Copper as Seed Particle Material for InP Nanowires

Karla Hillerich

Licentiate Thesis

Solid State Physics
Lund Institute of Technology
Lund University
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May 18, 2011

Opponent: Prof. Stig Stenström
Examiner: Ass. Prof. Magnus T. Borgström
Abstract

Even after two decades of research the interest in semiconducting nanowires is still high due to their remarkable electronic and optical properties. During the last few years, the focus within the nanowire growth community shifted from realizing new structures and devices to improving the performance of devices, and a deeper understanding of the growth mechanisms.

Nanowire growth is mostly seeded using gold particles. However, gold is not desirable in the existing silicon technology, as its presence results in poor electronic properties. Thus, new strategies are evaluated to avoid gold as particle material, for example by growing nanowires without particles or by using self-seeded growth. A recent approach is the growth based on alternative "foreign" seed particle materials which promise a better control over the growth compared to self-seeded growth.

In this thesis, copper seed particles were used for the first time to grow vertically-aligned epitaxial InP nanowires. Copper was chosen, because of its properties similar to those of gold. The slight differences between gold and copper allowed the identification of parameters which are crucial in understanding the necessary properties for a suitable seed particle material. The growth is limited to a narrow temperature regime between 340 °C and 370 °C. Two different types of nanowire growth were identified depending on the molar fraction of the precursor gas mixture, namely Cu₂In-seeded growth and self-seeded growth. High V/III ratios above 930 resulted in growth from Cu₂In-seed particles, while at lower V/III ratios both types of nanowires occurred. The studies have shown that gold particles can successfully be replaced using particles from other seed materials. These results bring us one step further in understanding particle-seeded nanowire growth.
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<tbody>
<tr>
<td>CCD</td>
<td>Charged-coupled device</td>
</tr>
<tr>
<td>CBE</td>
<td>Chemical beam epitaxy</td>
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<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron-beam lithography</td>
</tr>
<tr>
<td>EPC</td>
<td>Electronic pressure controller</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
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<tr>
<td>LPE</td>
<td>Liquid phase epitaxy</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass-flow controller</td>
</tr>
<tr>
<td>MO</td>
<td>Metal-organic</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal-organic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MOVPE</td>
<td>(also OMVPE) Metal-organic Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>PIN</td>
<td>Preferential interface nucleation</td>
</tr>
<tr>
<td>PLL</td>
<td>Poly-(L)-lysine</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy/Microscope</td>
</tr>
<tr>
<td>TBA</td>
<td>Tertiabutylarsine</td>
</tr>
<tr>
<td>TBP</td>
<td>Tertiabutylphosphine</td>
</tr>
<tr>
<td>TEG</td>
<td>Triethyl-Galllium</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy/Microscope</td>
</tr>
<tr>
<td>TMG</td>
<td>(or TMGa) Trimethyl-Galllium</td>
</tr>
<tr>
<td>TMI</td>
<td>Trimethyl-Indium</td>
</tr>
<tr>
<td>TPB</td>
<td>Three-phase-boundary</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>-------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
</tr>
<tr>
<td>VSS</td>
<td>Vapor-solid-solid</td>
</tr>
<tr>
<td>WZ</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-Ray Energy Dispersive Spectrometry</td>
</tr>
<tr>
<td>ZB</td>
<td>Zinc blende</td>
</tr>
</tbody>
</table>
List of papers

This thesis is based on the following papers. They will be referred to by their roman numbers:

I. Epitaxial InP nanowire growth from Cu seed particles,
   I planned the project, conducted all experiments, their characterization and their analysis, and I wrote the article.

II. Copper as Seed Particle Material for Epitaxial InP Nanowire Growth
    K. Hillerich, K.A. Dick, M.E. Messing, K. Deppert, J. Johansson, manuscript
    I planned the project, conducted all experiments, the characterization and their analysis, and I wrote the manuscript.

The following papers are not included in the thesis:

III. The use of gold for fabrication of nanowire structures
    I took part in the discussion of the concept of the article, contributed some parts of the text and illustrations and took part in the discussion of the article

IV. A comparative study of the effect of gold seed particle preparation method on nanowire growth
    I took part in the planning of the project, conducted large parts of the characterization and analysis, and developing the article.

V. Growth Mechanism of Self-Catalyzed Group III-V Nanowires
    I performed parts of the SEM characterization and dimension measurements. I took part in the discussion of the manuscript.

VI. The Periodically Changing Morphology of the Growth Interface in Si, Ge and GaP Nanowires
    I grew the GaP nanowires, took part in the in-situ experiments on them and took part in the discussion of the manuscript.
Acknowledgements

I am happy to be part of this very inspiring research group. Although one might think, nanowires are the main actors in the play, the people actually are! Thank you, Lars, for building up this nice group, for attracting great scientists and for promoting us so well out in the world.

There is a number of persons I would like to thank for their help or just for being there…

I thank the whole Crystal growth & Materials Science group for lively discussions, ideas and advices during our meetings. I learn a lot on Friday mornings.

I thank Knut for giving me the chance to do my PhD here in Lund, being a great supervisor, having time anytime, supporting, helping to improve and being a great source of ideas.

Kimberly, thank you for convincing Knut, that you need me here! It is great having you as a supervisor. Thank you for all your knowledge on nanowires, all the useful comments and discussions. It is a lot of fun working with you on the course.

Jonas, after some teething troubles, we are a great team. I appreciate a lot our meetings and your great contributions, your endless patience and kindness. You bring structure into my chaotic thoughts.

I have the possibility to spend some time at the in-situ TEM at IBM Yorktown Height. It has always been a great time in the lab with Frances and Cheng-Yen. I thank Frances’ family a lot for hosting me so warmly.

I thank the nCHREM people Reine, Martin and Gunnel for patiently teaching me the TEM and helping me with the troubles I tend to have with the instrument.

I thank Bengt for being such a great problem solver and for hours with Miss Swan (even though I would have preferred to spend them with something else). Apart from talking with you about the moods of an old lady, it is great to chat about anything else in life with you, too. Without Søren’s endless source of knowledge and his work on the machine, we would not have been able to finally start it again. Thank you.

I thank Magnus for answering all my questions on MOVPE and growth, you helped me a lot.

Without Kristian’s help on MATLAB I would not have come so far. Thank you for your patience and codes.

The people who make our lab working so smoothly, that we can concentrate on research and we tend to only recognize them, if something doesn’t work…Ivan, Peter, Mariusz, Håkan, George, Anders, Lena, Mona and Monica.

Bernhard welcomed me here, told me all important stories and made my time here much easier. I appreciate the hours of “sudern” and all the things I learned from you. I miss you.
Jessica, it was great working with you and thank you for all your help here and there. You see things differently and that is a great inspiration.

Jörgen, my coach, has accompanied me during the last month and helps me a lot to cope my (work) life. Thank you.

Maria and me – two persons could not be more opposite…But the passion for science and good looking men unifies us. It is wonderful to work with you, to have late lunches and to convince you that Germans aren’t that bad. Thank you for all your help!

Our little Dinner-Club is a great institution. Thank you, Anil, Bernhard, Nicklas, Maria and Mats, Kristian and Matilda for delicious food, lots of wine and great conversations. I look forward the next ones.

I thank all my friends in Germany, who haven’t forgotten me and welcome me in the rare moments I meet them as if I have never been away. I am especially happy that many of you find the way to Lund and visit me!

