nm} \) and \( h_1 = 30 \text{ nm}) \) as a reference, it is seen in Figure 19, that the other diameters lie within what we can expect from the uncertainty of the lithographic process and the NW diameter determination.
Figure 19: 5 different NW diameters are plotted as a function of the amount of Au in the seed particle. The graph is eq.32 with the values from the data point of 2 Au-droplets (2h). The diameters obtained from the few NWs in the images fit reasonable well with the graph.
4 Nanowire Heterostructure Growth

4.1 Introduction

Structures consisting of 2 or more materials are called heterostructures. Epitaxial growth of heterostructure nanowires has received increasing attention in recent years\cite{4,13,14}, due to a wide range of successful applications \cite{31,32,33}. Heterostructure growth confronts us with an extra challenge because of the fact that not only the different growth parameters such as temperature, pressure, flux ratios etc., have influence on the NW growth, but also the interface energies and the lattice mismatch$^{11}$ between the various materials at the junctions may play a important role on the wire growth and morphology. Of course the lattice mismatch which is about 7\% for GaAs and InAs’s respective bulk lattice constants, is an unjustable parameter. Fortunately, studies have shown that mismatch between the lattice parameters does not seem to have a major influence on NW heterostructure growth or morphology\cite{2,3}. Fabrication of intra-wire barriers in axial III-V heterostructures has so far been limited to an interchange of the group V elements arsenic and phosphorous. The primary reason for this limitation is that for most materials, axial growth of heterostructures consisting of two material combinations: A and B, is only possible with axial growth of either A on B or B on A, but not both. Another reason why group V materials are perferred as the changeable material, is that it is believed that group III materials have to diffuse through the Au cap before incorporation, which makes it difficult to get sharp junctions. The failure of axial growth of InAs/GaAs/InAs wires has been reported and studied intensively\cite{2,3}, and the conclusions are that the interfacial energy between the Au-catalyst and InAs is higher than the interfacial energy between the Au-catalyst and GaAs, which prevents axial growth of InAs on GaAs, as the system tries to minimize its free energy. This issue concerns other material combinations used for NW growth as well, and it is generally recognized that this is due to the difference in interfacial energies $\Delta \sigma = \sigma_{AC} - \sigma_{BC}$ between the catalyst particle C and the two wire materials A and B. Generally

$^{11}$Lattice mismatch is calculated using the respective bulk lattice constants, $(a_{GaAs} - a_{InAs})/a_{GaAs}$.
speaking, if $\sigma_{AC}$ is higher than $\sigma_{BC}$ axial growth of A on B fails, whereas axial growth of B on A is possible. Thus for B on A growth we get

$$\Delta \sigma = \sigma_{BC} - \sigma_{AC} < 0 \Rightarrow Straight$$

$$\Delta \sigma = \sigma_{BC} - \sigma_{AC} > 0 \Rightarrow Kinked$$

and vice-versa for growth of A on B. If $\sigma_{AC}$ and $\sigma_{BC}$ are almost equal, axial growth in both directions may become possible as in the case of the III-V nanowires, where the group V materials P and As are exchanged [4]. Specifically the division of Solid State Physics at Lund University has been growing heterostructure wires of a wide range of different material combinations by the Metal Organic Vapor Phase Epitaxy (MOVPE) method, and a complete overview of their results is made in a paper by Kimberly et al. in 2007 [2], see figure 20.

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<td>5.6886</td>
<td>straight</td>
<td>kinked to straight</td>
<td>-3.13</td>
</tr>
</tbody>
</table>

*Note that “straight” refers to continuation of growth in the same crystallographic direction, while “kinked” refers to a change of growth direction. *Mismatch is calculated with respect to material A, according to the formula mismatch = ($a_B - a_A$)/$a_A$. Therefore, a positive value of mismatch indicates that the lattice constant of material B is larger than that of material A. *The morphology type for InAs grown on InP depends on the growth conditions. See text for details.

Figure 20: Table taken from a article by Kimberly et.al 2007 [2] showing the heterostructure morphology of 13 of the most commonly used NW materials.

The development of axial heterostructures is of great interest in order to expand the range of device possibilities, but as seen in the table in Figure 20 it is not straight forward to do this.
4.2 InAs/GaAs single junction NWs

From Kimberlys table (table 20) it is seen that GaAs on top of InAs, retaining a straight NW configuration is possible, whereas InAs on top of GaAs is not. The possibility of growing straight GaAs/InAs heterostructures may be present under the right growth conditions, but several attempts with different temperature and pressures only resulted in kinked structures, as in the inset image in Figure 21. It might be that it is impossible with an Au catalyst, but possible with other catalyst materials. I have also grown straight InAs/GaAs heterostructures and a few have been examined with SEM and TEM.

![TEM image of a straight InAs/GaAs heterostructure and a SEM image of a kinked GaAs/InAs heterostructure in the upper inset. At the lower inset several characteristics of a straight InAs/GaAs NW is shown.](image)

Figure 21: A TEM image of a straight InAs/GaAs heterostructure and a SEM image of a kinked GaAs/InAs heterostructure in the upper inset. At the lower inset several characteristics of a straight InAs/GaAs NW is shown.
Because the diffusion length of Ga is relatively short (see section 3.3), a significantly amount of GaAs on the sidewalls of the InAs core develops during GaAs growth. The 2D nucleation of GaAs on the sidewalls does not seem to happen uniformly, which is seen in both SEM images (see Figure 22) and on TEM images (see Figure 23).

Figure 22: A) SEM images of InAs/GaAs NWs showing a nonuniform surface. The InAs wires are terminated with $\approx 150\text{nm}$ of GaAs. B) Pure InAs NW showing uniformity as a result of a very small nucleation rate of indium at the NW sidewall.

