Gold Particles for Growth of Semiconductor Nanowires

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Licentiate Thesis

Solid State Physics
Lund Institute of Technology
Lund University

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for Growth of
Semiconductor Nanowires

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Division of Solid State Physics
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Sweden 2009
Abstract

For more than a decade intense research on semiconductor nanowires has been ongoing, due to the potential that these structures offer for coming generations of electronic, optoelectronic and biosensor applications. However, if large-scale production of nanowire-based devices is to be realized better control and understanding of the nanowire growth process needs to be achieved.

Today particle-assisted growth is the most widely used method for production of epitaxial semiconductor nanowires. Nanoparticles of various different materials have been used to seed the growth of nanowires, but gold particles are by far the most common choice since gold is superior to other materials in most cases of nanowire growth. Although several nanowire growth models discuss the role of the seed particle, no clear understanding of why gold is such a suitable seed particle material exists. Furthermore, several different generation and deposition methods have been used to produce gold seed particles, but the effect of gold particle manufacturing method on nanowire growth is yet unclear.

In this thesis the effect of gold seed particles on growth of semiconductor nanowires is investigated. The first part of the thesis describes the most common seed particle generation and deposition methods and discusses the possible advantages and disadvantages of the resulting gold particle types. In the second part of the thesis the as-produced gold particles are used to seed the growth of semiconductor nanowires by Metal Organic Vapor Phase Epitaxy. The effects of gold particle diameter as well as gold particle manufacturing method on typical nanowire properties are directly investigated. In addition, the specific properties of gold are discussed in order to understand why gold is superior to other materials for mediating growth of nanowires.
Contents

Abstract iii

Contents iv

List of Papers v

List of Abbreviations vi

Acknowledgements vii

1. Introduction 1
   1.1 Nanoparticles 1
   1.2 Nanowires 2

2. Nanoparticle Generation and Deposition 5
   2.1 Aerosol Generated Particles (SDA & ECA particles) 6
   2.2 Colloidal Particles (DDC & ESC particles) 11
   2.3 Particles Produced by Annealing of Thin Films (TFA particles) 12
   2.4 Electron Beam Lithography Defined Particles (EBD particles) 12

3. Nanowire Growth 15
   3.1 Metal Organic Vapor Phase Epitaxy 15
   3.2 Gold Particle Assisted Nanowire Growth 16
4. **Transmission Electron Microscopy**  
   4.1 The Instrument  20  
   4.2 Imaging  22  
   4.3 Chemical Analysis  25  

5. **Gold Particle Effect on Nanowire Growth**  
   5.1 Particle Diameter  27  
   5.2 The Material Gold  29  
   5.3 Gold Particles of Different Origin  32  

6. **Conclusions and Outlook**  37  

References  39
List of Papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals:

I. 
Generation of size-selected gold nanoparticles by spark discharge – for growth of epitaxial nanowires
M. E. Messing, K. A. Dick, L. R. Wallenberg and K. Deppert
Gold Bulletin, 2009, 42 (1), 20

II. 
Controlled polytypic and twin-plane superlattices in III-V nanowires
P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert and L. Samuelson
Nature Nanotechnology, 2009, 4 (1), 50

III. 
The use of gold for fabrication of nanowire structures
M. E. Messing, K. Hillerich, J. Johansson, K. Deppert and K. A. Dick
Gold Bulletin, 2009, 42 (3), 172

IV. 
A comparative study on the effect of gold seed particle type on nanowire growth
M. E. Messing, K. Hillerich, J. Bolinsson, K. Storm, J. Johansson, K. A. Dick and K. Deppert
Submitted to Nanotechnology
The following papers are not included due to overlapping content or content beyond the scope of this thesis:

V. 
**InSb heterostructure nanowires: MOVPE growth under extreme lattice-mismatch**  
P. Caroff, M. E. Messing, B. M. Borg, K. A. Dick, K. Deppert and L.–E. Wernersson  
*Nanotechnology*, 2009, 20 (49), 495606

VI. 
**Control of III-V nanowire structure by growth parameter tuning**  
K. A. Dick, P. Caroff, J. Bolinsson, M. E. Messing, J. Johansson, K. Deppert,  
L. R. Wallenberg and L. Samuelson  
*Semiconductor Science and Technology* in press