My family, who supported my curiosity and fantasy and all my way to where and who I am now. Thank you so much. The uncountable parcels with food and precious things from the homeland made my life much nicer.

Elmar, what shall I say? You do not only love me and support me, you even encouraged me to live more than 1000 km apart from you, since you knew that this was my dream. And now you spend lots of time and money on flights just to see me. The time with you is so precious. To marry you is the best decision in my life.
Populärvetenskaplig sammanfattning


I vår forskning bedriver vi växt av enkristaller –välldigt små enkristaller. De är endast några tiotals nanometer tjocka och några mikrometer långa, de brukar kallas nanotrådar. En mikrometer är en tusendel av en millimeter och en nanometer är i sin tur en tusendel av en mikrometer.

Kristallerna vi producerar består av halvledande material. Halvledande material är material som bara leder ström vid speciella förutsättningar. Laddningsbärarna, det vill säga elektronerna, kan inte passera ett förbjudet energetiskt område mellan två tillståndsområde som är tillåten. I halvledare kan man ändra materialets egenskaper genom att dopa, vilket innebär att man tillsätter (eller tar bort) elektroner. På det viset kan fler elektroner finnas tillgängligt för t.ex. leda ström.

När kristaller är tillräckligt små, påverkar deras storlek elektronernas rörlighet. I de nanotrådar som vi jobbar med begränsar rörlighet i två dimensioner och bara i en dimension kan elektronerna flytta sig helt fritt. Att nanotrådar är så små gör att man kan kombinera olika material på ett bättre sätt än i mer storskaliga strukturer. Man har visat att det är möjligt att bygga transistorer, solceller och även lysdioder (LEDs) av nanotrådar.

Hur växten av nanotråder fungerar och hur man kan kontrollera den är i fokus i denna avhandling. Nanotråder växer på ett underlag, ett så kallat substrat. På grund av kristallordning växer de i lodrätt riktning i förhållande till ytan hos substratet. För att få nanotrådar i stället för en stor kristall måste man se till att växten är snabbare på höjden än vad den är på bredden. Detta gör att materialet kan kombinera olika material på ett bättre sätt än i mer storskaliga strukturer. Man har visat att det är möjligt att bygga transistorer, solceller och även lysdioder (LEDs) av nanotrådar.

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1 Introduction

The trend of miniaturization can be observed in almost all areas of technology. Examples are mobile phones, computers, medical operation tools or lab-on-a-chip applications. The reason for miniaturization lies not only within the possibility to fabricate smaller devices, but also the fact that new effects appear as soon as the size reaches the nanometer range. Nanostructures have a large surface-to-volume ratio. This increases the efficiency of catalysts or the sensitivity of sensors. In addition, the mechanical properties change with decreasing size, since certain deformation mechanisms are energetically not longer favorable. Some material phases that would not exist in bulk are also stable for small sizes. The size has even more severe effects on the electrical, optical, and magnetic properties. In this size range the carriers are confined and quantum effects play a major role.

To fabricate these nanostructures, two main fabrication concepts are applied: top-down and bottom-up. In top-down processes the nanostructure is fabricated from a macroscopic piece of material. A common method is lithography, where a pattern is transferred onto the material and the structures are then engraved or deposited along the pattern. The bottom-up approach uses self-organization of molecules and particles, which assemble to certain structures. Natural processes are bottom-up processes, and a lot can be learned by studying nature’s way of structure formation, such as DNA, membranes and minerals. Examples for bottom-up processes are the formation of colloids, quantum dots, nanowires and biomineralization. The top-down approach is mostly better controlled, but suffers from complicated and expensive processes. In addition, it is often difficult to form arbitrary small structures. With bottom-up processes, smaller objects can be achieved in a simple way, but the control is often more difficult. Often, a combination of bottom-up and top-down techniques is applied.

In crystal growth, miniaturization has taken place as well. Crystal growth is also a bottom-up technique, since atoms assemble in a crystal lattice. Epitaxy, a way of crystal growth to achieve perfect and oriented crystals, is presented in chapter 2 of this work. Besides the controlled growth of bulk crystals (3D), techniques have been developed to grow thin-films of high quality, such as liquid-phase epitaxy (LPE), molecular beam epitaxy (MBE), and VPE (vapor-phase epitaxy). Very low thicknesses can be achieved, leading to so-called quantum wells, where the electrons are confined in one dimension but are free in the other two (2D).
By refining the fabrication techniques, self-assembly of zero-dimensional (0D) crystals (in terms of the electron confinement), quantum dots, has been realized. These structures form due to differences in surface energy or strain. After 3D, 2D and 0D growth, also 1D growth has been realized, resulting in nanowires. Nanowires can be grown horizontally on a substrate or sticking out from a substrate. When they are grown epitaxially, they are usually vertically-aligned to the substrate, if the correct substrate orientation is used. Especially their electronic and optical properties as well as the possibility to combine materials, which cannot be combined in thin-films or quantum dots, triggers a high interest in growth of nanowires. A large number of nanowire devices have been realized, such as transistors [1, 2], light-emitting diodes [3, 4], solar cells [5] and biosensors [6].

The growth of nanowires is nowadays a research area with thousands of articles published per year. The growth of one-dimensional structures is rather old, but has disappeared from focus for a while. The fabrication of “hairy” silver crystals by heating argentite (Ag₂S) was reported already in 1778 [7]. In the 1950s to the 1970s, intensive research on whiskers with dimensions in the range of µm to cm was undertaken. The Proceedings of the International Conference on Crystal Growth 1958 [8] show this in an impressive way, where 275 pages from 24 authors were solely dedicated to whiskers. For a long time, research was more focused on metallic, oxide and carbide whiskers and their mechanical properties. In 1964, Wagner and Ellis proposed the famous vapor-liquid-solid (VLS) mechanism for the growth of Si whiskers with the help of Au seed particles [9]. Not much later GaAs and GaP whiskers were grown via VLS with the help of Au, Pd, Pt [10, 11] and even self-seeded with Ga [12]. However, whiskers were rather an undesirable effect in thin-film growth at that time [13]. Only a few researchers like Givarzigov continued to work on semiconductor whisker growth [14]. In 1991, Hiruma et al. discovered the growth of GaAs nanowhiskers in MOVPE, which were 10-20 nm wide and 1-5 µm long [15]. They first assumed a gold free growth, but admitted one year later that they had gold residues in their chamber [16]. The interest in single crystal semiconductor nanowhiskers or nanowires (the terms are synonyms) was and still is much higher than in microwhiskers, since they have interesting properties due to 2D carrier confinement [1, 17]. Within the last two decades, nanowire growth of group IV materials [18-20], virtually all III/V materials [21, 22] as well as the growth of II/VI [23, 24] nanowires has been showed. The first article on nanowire growth from Lund was published as late as 2001 [25], but was followed by more than 70 publications dedicated to nanowire
growth. The growth of nanowires is described in detail in chapter 4. As the research group at Solid State Physics in Lund University concentrates on III/V semiconducting materials, only those will be discussed further on.