In the lower inset in Figure 21 a Moiré pattern at the core-shell region is very clear. A Moiré pattern is an interference pattern which can arise due to two effects, either when two crystal structures are overlaid at an angle (rotational Moiré fringes), or if they are overlaid parallel but have slightly different lattice parameters (translational Moiré fringes). The mathematical description can be found in [8], chapter 22. Translational Moiré fringes are expected in the case of InAs and GaAs since these structures have a relatively large lattice mismatch of $\sim 7\%$. But as seen in the region at the InAs/GaAs junction a strain field of $\approx 50\text{nm}$ is present. This may be an indication of low lattice mismatch between core and shell since the GaAs shell, which is properly not more than $\sim 5-10\text{nm}$’s in thickness, is expected to have a lattice spacing close to the lattice spacing of the InAs core. The other probability of getting a Moiré pattern is as mentioned to have rotational Moiré fringes. A slight misalignment of $\approx 1.5^\circ$ of the core
and shell crystals is actually seen from DPs using a small aperture in Figure 23 C. This may be the primary reason for the Moiré fringes seen at the core-shell region. The misalignment may be a result of a strain relaxation due to the high lattice mismatch, but it will not be analyzed further here.
Figure 23: A TEM image of the InAs/GaAs junction. On these wires it is interesting to see that 2D nucleation of GaAs on the sidewalls has not occurred uniformly, since a pure InAs segment is present. A) A DP of the core-shell region showing a 2D Moiré pattern. B) A DP of the pure GaAs region. C) Two DPs where obtained of pure InAs core (red pattern) and of the GaAs shell (turquoise pattern). Core and shell crystals are slightly misaligned. The DPs tell us that the structure is WZ and the zone axis is $\mathbf{B} = [1\bar{1}00]$. The TEM images where achieved on a 300 kV probe-corrected FEI Titan microscope operated by Jakob Wagner, CEN, DTU.
4.3 Axial heterostructures using ternary compositions

Formation of other axial heterostructures will be accessible by tuning the $\sigma$ values during growth of ternary materials. This has been shown for GaAs/GaAsSb/GaAs [37] and for GaAs/GaInAs/GaAs NWs were the mid segment functions as a quantum well because of its lower bandgap compared to GaAs. Growth of InAs wires using $Ga_xIn_{1-x}As$ as barrier material have not yet been reported, and no well-defined junctions by changing group III materials have been achieved so far. Nevertheless, such structures have been achieved, and the work will be presented here.

4.3.1 $Ga_xIn_{1-x}As$ barriers grown in InAs NWs

Growth of straight NW heterostructures with diameters of $\sim$80nm consisting of A: InAs and B: $Ga_xIn_{1-x}As$ where x is in the range from 0 to $\approx$ 0.4 were performed. The bandgap energy as function of the GaAs mole fraction x in $Ga_xIn_{1-x}As$ is presently not known in such nanostructures, but it is reasonable to assume that it increases as function of x from the bandgap of pure InAs to the bandgap of pure GaAs like in the bulk materials[30]. Therefore the term 'barrier' will be used for the segments consisting of $Ga_xIn_{1-x}As$. Typically when dealing with In-Ga-As ternary materials the mole fraction x refers to the In fraction on the group III sites, but because we are interested in the rise of the bandgap caused by the Ga content, the Ga mole fraction notation will be used. The EDX measurements were performed in STEM mode on two microscopes, a 200 kV JEOL 2010F equipped with a JED-2200F JEOL EDX system, operated by Jun Yamasaki, and a 300 kV probe-corrected FEI Titan 80-300 equipped with an Oxford 7773 EDX detector, operated by Jakob B. Wagner. The line scans achieved with the JEOL microscope were obtained with a spot size of $\sim$ 1nm with typically 256 steps using high angle annular dark-field STEM imaging (HAADF) for drift correction. The linescans achieved with the Titan microscope were obtained in the same way but with 50 steps and longer dwell time. The EDX analysis procedure outlined in section 2.2.2 has been used. Several single barrier growths were carried out with different
barrier growth times and different group III flux ratios, and the results from the EDX analysis on few of the straight NWs from each sample are listed in table 7. RHEED intensity oscillation data, give a measure of the bulk InAs(GaAs) growth rate as function of the temperature in the In(Ga) cell. From this we extract an expected value of the gallium mole fraction $x'$ in the $Ga_xIn_{1-x}As$ bulk material during barrier growth.

<table>
<thead>
<tr>
<th>$Ga_xIn_{1-x}As$ growth time $[sec]$ (No. of samples)</th>
<th>x': GaAs mole fraction Expected</th>
<th>x: GaAs mole fraction EDX data</th>
<th>$Ga_xIn_{1-x}As$ Segment length [nm]</th>
<th>Fraction of kinked wires (estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 (3)</td>
<td>0.34</td>
<td>$\approx 0.15 - 0.25$</td>
<td>230-300</td>
<td>$\approx 0$</td>
</tr>
<tr>
<td>40 (2)</td>
<td>0.34</td>
<td>$\approx 0.15 - 0.25$</td>
<td>160-200</td>
<td></td>
</tr>
<tr>
<td>10 (3)</td>
<td>0.34</td>
<td>$\approx 0.15 - 0.25$</td>
<td>50-60</td>
<td></td>
</tr>
<tr>
<td>34 (3)</td>
<td>0.438</td>
<td>$\approx 0.25 - 0.4$</td>
<td>100-110</td>
<td>$\approx 0.12$</td>
</tr>
<tr>
<td>32 (2)</td>
<td>0.47</td>
<td>$\approx 0.25 - 0.3$</td>
<td>130-150</td>
<td>$\approx 0.35$</td>
</tr>
</tbody>
</table>

Table 7: Five different single barrier growths were carried out. 2-3 straight NWs from each sample were examined with EDX and the results are listed here.