This report is built up as follows. In chapter 2, the basic concepts of epitaxy are introduced. The applied experimental methods are described in chapter 3. In chapter 4, nanowire growth is discussed in detail, including the focus of the present work, epitaxial growth of InP nanowires from Cu seed particles; followed by conclusions and an outlook.
2 Epitaxy

Epitaxy comes from the Greek words "epi" (επι) meaning "above" and "taxis" (τάξις) meaning “in an ordered manner”. It is a version of crystal growth where arriving atoms are incorporated at certain positions on the surface in relationship to the underlying crystal structure. Epitaxial growth is used to produce high quality single crystal layers with low defect density for electrical, magnetic or optical applications, which cannot be achieved otherwise [26]. Epitaxy of the same material as the underlying substrate is denoted as homoepitaxy, where as growth of different materials on each other is called heteroepitaxy.

Crystal growth is controlled by thermodynamics and kinetics. Thermodynamics describes the driving force for all processes: reaching thermodynamic equilibrium which is the point of lowest free energy for the system. The rates at which processes take place are described by kinetics. In many cases, thermodynamic equilibrium is never reached, since the processes occur to slowly. These processes are referred to as kinetically hindered. In other words, thermodynamics determine what happens, kinetics determine how fast it happens. The occurrence of vapor pressure is an equilibrium effect, i.e. thermodynamic, whereas crystal growth from the vapor is a typical kinetic effect [27]. It is necessary to be able to distinguish between these two effects properly. They will be described on the following pages.

2.1 Surface processes

When atoms arrive on a surface the following processes can occur (Fig. 2.1): The atoms can adsorb (a) and desorp (b) later on. Once they are adsorbed, they can diffuse (c), until they meet other atoms and form nuclei (d) or incorporate at energetically favorable places such as edges (e) or corners (f).

![Figure 2.1: Processes on the substrate surface: adsorption (a), desorption (b), diffusion (c), nucleation (d) and incorporation at an edge (e) or a corner (f).](image-url)
2.2 Thermodynamic and kinetic aspects of crystal growth

Which of these processes happen preferentially depends on the surface properties, i.e. the roughness and the surface energy, the interaction between the substrate and adsorbate atoms, the temperature and the supersaturation, a concept which will be described in the next section.

2.2 Thermodynamic and kinetic aspects of crystal growth

The thermodynamic approach can be used to explain a number of phenomena during growth. The driving force for a phase change is the difference in the chemical potentials $\mu$ of the two phases:

$$\Delta \mu = \mu_1 - \mu_2$$  \hspace{1cm} (2.1)

At equilibrium, $\Delta \mu$ is zero. Let us assume phase 1 is vapor or liquid and phase 2 is solid. If $\Delta \mu > 0$, material would condensate, if $\Delta \mu < 0$, material would evaporate or dissolve/melt.

The difference in chemical potential can be expressed in terms of the temperature $T$ and the supersaturation $S$:

$$\Delta \mu = RT \ln S$$  \hspace{1cm} (2.2)

The supersaturation is the ratio between a quantity during the process $F$ and at equilibrium $F_{eq}$:

$$S = \frac{F}{F_{eq}}$$  \hspace{1cm} (2.3)

The quantity $F$ can be pressure, concentration, molecular fluxes amongst others. In some cases $\Delta \mu$ is referred to supersaturation instead.

The classical nucleation theory gives the Gibbs free energy $\Delta G$ for nucleation of an island depending on the number of atoms in the nucleus $j$ as follows [26]

$$\Delta G(j) = -j \Delta \mu + j^{2/3} X$$  \hspace{1cm} (2.4)

where $X$ is a surface energy term:

$$X = \sum_k C_k \gamma_k + C_{AB} (\gamma^* - \gamma_B)$$  \hspace{1cm} (2.5)
The first term stands for the surface energy of the different faces of the island \( (C_k\) is a geometrical factor, depending on the shape of the island), the second term stands for the interfacial energy between materials or layers \( A \) and \( B \); \( \gamma^* \) is the interfacial energy of the new interface with the area \( C_{AB} \); \( \gamma_B \) is the surface energy of \( B \).

The plot of \( \Delta G(j) \) vs. \( j \) (Fig. 3.2) has a maximum at the critical cluster size \( j^* \)

\[
j^* = \left( \frac{2X}{3\Delta\mu} \right)^3 \tag{2.6}
\]

The nucleation barrier is then given by

\[
\Delta G^*(j^*) = \frac{4X^3}{27\Delta\mu^2} \tag{2.7}
\]

Nucleation in nanowires can rather be treated as 2D growth [28], that is nucleation of a monolayer. The supersaturation is then in relation to the corresponding step in the adsorption isotherm [26] and expressed in terms of pressure \( p \), i.e.

\[
\Delta\mu' = RT\ln\frac{P}{P_1} \tag{2.8}
\]

and \( \Delta G(j) \) becomes then

\[
\Delta G_{2D}(j) = -j \Delta\mu' + j^{1/2}X \tag{2.9}
\]

The square root expression is due to the extra edge energy \( X \). The maximum is then at

\[
j^* = \left( \frac{X}{2\Delta\mu'} \right)^2 \tag{2.10}
\]

and

\[
\Delta G_{2D}^*(j^*) = \frac{X^2}{4\Delta\mu'} \tag{2.11}
\]

where \( \Delta\mu' = \Delta\mu - \Delta\mu_c \) and \( \Delta\mu_c = (\gamma_A + \gamma^* - \gamma_B)\Omega^{2/3} \), \( \Omega \) is the atomic volume of the deposit.
These considerations are not completely realistic, since it is questionable, how macroscopic concepts like surface energies are appropriate for monolayers. At this point, an atomistic approach should be applied, which still is in agreement with macroscopic thermodynamics for large $j$. Here kinetics comes into play. The atomic processes are described by rate equations, which have in the simplest case solutions in Arrhenius form:

\[
n = n_0 \exp \left( -\frac{\Delta G^*}{kT} \right)
\]

(2.12)

where $n$ could be the nucleation rate or a concentration along the surface, $n_0$ is a pre-exponential factor, which contains e.g. frequencies or mobilities. This equation shows the connection between thermodynamics and kinetics: The supersaturation as the driving force is contained in the exponential term. The rate model Venables [29] developed adds non-linear terms for surface processes (Fig. 2.1), nucleation, and growth. These processes are governed by energies, which appear in the exponentials, and by frequencies and entropic pre-exponential factors. The equations can be plotted in Arrhenius plots. These plots then reveal the dominant factors in certain temperature regimes. In Fig. 2.3, a schematic Arrhenius plot of the growth rate is shown. At very high temperatures atoms tend to desorb, the growth rate
drops. At intermediate temperatures the growth rate is governed by mass transport and stays constant with temperature. Ordinary epitaxial layer growth is performed in this temperature region. At lower temperatures surface reactions control the growth rate, which decreases with decreasing temperature. Nanowires are often grown in this temperature range, since here, layer growth is suppressed.

Figure 2.3: A schematic Arrhenius plot of the growth rate. The slope is a measure of the activation energy. At low temperature the growth is reaction controlled, here with two different activation energies. At intermediate temperature mass transport governs the growth rate, and at high temperature desorption takes place and the growth rate drops. Drawn after [30].
2.2 Thermodynamic and kinetic aspects of crystal growth
3 Methods

In this chapter, methods for fabrication and characterization of nanowires are introduced. Nanowires in our studies were grown by metal-organic vapor phase epitaxy (MOVPE). This process is illustrated first, including the growth system and the precursors used. We use seed particles to grow nanowires, which is the most common way. These particles can be generated and deposited in several ways. Some of them are presented and explained here. Finally, nanowires have to be characterized. Due to their small dimensions, the resolution of optical microscopy is not sufficient; electron sources have to be used instead. The overall morphology and dimensions of the structures are investigated by scanning electron microscopy (SEM). Deeper insight in the crystal structure and the chemical composition is given by (high-resolution) transmission electron microscopy ((HR)TEM) combined with X-ray energy dispersive spectroscopy (XEDS).

3.1 Metal-organic Vapor Phase Epitaxy

MOVPE\textsuperscript{1} is the most common method for growth of epitaxial layers in industry due to its high throughput compared to molecular beam epitaxy (MBE) or chemical beam epitaxy (CBE). However, the control of the process is complicated and not yet fully understood (operators call it often a black box). The only detailed textbook on MOVPE is written by G. Stringfellow [31] and is the source of most descriptions here. The growth depends on parameters such as substrate temperature, chamber pressure, molar fractions of the precursors, and their cracking efficiency and total gas flow. All these parameters are interdependent in themselves. Nonetheless, during the last four decades much development has taken place and the control of the process is now on a high level. Still, every machine is unique and leads to slightly different growth. In the next two subsections, the growth system will be explained, and then the precursors and their reactions are presented in detail.

\textsuperscript{1} The name comes from the precursor molecules that are used in the process. These are metal-organic compounds, where the metal (the growth species) is surrounded by organic functional groups. These precursors are cracked in the growth reactor in a vapor phase. Other names are organometallic vapor-phase epitaxy (OMVPE) or metal-organic chemical vapor deposition (MOCVD). We prefer MOVPE to underline the epitaxial character of the growth.
3.1 Metal-organic Vapor Phase Epitaxy

3.1.1 The growth system

The essential components of the MOVPE growth system are the reactor, the carrier gas, the precursors, the heating and the plumbing system including the valve system as well as the pressure and flow control.

The “heart” of the MOVPE system is the reactor. Here, the substrates are positioned, the temperature is applied, the precursors are mixed and cracked, and eventually the growth takes place. The carrier gas (H₂ or N₂, in our case H₂) transporting the precursor gases flows over the heated sample holder (susceptor) to the exhaust. At the solid surfaces of the reactor (susceptor, sample, wall) the velocity of the gas is zero, since the flow is laminar [32]. As a consequence of this boundary condition, a stagnant boundary layer is built up above the susceptor, where the velocity of the flow is decreased and the mass transport happens only by gas phase diffusion [32]. There are several types of reactors, e.g. with horizontal or vertical flow direction. We use here a cold wall horizontal reactor. The susceptor consists of an inert, high temperature stable material such as graphite or refractory metals, and can be heated by radio frequency, resistivity heating, or infrared lamps. A schematic outline of a MOVPE system is given in Fig. 2.1.

The precursors are fed to the reactor in separate lines for group V and group III materials. Gas sources (often used for group V materials) are provided either diluted or non-diluted from gas bottles. The metal-organic (MO) sources are provided in so-called bubblers, which are kept at a certain temperature. The carrier gas is led through the liquid or solid source material, thereby saturated with molecules. The molar fraction fed to the reactor is determined by the source flow, which is controlled by mass-flow controllers (MFCs). In addition, for the MO sources the molar fraction depends on the amount that is taken up by the carrier gas. It is determined by the vapor pressure of the precursor, which is controlled by the temperature, and the source pressure. The latter is controlled using electronic pressure controllers (EPC).

The system can be operated at atmospheric or at lower pressure down to a few tens of mbar. The total pressure influences the probability of parasitic reactions in the gas phase, the thermodynamics of the growth, and the diffusion of the growth species. Our standard pressure is 100 mbar.
3.1.2 Precursors

Two types of precursors are used in MOVPE. The MO sources can be used for providing both group III and group V materials. Common group III sources are sources with short alkyl groups, such as Trimethylgallium (TMG), Triethylgallium (TEG), or Trimethylindium (TMI). Typical MO-sources for group V materials are Tertiabutylphosphine (TBP) and Tertiabutylarsine (TBA). For group V materials, hydrides are often used instead, where the group V atom is surrounded by three hydrogen atoms, such as AsH$_3$ or PH$_3$.

The cracking, i.e. the dissociation of the precursors, occurs in multi-step reactions, until the metal or group V atom is set free [33]. This process can happen homogeneously, i.e. in the gas phase, or heterogeneously, i.e. on the substrate surface. The latter is the preferred situation, since homogeneous pyrolysis would cause parasitic reactions and the molecules would not end up in the growing crystals. The cracking efficiency of the precursors is a crucial factor in MOVPE. If it is low at growth temperatures a large excess of precursor has to be fed to the reactor to provide enough material for growth. If the cracking efficiency is so high at growth temperatures that homogeneous pyrolysis takes place, material will be consumed by parasitic reactions. Therefore, the choice of precursors has to take into account

![Figure 3.1 Schematic of a MOVPE system. Color coding of the valves: red valves are open and blue are closed when the source is used, and vice versa when it is not in use. Pink valves are opened when the source shall be fed to the reactor and the green valves are closed at the same time. Otherwise the flow from the sources is led through the vent line to the exhaust. [Courtesy of J. Bolinsson](image)]
the applied growth temperatures. An issue is the incorporation of carbon into the growing crystal, especially at low temperature growth. This has been attributed to the formation of CH$_3$ radicals, that decompose to carbon [34]. H radicals from the pyrolysis of group V hydrides or a higher total pressure help to avoid that process. The use of precursors with longer alkyl groups, such as TEG, reduces the effect as well.

3.2 Particle fabrication and deposition

Seed particles for nanowire growth can be produced in several ways. Purity, size selectivity, and position control are decisive factors for selection of a method. In the following, some common particle fabrication and deposition methods are introduced: particles from thin-films, lithographically defined particles, colloidal particles and aerosol particles [35]. Table 3.1 gives an overview of the different methods, their advantages, and drawbacks.

3.2.1 Particles generated by annealing of thin films

In this method, a thin metal film with a thickness of a few nanometers is deposited by evaporation on the substrate. The layer splits up into islands at elevated temperatures. This annealing step is mostly done in situ prior to growth. The size and surface density of the particles depends on layer thickness, annealing temperature and time, and the surface properties of the materials. Still, their surface density and size distribution can only be controlled to some extent. The process will always lead to a distribution in particle size, and the particle density cannot be controlled independently. This method is simple, clean and inexpensive and is mainly suitable for studies on the influence of the nanowire diameter, since it provides several particle sizes at the same time.

3.2.2 Lithographically defined particles

The definition of particles by lithography is an extension of the thin film method. It allows the precise control of size and position of the particles [36]. A resist is spun onto the substrate. The sample is then exposed to light through a mask, or, as in electron beam lithography (EBL), to an electron beam. The light/electrons change the solubility of the photo resist. By irradiation and subsequent dissolving of the resist, the substrate surface can be patterned, e.g. resulting in a surface pattern with holes. Then, a metal layer is deposited on the surface. After removing the photo resist completely, metal disks remain on the surface where here had originally been holes in the photo resist. This is a time consuming and expensive method. In addition, remnants of the resist may stay on the surface.
3.2.3 Colloidal particles

These particles are metal particles fabricated by a chemical reduction process [37] and stabilized in a colloidal suspension. Colloidal particles are commercially available in a wide range of sizes. The particles can either be directly deposited onto the substrate or by electrospray-deposition. If the particles are directly deposited, a surfactant layer of Poly-(L)-lysine (PLL) is often needed to compensate electrostatic repulsion. For a more homogeneous distribution the solutions can be spun on the substrate. This method is a simple method, but suffers from contamination due to the stabilizing ligands and the PLL, and an inhomogeneous surface distribution. The reproducibility of the particle density is increased by deposition via electrospray [38]. In this method, the solution is sucked through a capillary and split up into droplets in an electric field. Ideally, one droplet contains a single particle. The droplets are transported and dried in an N₂ stream and optionally annealed. Finally, the particles are deposited onto the substrate via an applied potential that attracts them to the surface. This leads to a homogeneous and controlled distribution of the particles. Compared to the direct deposition, the amount of organic remnants is reduced, but the setup is more complicated.