The first three samples are identical except for a change in the barrier growth time. From the EDX data the barrier thickness was determined and plotted in Figure 24B as function of the barrier growth time. I expected a linear relationship between growth time and barrier length for these small growth periods, but from these few data points, the growth rate seems to ease slightly off as the growth time increases. As seen in table 7 axial growth in both directions (A on B as well as B on A) with an x-value of up to $\approx 0.4$ have been obtained. From the EDX analysis we get large deviations on both the x values and barrier length values within each sample. This tells us that the growth conditions for the individual wires which are collected randomly on the wafer can vary substantially within a single growth experiment. Detailed analysis on positioned wires with barriers which have almost same growth conditions as presented in section 3.4, is left to be done.
Figure 24: (A) EDX line scan from sample 2, which is used to determine not only the barrier thickness but also the gallium mole fraction $x$ in the barrier. During GaInAs growth an InAs-GaInAs core-shell structure develops with a high content of Ga in the shell as a result of the short diffusion length of Ga. This is observed from 400 to 800 nm as a gradually increasing Ga content. When the growth time of GaInAs was only 10 sec the shell is very thin and could not be resolved from the background in the EDX analysis. (B) Barrier thickness as a function of GaInAs growth time for the samples with flux ratios of $x'=0.34$.

### 4.3.2 Estimate of the threshold value of $x$ for axial growth

In sample 4 and 5 (table 7), the In flux was held constant while the gallium flux was set corresponding to $x'=0.44$ and $x'=0.47$ during barrier growth, where $x'$ is the expected GaAs mole fraction (determined as explained in section 4.3.1). The wires are distributed randomly on the substrate and the local wafer area from which a single wire collects material (with different diffusion lengths) for its growth is different for each individual wire. Therefore it has not been possible to determine a detailed relationship between $x'$ and $x$. However, using SEM images (see Figure 25) the abundance of kinked wires has been determined by counting over a large area of each sample, and in Figure 25D the fraction of kinked wires has been plotted as function of $x'$. 

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Figure 25: A,B,C) SEM images of samples with \( x' = 0.34 \), \( x' = 0.44 \) and \( x' = 0.47 \), respectively (the scale bar in A applies also for B and C). Sample 2 (image A) shows no kinked wires, while in sample 4 (image B) and sample 5 (image C) we see an increase in the fraction of kinked wires. D) Plot of the fraction of kinked wires as a function of GaAs mole fraction \( x' \) (using the fact that all wires are straight when \( x' = 0 \) and all are kinked when \( x' = 1 \)). The maximum mole fraction that can sustain axial growth is around \( x' \approx 0.5 \). The inset shows an image of a typical kinked wire when the amount of gallium in the barrier is too high for axial growth.

If all wires had exactly the same growth conditions within a given sample we would expect the majority of all wires to be either straight or kinked, depending on whether the \( x' \)-value are either under or over the threshold value, respectively. Due to the large difference in the surface diffusion lengths between In and Ga, with
In being the more mobile species, it is reasonable to assume that the threshold value for $x'$ is not smaller than $x$. This assumption is supported by our EDX measurements on the samples with only straight wires, where all wires had $x$-values lower than $x'$. From Figure 25D the threshold value of $x'$ appears to be around $\approx 0.5$, and it is therefore expected (as a rough estimate) that the threshold value for $x$ in straight wires will be in the range

$$x_{\text{threshold}} \approx 0.4 - 0.5$$  \hspace{1cm} (34)

I should emphasize that this estimate applies to the growth conditions and NW diameters used. The threshold value for $x$ and therefore also the interfacial energies may depend on parameters such as temperature and pressure used during growth. Earlier studies \cite{2},\cite{13} have shown that these parameters have an effect on the morphology, indicating that the threshold values for $x$ might be optimized to higher values under other growth conditions. As already mentioned, all growths presented here were done with a substrate temperature of $423^\circ C$, a temperature which was found from optimized pure InAs nanowire growth conditions. Parameter optimization for higher threshold-values of $x$ on these types of wires still has to be addressed.

### 4.3.3 HAADF-STEM and EDX analysis of double barriers

Using the same growth conditions as sample 3 in table 7 but with a flux ratio of $x' = 0.44$ during barrier growth, two barriers were grown with a 20 sec (or approximately 50-100 nm) InAs separation. The sharpness of the interfaces was determined by HR HAADF-STEM image contrast, see Figure 26, which is not linear although it is a monotone function of $x$. As described in section 2.3, HAADF-STEM mode only detect high angle scattering which is highly dependent on the atomic number $Z$. The experiments where done by Jun Yamasaki and the microscope used for this purpose was an 200kV JEOL 2100F equipped with a STEM Cs probe corrector (CEOS GmbH) located at EcoTopia Science Institute, Nagoya, Japan.

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Figure 26: (A) HAADF STEM image showing a double barrier NW. The two barriers can be seen as two slightly darker bands in the image. The blow-ups of the barriers in (B) and (C) clearly show the contrast difference between the darker Ga\textsubscript{x}In\textsubscript{1−x}As and brighter InAs regions. The sharpness of the junctions can be resolved at the atomic level in (D) for the InAs/Ga\textsubscript{x}In\textsubscript{1−x}As junction. For the Ga\textsubscript{x}In\textsubscript{1−x}As/InAs junction in (E) a more blurred transition is typically completed within 5-15 atomic layers.

The atomically sharp InAs/Ga\textsubscript{x}In\textsubscript{1−x}As junction implies an instant incorpora-
tion mode of Ga. This was not expected from the VLS or VSS theory since as explained in the previous section, group III materials are believed to diffuse through the catalyst before incorporation. This would blur the interface since the Ga content which is absent in the catalyst before growth of $Ga_xIn_{1-x}As$, will increase slowly until an equilibrium ternary alloy state is established. Therefore an atomically sharp junction is unlikely with this growth mode only. However, although the atomically abrupt junction implies an instant incorporation mode of Ga, the transition from $x=0$ to the maximum value in the barrier is from EDX data seen to be less steep at this interface than at the $InAs/Ga_xIn_{1-x}As$ interface, see Figure 27. (A detailed description of the EDX data processing method is given in section 2.2.)