3.2.4 Aerosol particles

A very clean and controlled method is the production of aerosol particles. Material is evaporated, either by heating [39] or by spark discharge [40], the vapor is transported in an inert gas to a cooler region, where the material condensates and primary particles are formed. These particles are size selected with the help of a differential mobility analyzer (DMA). The particles are sintered in a second furnace and again size selected according to the desired size. The particles are then deposited by applying an electric field to the substrate. The method is very clean and both the size and the surface density can be controlled accurately.
3.2 Particle fabrication and deposition

Table 3.1 Overview of the general characteristics of different particle types[41].

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Diameter range</th>
<th>Diameter Control</th>
<th>Density Control</th>
<th>Position Control</th>
<th>Throughput</th>
<th>Cleanliness</th>
<th>Simplicity</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol Spark Generated (SDA)</td>
<td>Limited</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Limited</td>
<td>Reasonable</td>
<td>Very Clean</td>
<td>Reasonable</td>
<td>High</td>
</tr>
<tr>
<td>Aerosol e/c Generated (ECA)</td>
<td>Broad</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Limited</td>
<td>Reasonable</td>
<td>Very Clean</td>
<td>Reasonable</td>
<td>High</td>
</tr>
<tr>
<td>Colloid Directly Deposited (DDC)</td>
<td>Very Broad</td>
<td>Very Good</td>
<td>Limited</td>
<td>Uncontrolled</td>
<td>Very High</td>
<td>Contaminated</td>
<td>Simple</td>
<td>Low</td>
</tr>
<tr>
<td>Colloid Electrospray Deposited (ESD)</td>
<td>Very Broad</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Limited</td>
<td>Low</td>
<td>Contaminated</td>
<td>Reasonable</td>
<td>High</td>
</tr>
<tr>
<td>EBL Generated (EBD)</td>
<td>Limited (small difficult)</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Low</td>
<td>Contaminated</td>
<td>Reasonable</td>
<td>Very High</td>
</tr>
<tr>
<td>Thin film Generated (TFA)</td>
<td>Broad</td>
<td>Very Limited</td>
<td>Uncontrolled</td>
<td>Very High</td>
<td>Very Clean</td>
<td>Simple</td>
<td>Medium</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Characterization

Due to their small size, nanowires have to be characterized using electron beam techniques. For topographical characterization scanning electron microscopy (SEM) is applied. To investigate the structural and compositional state of the nanowires transmission electron microscopy (TEM) is used. The general features for both SEM and TEM described in the first section.

3.3.1 Electron Microscopy

The electron microscope consists mainly of four parts:

- The electron gun, which is used to generate and accelerate the electrons
- The lens system, which is used to focus the electrons on the sample
- The sample, which the electrons interact with
- The detection system, which convert the signal of the electrons into a visible image

The electron gun: The electrons are generated via thermionic emission or field emission. In the first method, a wire (most often tungsten or LaB₆) is heated up so that the energy of the electrons exceeds the work function of the material and thereby the electrons can leave it. In the second method, electrons are extracted from a tungsten tip with the help of an electric field. The first method is less expensive than the second method, which creates a brighter electron beam with a narrower energy spread. The electrons are then accelerated to the desired energy. The energy determines the wavelength of the electrons, as defined in de Broglie’s equation [42]:

$$\lambda \sim \frac{1.22}{\sqrt{E}}$$  \hspace{1cm} (3.1)

From the concept of resolution for visible light according to the Rayleigh criterion, the resolution (meaning the smallest distance between to points that can be distinguished) is proportional to the wavelength. This concept was the driving force to use electrons for imaging in the beginning. Although, the Rayleigh criterion is not valid for electrons, since it only applies for incoherent light (whereas electron sources produce coherent light). The limiting factor for resolution, however, is not the wavelength but the quality of the lens system.
3.3 Characterization

The lens system: Since electrons do not interact with any material in the same way as visible light does with glass, electron lenses are based on a different concept. Electron lenses are magnetic lenses that consist of a soft magnetic core with a hole in it, the so-called polepiece surrounded by a copper coil. Current through the copper coil induces a magnetic field in the hole. The current controls the strength of the magnetic field and thereby the path the electrons take through the lens. The electrons move with a helical trajectory through the field due to the Lorentz force. Magnetic lenses act like convex glass lenses. The quality of magnetic lenses is fairly poor; Williams and Carter [43] compare them with “using the bottom of a […] bottle as a magnifying glass”. There are several lens defects, whereof the spherical aberration, the chromatic aberration, and the astigmatism are the most important ones. The first, spherical aberration, is the main error limiting the resolution. During recent years, a correction for the spherical aberration in TEM was developed, but not all microscopes are equipped with one yet. Spherical aberration is the effect that electrons, which are off-axis, are bent back towards the axis leading to image disks instead of image points and thereby limiting the resolution. By inserting apertures, the off-axis electrons are screened from the beam and fewer distortions are induced.

The chromatic aberration is due to electrons with a spread in energy. The spread from the sources is very small and can be neglected. But inserting the sample into the electron beam produces electrons of a wide range of energies which are then bend differently by the following lens leading to a disk image (this holds for TEM, not for SEM).

Astigmatism is a lens error caused by imperfect lenses. If the electrons sense a non-uniform magnetic field, the focal planes will be different for perpendicular rays. In practice, defocusing leads to distortions in different directions. Astigmatism can be compensated by stigmators, small magnets in the lens, which balance the inhomogeneities of the lens leading to a uniform magnetic field.

The sample and the detectors are different for SEM and TEM and therefore treated in the corresponding sub-chapters.
3.3.2 Scanning Electron Microscopy

In scanning electron microscopy, the image is generated by the electron beam scanning over the surface. The beam is deflected by scanning coils. The sample is illuminated by the electrons from the top. The electrons interact with the sample. Therby they generate secondary electrons X-rays and Auger electrons via inelastic scattering, and backscatter electrons via elastic scattering. The sample has to be conductive, otherwise the electrons accumulate in the sample and lead to charging effects, i.e. incoming electrons are deflected. For imaging, secondary electrons which come from areas close to the surface and backscattered electrons coming from deeper regions are used. The penetration depth is mainly dependent on the acceleration voltage. SEMs are mostly run with 5-20 kV. The emitted electrons are attracted to a detector by an electric field. The signal is processed and leads to an image, which gives information on the surface and topography. The resolution of SEMs can be a few nm, depending on sample and conditions.