Figure 27: (A) HAADF STEM and EDX data of a double barrier nanowire with Ga mole fraction of $x \sim 0.25$. The EDX line scans show the As, In, and Ga content along the wire. The distance between the EDX steps is 1.9 nm, but these data are expected to include blurring of some nanometers, which is due to the probe size and imperfect drift correction. At (I) a sharp transition at the $InAs/Ga_xIn_{1-x}As$ junction to typically around half of the maximum value of $x$ is observed. A slower transition to the maximum value of $x$ appears at (II). Finally a fast transition back to $x=0$ is seen at the $Ga_xIn_{1-x}As/InAs$ junction (III). This is the typical profile of the compositions across the junctions as seen on several single barrier wires and three different double barrier wires in (A), (B) and (C).

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These results which will be discussed in section 4.4, suggest that the route to the incorporation site of Group III materials comes from two distinct diffusion mechanisms, interface and volume diffusion, and although Ga only alloys weakly with the solid Au-In cap, a certain amount will diffuse through it during growth.

4.3.4 Structure of the $Ga_xIn_{1-x}As$ and InAs segments

High supersaturation of the nanowire growth environment favors formation of the wurtzite (WZ) structure, while low supersaturation favors the zinc blende (ZB) structure [37]. The introduction of Ga gives a lower supersaturation of the environment at the growth interface, which is responsible for the high abundance of ZB segments (see Figure 28) in the barrier, in otherwise pure wurtzite (WZ) wires. To use the barriers for quantum electrical transport measurements, pure monostructures may be preferred, since the potential outcome would be easier to interpret. However, changing the growth parameters or nanowire diameters to get either pure ZB or pure WZ in the barrier is left to be done.
Figure 28: (A) A TEM image (left) showing structural change in the barrier region, due to a supersaturation change during growth, and a HAADF-STEM image (right) showing the compositional change in the barrier region (images from two different wires). The square in the HAADF-STEM image indicates the region corresponding to the image in (B). (B) HR-HAADF-STEM image revealing the structural composition near a barrier. C) Close up of the structural composition cross the junction going from pure WZ in the InAs region to an interchange of WZ and ZB in the barrier. The zone axis is [011] (cubic). D) Zoom in (B) showing that the individual In and As columns in the InAs region with a spacing of 1.5 Å are clearly resolved by HR-HAADF-STEM. These HR images also show unambiguously that the wires grow along the [111]B growth direction, and that they have the same polarity as the substrate. The HR-STEM images have been made with an aberration-corrected high-resolution STEM (JEOL 2100F equipped with a third-order spherical aberration corrector) operated at an acceleration voltage of 200 kV (Yamasaki, Japan.).
4.4 The atomic route to the nucleation site: Interface Diffusion vs. Solid Phase Diffusion

The purpose of this section is to describe how the adatoms are transferred to the incorporation site at the growth interface for temperatures below the eutectic melting point of the catalyst. In polycrystalline materials it is well known that the rate of atomic diffusion along interfaces generally differs significantly from the volume diffusion rate in the adjoining crystal lattices [38],[42]. Based on the information obtained in this study I believe that catalytic nanowire growth is not an exception. So there will be distinguished between the two diffusion mechanisms of how the materials are transferred to the nucleation site at the growth interface;

- **Interface diffusion** (IFD) most likely occurs at the growth interface between the Au cap and the wire. However, other possible fast IFD paths for the adatoms could come via grain boundaries, or possible interphase boundaries, within the Au-cap. Recent x-ray analysis [40] on the Au caps terminating GaAs wires has shown several peaks from different Au-Ga structural phases after growth, see Figure 29. The structure of the narrow interface region varies with distance from the interface midplane, and the diffusivity will therefore be a function of distance away from the midplane. As an approximation we will assume a thin plate with an effective averaged diffusivity denoted $D_{IFD}$.

- **Volume diffusion** (VSS) [19] is referring to the atomic diffusion induced by a concentration gradient in the solid catalyst with an average effective diffusivity denoted $D_{VVS}$.
Figure 29: An illustration of an axial heterostructure nanowire. The zoom on the Au cap gives us an idea of how the two types of mechanisms for the group III elements could look like. It is likely that the IFD process occurs at the growth interface, but also grain boundary diffusion or even phase boundary diffusion within the catalyst may play an important part.

The overall effective diffusivity of the incorporation system (i.e., the catalyst and growth interface) are given by

$$Dt \approx D_{IFD}\eta t + D_{VVS}(1 - \eta)t$$

(35)

where $\eta$ is the fraction of the total diffusion time spent by the migrating atoms at the interface regions with diffusivity $D_{IFD}$. As the diffusion distance in solid materials can be approximated by $(Dt)^{\frac{1}{2}}$[41] where $t$ is the total diffusion time, the value of the two terms $D_{IFD}\eta t$ and $D_{VVS}(1 - \eta)t$ represents the relative amount of interface and volume diffusion respectively. We assume that $\eta \ll 1$, but at the same time $D_{IFD} \gg D_{VSS}$, and we can therefore not neglect any of the two terms a priori. So we will distinguish between three diffusion regimes;
• A: $\eta D_{IFD} \gg (1 - \eta) D_{VSS}$, Under this condition the adatoms are transferred to the nucleation sites at the growth interface only along interfaces. Since $D_{VVS}$ is more temperature dependent than $D_{IFD}$ [38], this regime is favored at sufficiently low temperatures, but also at higher $\eta$ values and lower solubility of the diffusant in the catalyst material.