3.3.3 Transmission Electron Microscopy

In the transmission electron microscopy the sample is placed in the middle of the ray path, i.e. between the two pole pieces of the objective lens. The electrons interact with the sample and those transmitted through the sample are magnified and focused by the image lens system onto a fluorescent screen or a CCD (charge-coupled device) camera. Since the electrons have to pass through the sample, it has to be sufficiently thin, i.e. thinner than about 100 nm depending on the material and the acceleration voltage. The interaction of the electrons with the material gives not only a projection image of the sample, but also information about the crystal structure via diffraction images, the composition via X-rays or energy-loss and can reveal the atomic structure in high resolution mode. The beam can even be converged and then scanned over parts of the sample, in the so called STEM – mode. This allows small probe sizes and is therefore necessary for a locally-resolved chemical analysis.

3.3.4 Chemical Analysis

X-ray energy dispersive spectroscopy is used to analyze the composition of the sample. This method uses the fact that incoming electrons eject core electrons from atoms, electrons from higher energy levels fall down to the empty states and thereby emit X-rays. The energy of these X-rays is specific for each level in each element. The X-rays can thus be detected according to their energy and can then be correlated to the elements in the sample.
3.3 Characterization
4 Nanowire growth

As described in the introduction, research on nanowires started about two decades ago. During that time period nanowire growth of group IV materials [18-20], virtually all III/V materials [21, 22] has been shown, as well as the growth of II/VI nanowires [23, 24]. Since mainly III/V materials are grown by our research group, the focus of this chapter will lie on these materials.

The growth of nanowires has advanced, and heterostructures, both axial [44-48] and radial [49-53] have been realized. The fact, that nanowires of materials, that grow in bulk only in zinc blende (ZB) crystal structure, can also grow in wurtzite (WZ) structure\(^2\) has opened up a new field of research [54]; the control of crystal structure, which also influences the electronic properties [55]. Nowadays challenges for growers are doping [56-58], the tuning of the crystal structure [54, 55, 59-61], new materials such as antimonides [62-65], and alternative seed particle materials [19, 20, 66-74].

To generate nanowires, growth in one direction has to be enhanced and suppressed in the other two directions at the same time. A number of mechanisms to explain semiconducting nanowire growth have been proposed during the last years. The most common is still particle assisted growth [21], furthermore selective-area growth [75] and oxide-assisted growth [76] are proposed. Mandl et al. evaluate these hypotheses thoroughly [66]. Since we use particle assisted growth, only that mechanism is discussed further here.

4.1 Particle assisted nanowire growth

Particle assisted growth is the most common method for semiconducting nanowire growth [21]. In this method metal particles are deposited onto a substrate (Fig 4.1 a)) (for particle fabrication and deposition methods see chapter 3.2); particles from thin-films can even form in-situ. The substrate is transferred to the growth chamber. For self-seeded growth, the particles are formed \textit{in-situ} by accumulation of group III to droplets. The source material

\[\text{Zinc blende (ZB) has a face-centered cubic (fcc) unit cell with an ABCABC stacking of the closely packed (111) planes. The hexagonal counterpart wurtzite (WZ) has the corresponding planes in the (0001) direction with an ABAB stacking. These directions are also the growth directions in most cases. A change of stacking leads to stacking faults or inserts of the other crystal structure. Rotational twin-planes are also common lattice defects found in ZB nanowires.}\]
4.1 Particle assisted nanowire growth

is fed to the sample at elevated temperatures (Fig. 4.1 b). The growth process is understood as follows: The particles serve as preferential deposition sites and form an alloy with the growth species (mostly group III). As soon as the particles are supersaturated, the excess material precipitates at the interface between particle and substrate (Fig 4.1 c). The crystal grows as long as growth material is provided (Fig 4.2 d). Heterostructures can be produced by changing the growth temperature and/or the source materials. Increasing the temperatures to layer growth conditions leads to radial heterostructures (Fig. 4.1 e). Axial heterostructures can be produced as well for many material combinations (Fig. 4.1 f).

Figure 4.1: Schematics of the particle assisted nanowire growth process a)-d) and possible advanced structures e)-h). a) Particles are deposited on the surface, b) the source are fed to the reactor and the particles form an alloy until they are supersaturated and c) solid nanowires are precipitated at the interface between substrate and particle, d) the wires grow as long as precursors are supplied. e) and f) by changing growth temperature and material e) radial and f) axial heterostructures can be grown. Branched nanowires can be fabricated by g) deposition of a 2. generation of particles and then h) a repetition of the growth process.

The preferential growth direction of III/V nanowires is the $<111>$B direction. Under certain conditions they can be forced to grow in other directions [77]. Using $\{111\}$B substrates leads to vertically aligned nanowires, if they grow epitaxially.

The state of the particle has been under discussion for some time. The mechanism proposed by Wagner and Ellis [9], vapor-liquid-solid (VLS), assumes a liquid particle. Following this assumption, nanowires have been grown above the eutectic temperature to assure a liquid particle. It was found, however, that nanowires even grow below the eutectic temperature

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3 B denotes the termination with group V atoms, whereas A would be terminated with group III atoms.
This goes along with a drop in growth velocity, indicating a solid particle, since the diffusion through a solid particle is slower than through a liquid particle [81]. In in-situ TEM investigations, it was found that both, solid and liquid particles can exist at the same sub-eutectic temperature [82, 83]. In the meantime, the state of the particle is not considered to be that important anymore, especially since it is questionable how much you can distinguish between solid and liquid at the nanoscale. Therefore, the more general concept of preferential interface nucleation (PIN) was proposed [84]. The concept considers that the state of the particle is not important, but the stability and the ability to collect material. Furthermore, the nucleation occurs at the three-phase boundary (TPB) (where vapor, particle and nanowire meet), since the Gibbs free energy can there be minimized and the local supersaturation is relatively high. These factors together lead to unidirectional growth. After nucleation, the growth is quick compared to the nucleation and occurs as step-flow [85, 86]. Step-flow means, that the growth front of the new layer (usually a bilayer) moves along the the plane from one side of the nanowire to the other.

Quite recently, however, it has been shown by in-situ TEM growth, that nanowire growth is more complicated: The morphology of the growth interface changes periodically. Small facets are formed at the edges of the nanowire. They shrink (material precipitates), then nucleation and growth of a (bi-) layer occurs on the main facet. Material is dissolved and the facet returns to its maximum size and starts to shrink again. This phenomenon has been observed in the self-seeded growth of Al$_2$O$_3$ nanowires [87], Au-seeded growth of Ge nanowires [88, 89], for Si nanowires seeded by several Au alloys, and even Au-seeded GaP nanowires [89]. These three groups have different explanations and models for their observations. Oh et al. [87] suspect that the rim is dissolved to provide oxygen for the growth of a layer on the nanowire. They assume that nucleation still takes place at the TPB. Gamalski et al. [88] and Wen et al. [89] dedicate the formation of the truncations to thermodynamic effects. The size of the truncated facet is a measure for the supersaturation in the particle. Both state that the nucleation of the layer happens away from the TPB. The main difference between these two models is, that the first assume that the small facet is atomically rough, and can therefore change shape easily, whereas the second suppose that the small facet can easily equilibrate due to lower nucleation barrier at the TPB. These new findings will radically change the view on nanowire growth mechanisms and make new models for stacking fault formation and polytypism necessary.
4.2 Gold seeded nanowire growth

Nanowires have been grown from gold particles for years. Up till now, no alternative material has been found which is that versatile. Gold leads with almost all (semiconducting) materials to epitaxial nanowire growth, mostly in a wide parameter window [21]. The reason for the high versatility has not been fully understood yet. It is not clear, which property is the decisive one for successful nanowire growth or whether it is rather the unique combination of properties that gold possesses [35]. These properties are chemical inertness, thermal stability, the ability to form liquid alloys with a large number of growth species, softness, which enables good particle/wire alignment even in VSS growth mode.

Different scientific groups use a number of methods to prepare gold seed particles for nanowire growth (for preparation methods see Chap.3.2). We wondered how comparable the results of different groups are, if they use different preparation methods. In our study on the influence of different gold particle preparation methods on the growth of GaAs nanowires [41], we found, that the particle type has little influence on the nanowire growth concerning growth rate and crystal structure. Differences occur only in incubation time and in sensitivity to annealing. The incubation time is the shortest for the cleanest particles (the aerosol particles) and the longest for particles with remnants from the preparation process (EBL defined and directly deposited colloids). The annealing step strongly improves the quality of growth of nanowires grown from EBL defined particles and thin-films. This is not surprising, since these particles form during the annealing step. These observations led to the conclusion, that results from different groups using different particle preparation methods can be compared. Differences occur rather due to the influence of different designs of growth systems or cleaning procedures.

The influence of the particle preparation method on the cathodoluminescence (CL) of the nanowires was also investigated (unpublished results). Only wires grown at 480 °C showed enough emission intensity to be investigated. Nanowires grown from different particle types, which had been grown including an annealing step, showed very similar emission. Only nanowires grown from aerosol spark-discharge particles showed a severe bleaching.
Figure 4.2: SEM micrographs of GaAs nanowires grown at 430°C for 4 min from different seed particles with 30 nm diameter: a) Spark generated aerosols b) evaporation/condensation aerosols c) directly deposited colloids d) electrosprayed colloids e) EBL patterned, and f) particles from annealed thin film [41]. The difference of the nanowires in f) compared to the others is due to the higher surface density. Sample tilt 30°

When growth was performed without annealing step, there was a larger variation in emission between the samples. Nanowires grown from aerosol particles (both evaporation/condensation and spark-discharge) and EBL defined particle did not show significant difference from their annealed counterparts; except that they tend to charge under the beam. Nanowires grown from colloidal particles show significantly weaker emission without annealing. The weakest emission show nanowires grown from directly deposited colloidal particle, electrospraying improves the performance. Electrosprayed particles, that were heated before deposition, lead to nanowires with stronger emission, but still weaker than with annealing step before growth. It seems that carbon remnants from the preparation are incorporated into the nanowires and thereby influence the optical properties. An annealing step as applied in the experiments (650 °C for 6 min), however, seems to be enough to remove the remnants and lead to similar optical properties for nanowires grown from particles with different cleanliness.

4.3 Alternative seed particle materials

Gold has the major disadvantage that it is not compatible with existing silicon technology, since it causes deep traps for carriers in the bandgap of semiconductors [90]. Another disadvantage is the high solubility of most growth species in gold. On the one hand, this enables nanowire growth; on the other hand, it prevents sharp interfaces in heterostructures, since the particle acts as reservoir and releases remaining material over a certain time.
4.4 Cu seeded InP nanowire growth

Therefore, people have been looking for alternative seed particle materials. Self-seeded growth can be an alternative as well, but it suffers a number of problems, such as limited control over size and aspect ratios, heterostructures and crystal phase, and will not be discussed here. Si and Ge nanowires have been grown with a number of metals including Cu, Al, Ti, Ni [19]. In many cases it was possible to achieve sharp interfaces. This is due to a higher eutectic temperature of these material combinations, leading to growth from a solid particle and a limited solubility. III/V nanowires have been grown from Fe [74], Mn [72, 91], and Ni. These nanowires were, however, not vertically aligned to the substrate. Only very recently, this was obtained for Pd seeded InAs nanowires [70, 92], for Ag seeded InSb nanowires [71] and for Cu seeded InP nanowires [I], as discussed in the next section.

4.4 Cu seeded InP nanowire growth

Copper was chosen as model system, since it has a lot in common with gold, but has several different properties. This knowledge will help us to map the essential properties for seed materials. Cu is also a noble metal and in the same group of the periodic system. It is ductile, has the same crystal structure, almost the same melting temperature, and is expected to have – unfortunately – similarly severe electronic properties for the integration with silicon technology; although it seems to have a less severe effect of Si solar cells [93]. The actual effect of Au and Cu in nanowires has not been proven yet, if it turns out to be harmless, Cu will be the cheaper materials choice for large-scale production. There are certain distinct differences between the two metals: Cu is not inert, interacts differently with In, i.e. In has a lower solubility in Cu and the eutectic temperature is higher, and has a different surface energy.

Vertically-aligned InP nanowires were grown from Cu seed particles [I, II]. The influence of temperature at a V/III ratio of 940 [I] and of molar fraction at 350 °C [II] was investigated. The V/III ratio of 940 was chosen for the temperature study, since there the highest yield of vertically-aligned nanowires in the <111>B direction could be achieved. The same reason has the choice of 350 °C as standard temperature for the flow study. Experimental details can be found in papers I and II, respectively.
4.4.1 Temperature study on the growth of Cu seeded InP nanowires

In Fig. 4.3, SEM micrographs show the growth of InP nanowires in the temperature range of 310 °C to 400 °C. The temperature range, where InP nanowires successfully can be grown from Cu seeds, is quite limited to 340 °C to 370 °C and low compared to InP nanowire growth from Au particles. Beyond this range the fraction of epitaxial nanowires decreases considerably. Below 340 °C nucleation and growth might just be too slow to lead to nanowire structures in reasonable time. Above 390 °C growth of nanowires cannot be observed anymore.

The diameters of the nanowires range from 10 to 100 nm due to the preparation of the seed particles from thin films. In this case the fabrication method is very useful, since it provides a wide range of diameters, so that the dependence of the growth behavior on the diameter can easily be studied. The length of the nanowires is inversely dependent on the diameter for small diameter and then independent for diameters larger than about 50 nm, as described by Dubrovskii and Sibirev [94]. Both very thin and very thick nanowires have a tendency to kink. Thin nanowires kink mostly directly from the beginning and grow straight afterwards in the new direction, while thicker nanowires either grow curly or start vertically-aligned and kink later.

Those nanowires which grow epitaxially along <111>B direction have a hexagonal cross section and {112} oriented sidewalls with alternating {111} A and B micro facets. The nanowires exhibit a zinc blende (ZB) crystal structure with random stacking faults and twin

Figure 4.3: SEM micrographs of InP nanowires grown from Cu seed particles at growth temperatures of a) 310, b) 340 d) 350, e) 360, f) 370, g) 380, and h) 400 °C; scale bar 500 nm, tilt 30°. Taken from [I].
4.4 Cu seeded InP nanowire growth

planes for the investigated temperatures 350 °C and 370 °C in HRTEM (Fig. 4.4). This is in agreement with crystal structure of Au seeded InP nanowires grown below 380 °C [59]. It seems that the change of seed material does not have an influence on the crystal structure - at least at our conditions.