• B: $\eta D_{IFD} \approx (1 - \eta) D_{VSS}$ Here both diffusion processes contribute to the nanowire growth.

• C: $\eta D_{IFD} \ll (1 - \eta) D_{VSS}$ This volume diffusion regime is favored at higher temperatures, lower $\eta$ values and higher solubility of the diffusant in the catalyst material.

It is known that the solubility of As in Au is negligible under typical growth conditions [1], and therefore we assume this element to be a diffusant of regime A. This assumption is supported by studies [4] on InAs/InP nanowires, where the exchange of As and P occurs instantly, giving atomically sharp junctions. On the other hand, the solubilities of both Ga and In in Au are known to be high although they will depend on the growth conditions, making the system more complex. However, by selecting appropriate growth parameters it may be possible to have a situation where the solubility of one of the elements in the Au particle is much higher than the other, thus providing equilibrium conditions where only one element will alloy with the Au particle. EDX measurements that have been carried out on the InAs nanowires (same wires as presented in section 4.2) terminated by growth of $\approx 150\,nm$ of GaAs below the Au cap, and grown under the same conditions as the barrier wires presented here, have shown that the Au cap contained about 20-30 % In and virtually no Ga, see Figure 30.
Nanowire heterostructure growth

Figure 30: A InAs/GaAs NW. The red line in the image shows the path of the EDX line scan. The Au concentration tells us where the Au cap begins. As seen from the Ga profile there is no Ga left in the Au catalyst while a high concentration of In is still present. The In peak close to the interface might be a result of In precipitation towards the eutectic Au-In concentration during cooling. The concentrations shown are in weight percentage. The weight percent of In in Au at the eutectic melting point is 23% [17], which seems to be in good agreement with these EDX data.

These results are confirmed by other studies [39],[19]. This is an indication of either a low solubility of Ga in Au during growth in the presence of In or that Ga may be released from the Au cap during cooling after growth. However, studies on GaAs/InAs NW heterointerfaces[39] show that when the Au-Ga alloyed catalyst

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is exposed to the In flux, the catalyst quickly changes its composition by expelling Ga and absorbing In, where in the opposite case In tends to stay in the catalyst. These differences suggest that In might have more thermodynamic affinity toward Au than Ga, and tells us that the $Ga_xIn_{1-x}As/InAs$ junction will be completed faster than the $InAs/Ga_xIn_{1-x}As$ junction.

Arguments of why I expect regime B to apply for Ga incorporation will be presented here; In the case of solely IFD growth (regime A), Ga will be incorporated instantaneously as in the case of As and therefore both junctions are expected to be atomically sharp. For the wires with short barriers and no core-shell structure the EDX data show that the transition from the minimum to the maximum value of $x$ in the barrier was slightly slower at the $InAs/Ga_xIn_{1-x}As$ interface than at the $Ga_xIn_{1-x}As/InAs$ interface. High Resolution STEM images of the $InAs/Ga_xIn_{1-x}As$ interface on the other hand, show that a substantial compositional change happens at the atomic level. These informations indicate that both incorporation modes for Ga are present, and Ga therefore is a diffusant of regime B. From the EDX data I estimate the fraction of Ga incorporated from the two mechanisms to be comparable, as the width of the transition zone from $x=0$ to typically around half of the maximum value in the barrier is below the lateral EDX resolution. HR HAADF STEM images of the $Ga_xIn_{1-x}As/InAs$ junction (see Figure 26E) also show a slightly darker band with higher concentration of Ga, followed by a slight decrease in intensity over typically the following 5-10 atomic layers. This may be an indication that a small amount of Ga is left in the catalyst after barrier growth, and that this Ga is incorporated in the wire shortly after the beginning of InAs growth. Since we know that $\sigma_{AC} > \sigma_{BC}$, other reasons may also contribute to this profile such as beginning island formation [2] which will give a rough interface and therefore a blurred contrast profile. It could also be due to surface segregation, as observed in bulk $Ga_xIn_{1-x}As/GaAs$ interfaces, but this cannot contribute much since we would expect to see similar segregation effects at the $InAs/Ga_xIn_{1-x}As$ junction. Based on the NWs presented here, it is difficult to say which diffusion regime indium belongs to, but the higher thermodynamic affinity of In in Au relative to Ga [39], suggests that In is somewhere in between regime B and C. From these arguments a list of the diffusion regimes of the respective elements used is given in table 8.
Growing other axial heterostructure NWs using different ternary compositions would be interesting because such NWs would properly not only tell us more about the diffusion regimes of presented elements when combining some of these elements with new ones, but also include new elements to the list (Table 8).

<table>
<thead>
<tr>
<th>Element</th>
<th>Diffusion regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>B</td>
</tr>
<tr>
<td>In</td>
<td>B - C</td>
</tr>
<tr>
<td>As</td>
<td>A</td>
</tr>
</tbody>
</table>

Table 8: Diffusion regimes of Ga, In and As
5 Conclusions

As seen this thesis has been split into three parts, and overall conclusions on each part will be presented here.

The first part  'Characterization of Nanowires’, a framework of how to handle and process data from relevant electron probe techniques used on III-V nanowires has been presented. It includes:

- A general and detailed procedure for identifying and indexing a nanowire diffraction pattern has been developed. The requirements for using this method is that the nanowire growth direction is known and the nanowire structure is either zincblende or wurtzite.

- A theoretical framework of the two possible structures using the kinematical approximation has been derived, including the unit cell structure factor of the two structures. It has not been possible to find any previous attempt to derive the unit cell wurtzite structure factor.

- A general procedure for processing and quantifying raw EDX data has been developed, which makes it possible to make a reliable and relatively accurate composition determination in either atomic or weight percentage using the Cliff-Lorimer ratio technique.

The second part  ‘Nanowire growth’, thermodynamic and kinetic properties of crystal growth which may be relevant for further understanding of nanowire
growth have been described. This theoretical discussion on growth develops mostly a qualitative and conceptual framework, as the detailed growth process is very complex. Positioned nanowires with diameters defined by the size of the positioned Au-droplets via a lithographic E-beam process are presented together with a model describing the NW diameter as function of the applied Au in the E-gun chamber.

The third part 'Nanowire Heterostructure growth’ presents results on some of the experimental work and new ideas on NW growth. Growing relatively long segments of GaAs on top of InAs results in a nonuniform shell structure due to a nonuniform nucleation process. This effect may be minimized with other growth conditions. The effect is seen in SEM images, TEM images, and from EDX data. Growing short segments (< 50 nm) of $Ga_xIn_{1-x}As$, sidewall growth is not seen in the images and are below the detection limit in the EDX data. It has been shown that it is possible to grow well-defined barriers in straight axial nanowires by changing the group III-components using ternary compositions. Here $Ga_xIn_{1-x}As$ has been used as barrier material in InAs nanowires. The threshold value of the GaAs mole fraction in the barrier for successful axial barrier growth is estimated to be $\approx 0.4-0.5$ under the growth conditions presented. The width of the interfaces between $Ga_xIn_{1-x}As$ and InAs is the limiting factor for how thin barriers can be grown. From HAADF-STEM images the interfaces have been shown to be sharp at the atomic level although from the EDX data we have seen that the $InAs/Ga_xIn_{1-x}As$ interface is only atomically sharp up to a certain level of the maximum GaAs mole fraction found in the barrier. A growth model is proposed, which assumes that the route of the adatoms to the incorporation site involves two different diffusion mechanisms; an instant incorporation mode where the materials are transferred to the incorporation site via interface diffusion, and a slower incorporation mode where the group III elements diffuse through the solid catalyst.

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6 Appendices

A1. IDL program for calculating the R-ratios and intermediate angles of two reflections in a DP of ZB or WZ structure

```
pro calculation_of_angles_and_spots_ratios_in_ZB_or_WZ_DPs

print, 'For Zinc Blende type 1, for Wurtzite type 2:'
read, structure
if structure eq 1 then print, 'Type the 3 miller index ZB growth direction h,k,l of the NW:'
if structure eq 2 then print, 'Type the 3 miller index WZ growth direction h,k,l of the NW:'
read, h
print, h
read, k
print, k
read, l
print, l=-(h+k)
for U=-2,2 do begin $
  for V=-2,2 do begin $
    for W=-2,2 do begin $
      T=-(U+V)
      dot_wz=h*U+k*V+i*T+l*W
      dot_zb=h*U+k*V+l*W
      if dot_wz eq 0 and structure eq 2 and U+V+W ge 0 and U^2+V^2+W^2 ne 0 then
        print, '--------------------'
        print, 'Zone Axis [UVW]:',U,V,W
        print, 'Zone planes (hkl):'
      if dot_zb eq 0 and structure eq 1 and U+V+W ge 0 and U^2+V^2+W^2 ne 0 then
        print, '--------------------'
        print, 'Zone Axis [UVW]:',U,V,W
        print, 'Zone planes (hkl):'
    endfor
  endfor
endfor

print, 'Type the 3-index miller indices for the first reflection ', 'i_1='
read, h_1
print, h_1='
read, k_1
print, k_1='
read, l_1
print, l_1=-(h_1+k_1)
for h_2=-2,2 do begin $
  for k_2=-2,2 do begin $
    for l_2=-2,2 do begin $
      i_2=-(h_2+k_2)
      dot1_wz=h_1*U+k_1*V+i_2*T+l_2*W
      dot1_zb=h_1*U+k_1*V+l_2*W
      if dot1_wz eq 0 and structure eq 2 and dot_wz eq 0 and sqrt(h_1^2+k_1^2+l_1^2) lt sqrt(12) and h_1+k_1+l_1 ge 0 
        and h_1^2+k_1^2+l_1^2 ne 0 and U+V+W ge 0 and sqrt(U^2+V^2+W^2) lt sqrt(12) and U^2+V^2+W^2 ne 0
        print, h_1,k_1,l_1, ' R= ', sqrt(4./3.*(h_1^2+h_1*k_1+k_1^2)+3./8.*l_1^2)
      if dot1_zb eq 0 and structure eq 1 and dot_zb eq 0 and sqrt(h_1^2+k_1^2+l_1^2) lt sqrt(12) and h_1+k_1+l_1 ge 0 
        and h_1^2+k_1^2+l_1^2 ne 0 and U+V+W ge 0 and sqrt(U^2+V^2+W^2) lt sqrt(12) and U^2+V^2+W^2 ne 0
        print, h_1,k_1,l_1, ' R= ', sqrt(h_1^2+k_1^2+l_1^2)
    endfor
  endfor
endfor

print, 'Type the 3-index miller indices for the second reflection ', 'i_2='
read, h_2
print, h_2='
read, k_2
print, k_2='
read, l_2

R12=sqrt(4./3.*(h_1^2+k_1^2+l_1^2)+3./8.*l_1^2)/sqrt(4./3.*(h_2^2+k_2^2+l_2^2)+3./8.*l_2^2)
theta=sqrt((h_1+k_1+l_1)^2/2*(h_2+k_2+l_2)^2/2)/sqrt((h_1+k_1+l_1)^2/2*(h_2+k_2+l_2)^2/2)
```