The particles on top of the nanowires are strongly faceted. At 350 °C and below the particles have the form of a hexagonal pyramid (Fig. 4.4 a) and c)). At 370 °C and above the particles have an irregular shape, but still faceted (Fig. 4.4 b) and d)). At 360 °C both shapes coexist. The particles have a composition of 64 at.% Cu and 36 at.% In as revealed by point XEDS measurements (the P content was below the detection limit of 2 at.%). In combination with diffraction patterns and atomic distances the phase of the particle is identified as a form of the \( \eta \) (Cu\(_2\)In), which has a NiAs basic structure. The particle is epitaxially related to the nanowire with c-axis is parallel to the growth direction InP (\( \bar{1} \bar{1} \bar{1} \)) //Cu\(_2\)In (000\( \bar{1} \)) and InP[1\( \bar{1} \bar{0} \)]/Cu\(_2\)In[1\( \bar{1} \bar{0} \bar{1} \)]. The lattice mismatch in the parallel densely packed planes (\( \bar{1} \bar{1} \bar{1} \)) in InP and (000\( \bar{1} \)) in Cu\(_2\)In is very small with 0.7%. Although these are room temperature and post-growth observations, they are strong indications that the nanowires grow from a solid particle. In the binary Cu-In phase diagram\(^4\) [95] the temperature range for successful nanowire growth lies more than 300 K below the eutectic temperature. It has been shown that liquid seed particles still can exist far below the eutectic temperature due to temperature and pressure effects [82] or due to supersaturation [83]. Still, the large required undercooling and the good epitaxial relation and the small lattice mismatch make it reasonable to assume solid particles during growth.

\(^4\)The application of phase diagrams on nanowire growth processes is problematic: Phase diagrams represent the phases occurring at thermodynamic equilibrium at atmospheric pressure. This is not given during the growth process. Nonetheless, phase diagrams can give indications for phases existing during growth. In this case for example, due to low temperatures and fast cooling times, it can be assumed that the state of the particle during growth is “frozen” due to kinetic hindering.
4.4.2  Flow study on the growth of InP nanowires from Cu particles

More or less epitaxial nanowires can be grown in the range of V/III between 175 and 1860 with varying total molar fractions [II]. Higher molar fractions of PH\textsubscript{3} lead to enhanced growth of non-straight structures (Fig 4.5).

The vertically aligned nanowires have a hexagonal cross section with \{112\} oriented side walls consisting of alternating \{111\} A and B microfacets. Their crystal structure is ZB with random stacking faults and twin planes without obvious change over the investigated range of temperatures and molar fractions.

There are two types of nanowires growing in the investigated range of molar fractions and V/III ratios. One type are nanowires described in section 4.4.1, with facetted Cu\textsubscript{2}In particle (Fig 4.6 a)-b)). The second type are nanowires with an about 4 times higher growth rate compared to the other type and with a roundly shaped, often oversized particle (Fig 4.6 d-b)). The first type grows under all investigated conditions, the second only at V/III ratios from
4.4 Cu seeded InP nanowire growth

470 and below. Interestingly enough, the growth rate of type I nanowires is almost the same for a V/III ratio of 930 and for 175, suggesting that their growth rate is independent of the In molar fraction at low molar fractions of PH₃.

HRTEM and XEDS investigations show that the particles of type II nanowires consist mostly of two phases (Fig 4.6 e)); a Cu rich part and a pure In part or shell. The In content varies with time and V/III ratio. At a V/III ratio of 175 the In content is around 70 at.% for growth times of 15 to 30 min, and jumps to 90 at.% for 45 min and 60 min. At a V/III ratio of 470, the In content is about 65 at.% after 10 min growth.

The large difference in growth rate between the two types of nanowires strongly suggests that type I nanowires grow from a solid particle, confirming the considerations in 4.4.1 and paper I, and type II nanowires grow from a liquid particle. Kodambaka et al. [82], who investigated in-situ VLS and VSS growth of Ge nanowires side by side, observed growth rates 7 times faster for VLS than for VSS growth.
Whereas the particle phase during growth is quite obvious for type I wires, it is not for type II wires. The phase boundary between the copper rich phase and the pure In is often perpendicular to the nanowire-particle interface and it is hard to imagine, that this would give straight nanowires. It is more likely, that this phase separation (or at least a shape change) takes place during cooling.

The most probable constitution is actually self-seeded growth. The copper particle acts probably as collection site for In, such as holes in a dewetting SiO layer stabilize In droplets [66]. Vogel et al. observe a similar behavior for growth of InSb nanowires from Au [65] and Ag [71]. In the Au seeded case, the post-growth particle consists mostly of In with a small part of AuIn$_2$ at low temperatures and low V/III ratios. At high temperatures and higher V/III ratios the nanowires have AuIn$_2$ particles. For all growth conditions they used for Ag seeded growth, they only found In-rich particles.

Two configurations of the particle are imaginable. A completely liquid In-rich particle or a particle with a liquid In shell and a Cu-rich, presumably Cu$_2$In core. The latter would be in accordance to the Cu-In binary phase diagram [95], which predicts two phases of $\eta$ and an In-rich liquid at growth temperature and the post-growth compositions. Presumably, the solid Cu$_2$In part is situated in the middle of the particle and the liquid In-rich shell is in contact with the vapor and the growth interface. This configuration could also explain kinking. The solid Cu$_2$In particle is probably not static, but moves a bit. If it moves so much that it reaches the corner of the nanowire and the In-rich liquid dewets it, the liquid might be pushed to the side, and the growth cannot occur straight anymore.

A completely liquid particle is also probable, even if the phase diagram predicts something different. During cooling in PH$_3$, the nanowire can continue to grow and thereby In is removed from the particle. The In concentration might therefore be higher during growth and the particle could even in accordance with the phase diagram be liquid. Other effects, such as undercooling [82] or a metastable liquid [83] could moreover play a role. During cooling the phase separates, leading to the two observed phases.
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The most intriguing question is why the two types of nanowires appear side by side under the same conditions. It might be, that there are two growth regimes and these tested V/III ratios are at the transition of the two regimes. Still, what is the reason that some particles form Cu$_2$In and others accumulate much more In? Some kind of Oswald-ripening could explain their occurrence. On samples with two types, type I nanowires have smaller diameters and type II nanowires larger diameters. At higher V/III ratios all nanowires are of type I, also at large diameters. The suggestion is, that all particles form Cu$_2$In particles first, additional In attaches, but diffuses then from smaller particles to larger ones, in an Ostwald-ripening process.
Chapter 5 Conclusions and Outlook

5 Conclusions and Outlook

This work shows that it is possible to grow epitaxially aligned InP nanowires from Cu seed particles. The growth regime is very limited compared to the growth from Au particles. The temperature ranges only within a few tens of Kelvin. At higher V/III ratios, the nanowires grow slowly from a solid particle. At lower V/III ratios, a second type of nanowires occurs side by side to nanowires seeded by a solid particle, which apparently grow self-seeded from an In-rich particle. Growth of nanowires with different characteristics on one sample is not desirable. It is therefore reasonable to use only higher V/III ratios, since the growth is more controlled. Otherwise, if self-seeded growth is desired, no Cu particles should be deposited to avoid contaminations.

The next steps in this project are: improving the growth and the use of Cu as seed particle material for other nanowire materials, a size selected generation of Cu particles and the application of other metals as seed material. It is interesting that several research groups have succeeded to grow epitaxial nanowires from alternative seed particle materials within the last year. The application of alternative seed particle materials has just started and the results cannot yet be compared with those from the quite mature growth from Au seed particles.

Nanowire growth from new seed particle materials is an important research field which will be closely investigated within the growth community for the following years. Upcoming studies will lead to new insights in, and a better understanding of, nanowire growth. These investigations may allow the growth of new nanowire-based materials hitherto unknown.
6 References