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\((h_2^2+k_2^2+h_2*k_2+9./32.*l_2^2))\)

\[R^2 = (R_{21})^{-1}\]

\[\theta = \theta \times 360/(2 \times 3.14159265)\]

if structure eq 2 then print, "WZ, The spot spacing ratio for the reflections: '1: (',h_1,k_1,l_1,')',' and ','2: (',h_2,k_2,l_2,')'
if structure eq 2 then print, 'R12=', R12, ' R21=', R21
if structure eq 2 then print, 'And the intermediate angle:', theta, 'degrees'

if structure eq 2 then print, '---------------ZB--------------------------'

\[R_{13} = \sqrt{(h_1^2+k_1^2+l_1^2)/\sqrt{(h_2^2+k_2^2+l_2^2)}}\]

\[R_{31} = (R_{13})^{-1}\]

\[\theta_1 = \arccos((h_1*h_2+k_1*k_2+l_1*l_2)/\sqrt{(h_1^2+k_1^2+l_1^2)*(h_2^2+k_2^2+l_2^2)})\]
\[\theta_1 = \theta_1 \times 360/(2 \times 3.14159265)\]

if structure eq 1 then print, 'ZB, The spot spacing ratio for the reflections: '1: (',h_1,k_1,l_1,')',' and ','2: (',h_2,k_2,l_2,')'
if structure eq 1 then print, 'R12=', R13, ' R21= ', R31
if structure eq 1 then print, 'And the intermediate angle:', theta, 'degrees'

end
A2. IDL program for Cliff-Lorimer factor determination for EDX analysis

```idl
pro alpha_beta_determination

; This program determines the alpha value (K_ga/K_as) from a background corrected pure GaAs region, or the beta value (K_in/K_as) from a background corrected pure InAs region.

print, 'For alpha determination type 1, for beta determination type 2:
read, ab
if ab eq 1 then goto, alpha_det
if ab eq 2 then goto, beta_det

alpha_det:
print, '------------Alpha determination NBI257--------------

; Type the path of the 'GaAs' datafile
readcol, 'datafile.txt', dist, Y_ga, Y_as, Y_in,

u=n_elements(dist)
print, 'Type the number of the first line of the pure GaAs region:'
read, w2
print, 'And the number of lines in that region:'
read, v2

Y_ga0=fltarr(1,u)
for i=0,u-1 do begin
  Y_ga0(i)=Y_ga(i)
endfor

Y_as0=fltarr(1,u)
for i=0,u-1 do begin
  Y_as0(i)=Y_as(i)
endfor

; ----------------Quantification--------------------
print, 'Type the alpha value:'
read, alpha

C_as=fltarr(1,v2+1)
C_ga=fltarr(1,v2+1)
for i=w2,w2+v2 do begin
  C_ga(i-w2) = 1/(1+alpha*(Y_as0(i)/Y_ga0(i)))
  C_as(i-w2) = alpha*(Y_as0(i)/Y_ga0(i))*C_ga(i-w2)
endfor

C_as2=0
for i=w2,w2+v2 do begin
  C_as2=C_as(i-w2)+C_as2
endfor
print, 'Average value of quantified arsenic:', C_as2/(v2+1)

C_ga2=0
for i=w2,w2+v2 do begin
  C_ga2=C_ga(i-w2)+C_ga2
endfor
print, 'Average value of quantified gallium:', C_ga2/(v2+1)

plot, dist, Y_ga, xtitle='Position [nm]', ytitle='Counts', title='Unquantified EDX data'
oplot, dist, Y_ga, color='0000FF'
oplot, [dist(u/1.2),dist(u/1.1)], [Y_ga(u/2),Y_ga(u/2)], color='00FF00'
xyouts, dist(u/1.05),Y_ga(u/2), 'Arsenic', charsize=1,charthick=1
xyouts, 0.195,280, 'GaAs', charsize=1,charthick=1
xyouts, 0.13,160, 'Catalyst', charsize=1,charthick=1
xyouts, 0.451,200, 'InAs', charsize=1,charthick=1
plot, dist*1000, C_ga, yrange=[0,1], xtitle='Position [nm]', ytitle='Concentration', title='Quantified EDX data'
oplot, dist*1000, C_ga, color='FF0000'
oplot, [2,4], [0.9,0.9], color='FF0000'
oplot, [2,4], [0.85,0.8], color='0000FF'
```

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beta_determ:
print, '----------Beta determination--------------'
;Type the path of the 'InAs' datafile
readcol, 'datafile.txt', dist, Y_ga, Y_as, Y_in
u=n_elements(dist)
;--------Gallium background substraction and background ratios------------------
print, 'Type the number of the first line of the pure InAs region:'
read, w
print, 'Type the number of lines in this region:'
read, v
print, 'Type the beta value:'
read, beta
C_as=fltarr(1,v+1)
C_in=fltarr(1,v+1)
for i=w,w+v do begin
    C_in(i-w) = 1/(1+beta*(Y_as(i)/Y_in(i)))
    C_as(i-w) = beta*(Y_as(i)/Y_in(i))*C_in(i-w)
endfor
C_as2=0
for i=w,w+v do begin
    C_as2=C_as(i-w)+C_as2
endfor
print, 'Average value of quantified arsenic:',C_as2/(v+1)
C_in2=0
for i=w,w+v do begin
    C_in2=C_in(i-w)+C_in2
endfor
print, 'Average value of quantified indium:',C_in2/(v+1)
;---------------plotting----------------
!p.multi=[0,0,2]
plot, dist, Y_as, xtitle='Position [!7l!3m]', ytitle='Counts', title='Unquantified EDX data'
oplots, dist, Y_as, color='0000FF'
oplots, dist, Y_in, color='00FF00'
oplots, [0.09*dist(u-1),0.09*dist(u-1)], [Y_as(u-1),Y_as(u-1)], color='0000FF'
oplots, [0.09*dist(u-1),0.09*dist(u-1)], [0.9*Y_as(u-1),0.9*Y_as(u-1)], color='00FF00'
oplots, [0.09*dist(u-1),0.09*dist(u-1)], [0.8*Y_as(u-1),0.8*Y_as(u-1)], color='FF0000'
oplots, [0.09*dist(u-1),0.09*dist(u-1)], [0.8*Y_in(u-1),0.8*Y_in(u-1)], color='FF0000'
oplots, [0.09*dist(u-1),0.8*Y_as(u-1)], 'Arsenic', charsize=1,charthick=1
oplots, [20,25], [0.9,0.9], color='0000FF'
oplots, [20,25], [0.8,0.8], color='00FF00'
oplots, [20,25], [0.7,0.7], 'Indium', charsize=1,charthick=1
plot, Y_ga*1000, C_in, yrange=[0,1], xtitle='Position [nm]', ytitle='Concentration', title='Quantified EDX data'
oplots, Y_ga*1000, C_in, color='00FF00'
oplots, Y_ga*1000, C_as, color='0000FF'
oplots, Y_ga*1000, C_as, 'Arsenic', charsize=1,charthick=1
oplots, Y_ga*1000, C_in, color='00FF00'
oplots, Y_ga*1000, Y_in, color='0000FF'
oplots, Y_ga*1000, Y_in, 'Arsenic', charsize=1,charthick=1
oplots, Y_ga*1000, Y_in, 'Indium', charsize=1,charthick=1
end
A3. IDL program for quantification of EDX data

```IDL
pro edx_quantification
print, 'Remember to type in the alpha and beta value and type in the barrier region for x value.'
alpha = ?
beta = ?
readcol, 'Special wire2_EDXprofile.txt', dist, C_K, O_K, Yga, Yas, YIn, Au_M
u = _element(dist)
print, 'number of line: ', u
for i=0,u-1 do begin
  C_in(i) = 1/(beta/alpha*(Yga(i)/YIn(i)) + beta*(Yas(i)/YIn(i)) + 1)
  C_as(i) = beta*(Yas(i)/YIn(i))*C_in(i)
  C_ga(i) = (beta/alpha)*(Yga(i)/YIn(i))*C_in(i)
endfor
for i=0,u-1 do begin
  C_in2(i) = 1/(1+(alpha/beta)*(YIn(i)/Yga(i)))
  C_ga2(i) = (alpha/beta)*(YIn(i)/Yga(i))*C_in2(i)
endfor
C_as4 = 0
for i=0,u-1 do begin
  C_as4 = C_as(i) + C_as4
endfor
print, 'average value of quantified arsenic:', C_as4 / u
for i=0,u-1 do begin
  C_ga1 = C_ga(i) + C_ga1
endfor
C_ga5 = C_ga1 / (endpoint - startpoint + 1)
for i=0,u-1 do begin
  C_in1 = C_in(i) + C_in1
endfor
C_in5 = C_in1 / (endpoint - startpoint + 1)
print, 'Gallium in barrier', C_ga5
print, 'Indium in barrier', C_in5
a = 1/(C_ga5 + C_in5)
print, 'Gallium mole fraction (x) in barrier:', a * C_ga5

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```
B. Producing an array of gold dots on an GaAs wafer

(This recipe is described in great detail so other people should be able to use it)

**Cutting out pieces of the GaAs wafer**  Clean the cutting table, tweezers and other surfaces which might come in contact with the wafer. This is mandatory throughout the process. The GaAs wafer should be cutted out in pieces of 8x6mm. 8mm along 'major flat' and 6 mm along 'minor flat'. To avoid GaAs splinter on the surface of the wafer, there must not be any weight on the cutter.

**Double layer resist application**  Before the resist application the wafer, spinner and the glass which lies on the baker should be clean. Do not use the o-ring at the spinner. If it is uncertain whether the wafer is clean or not, clean it in acetone, methanol and IPA and bake it in approximately 5 minutes at $185^0C$. At the same time find the 6% copolymer and the 2% PMMA and stir the mixtures. Now the two resists should be applied in the following order:

- 6% copolymer, 4000 o/m in 45 sec and bake it in 90 sec at $185^0C$.
- 2% PMMA, 4000 o/m in 45 sec and bake it in 90 sec at $185^0C$

Make sure that the spinner acceleration is on max.

**E-beam lithography**  Before loading of sample in the SEM, scratch a little focusing point in the top left corner. Load the sample, blank the beam and turn on V7G. Go to the faraday-cop, open the beam and focus. Find the top left corner (closest to the faraday cop) on the chip, and focus with wobbler and astigmatism until a nice round spot appears. Align 'minor flat' to the x direction.

---

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To make well-defined dots with the electron beam it is important that it is well focused. Hereafter:

- Find the top left corner and place the beam as shown in the figure. Blank the beam and press 'go rel' (-3, 3.5, 0) (Elphy has to be turned on). Store the position! and focus.

- Open the pattern in Elphy, set a mark in 'dot' and type the dwelltime in msec. \( t(\text{ms}) = \frac{\text{charge}}{\text{current}} \). Remember to set the magnitude at 2000x.


- Hereafter follow the planned e-beam process with elphy.

**Resist development**  Clean 2 glasses in acetone and IPA, and pour IPA in one glass and PMMA developer 1:3 in the other. Develop in PMMA developer 1:3 for 45 sec and flush in IPA immediately after. Dry with nitrogen. Check if the focusing spots are visible in the optical microscope.

**Evaporation of gold**  After the chip is mounted on the E-gun sample holder, blow it with nitrogen. The chamber pressure must be below \( < 5 \cdot 10^{-8} \) before starting to evaporate. The wanted amount of gold are deposited with a rate of approximately 2 Å/s.

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Dissolving the resist  Put the chip in hot acetone (approximately 50 – 60$^\circ$C) in a couple of minutes. Hereafter the gold should be washed off with acetone, methanol and IPA. Dry it with nitrogen.

Preparing for MBE growth  Before introducing the chip in the MBE chamber, ash it for 60 sec, deoxidize in HF or $NH_3$ and flush it in pure methanol. The chips are mounted on a GaAs substrate with liquid Ga as a glue.
References


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