VII. 
**Diameter dependence of the wurtzite–zink blende transition in InAs nanowires**  
J. Johansson, K. A. Dick, P. Caroff, M. E. Messing, J. Bolinsson, K. Deppert and  
L. Samuelson  
Submitted to *Journal of Physical Chemistry C*
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>AsH₃</td>
<td>arsine, precursor for arsenic</td>
</tr>
<tr>
<td>CBE</td>
<td>chemical beam epitaxy</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CTF</td>
<td>contrast transfer function</td>
</tr>
<tr>
<td>DDC</td>
<td>directly deposited colloid particles</td>
</tr>
<tr>
<td>DMA</td>
<td>differential mobility analyzer</td>
</tr>
<tr>
<td>DP</td>
<td>diffraction pattern</td>
</tr>
<tr>
<td>EBD</td>
<td>electron beam lithography defined particles</td>
</tr>
<tr>
<td>EBL</td>
<td>electron beam lithography</td>
</tr>
<tr>
<td>ECA</td>
<td>evaporation/condensation generated aerosol particles</td>
</tr>
<tr>
<td>ESC</td>
<td>electrospayed colloid particles</td>
</tr>
<tr>
<td>ESP</td>
<td>electrostatic precipitator</td>
</tr>
<tr>
<td>FEG</td>
<td>field emission gun</td>
</tr>
<tr>
<td>FET</td>
<td>field effect transistor</td>
</tr>
<tr>
<td>GaAs</td>
<td>gallium arsenide</td>
</tr>
<tr>
<td>GaP</td>
<td>gallium phosphide</td>
</tr>
<tr>
<td>GaSb</td>
<td>gallium antimonide</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscope/microscopy</td>
</tr>
<tr>
<td>InAs</td>
<td>indium arsenide</td>
</tr>
<tr>
<td>InP</td>
<td>indium phosphide</td>
</tr>
<tr>
<td>InSb</td>
<td>indium antimonide</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diode</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>MOVPE</td>
<td>metal organic vapor phase epitaxy</td>
</tr>
<tr>
<td>PH₃</td>
<td>phosphine, precursor for phosphorus</td>
</tr>
<tr>
<td>PLL</td>
<td>poly-L-lysine</td>
</tr>
<tr>
<td>SDA</td>
<td>spark discharge generated aerosol particles</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope/microscopy</td>
</tr>
<tr>
<td>-SH</td>
<td>thiol</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope/microscopy</td>
</tr>
<tr>
<td>TFA</td>
<td>particles generated by annealing of thin films</td>
</tr>
<tr>
<td>TMGa</td>
<td>trimethylgallium, Ga(CH₃)₃, precursor for gallium</td>
</tr>
<tr>
<td>TMI</td>
<td>trimethylindium, In(CH₃)₃, precursor for indium</td>
</tr>
<tr>
<td>VLM</td>
<td>visible light microscope/microscopy</td>
</tr>
<tr>
<td>VLS</td>
<td>vapor liquid solid</td>
</tr>
<tr>
<td>VPE</td>
<td>vapor phase epitaxy</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 spectrometer/spectrometry</td>
</tr>
<tr>
<td>ZB</td>
<td>zinc-blende</td>
</tr>
</tbody>
</table>
Acknowledgments

This work would not have been possible without the help from a large number of people that I am very grateful to. First of all I have to acknowledge my main supervisor Prof. Knut Deppert. Thank you for showing me how much fun it is to do research, for always taking time, for enormous inspiration and for improving my skills with wrenches and screwdrivers. You truly are a great supervisor!

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Chapter 1

1. Introduction

Nanostructures attract considerable attention these days, due to their interesting properties not found in their bulk structure counterparts. Surface effects and quantum mechanical effects are found in nanostructures because of their large surface-to-volume ratio and dimensions of the same order as the electron wavelength, respectively. Such effects are utilized in order to produce novel medical, optical and electronic devices. A highly promising nanostructure for novel device design is the so called nanowire [1]. The first step towards nanowire applications, however, involves a complete control of the nanowire production itself. One of the most widely used techniques for production of nanowires is the gold particle induced epitaxial growth technique [2]. In this thesis the effect of the gold particle on nanowire growth control has been investigated. The aim of the work has been to achieve more fully controlled nanowire growth as well as an enhanced understanding of how the gold particle affects growth.

1.1 Nanoparticles

All human beings are exposed to nanoparticles in their everyday life. Nanoparticles are generated by several sources such as nature itself, combustion engines, car tires, coal fires, cooking and construction areas, to only mention a few. It is well known that nanoparticles could have a major impact on climate [3] and public health [4], and therefore considerable amounts of research dealing with these issues are ongoing. However, nanoparticles are not only harmful, several useful applications of nanoparticles exists. A few examples in the field of optics and optoelectronics include light emitting diodes (LED:s) [5], gas sensors [6] and solar protection creams [7] based on nanoparticles. In biology nanoparticles are used for drug delivery, as fluorescent biological labels and as MRI contrast enhancement [8] among other things. In addition, nanoparticles can be used as seed particles for growth of epitaxial nanowires, which is the application discussed in this thesis.

The word nanoparticle is used for particles with diameters ranging from 1 to more than 1000 nm, and no accepted definition of nanoparticle diameter exists. However, throughout this thesis nanoparticles are considered to have a diameter between 1 and 150 nm. Moreover several different techniques can be used to generate nanoparticles, including vapor phase methods and chemical methods. Some of these techniques are more commonly used for
Chapter 1. Introduction

generation of nanowire seed particles and will be further discussed. These methods include the production of aerosol generated particles, colloidal particles, electron beam lithography defined particles and particles generated by annealing of thin films. Here, main focus will be on aerosol generated particles.

The precise definition of an aerosol is a solid or liquid particle suspended in a gas [9], thus the term aerosol refers to both the particle and the gas. It should be noted, however, that this expression is often used for the particle only. According to this definition almost all nanoparticles could be considered being aerosol particles. To slightly limit this definition, only particles suspended in an ultra-pure gas, such as nitrogen, will be regarded aerosol particles throughout this work.

1.2 Nanowires

Nanowires are one-dimensional (1D) rod shaped structures characterized by a large length-to-width ratio. Two dimensions are in the size range of tens of nanometers or less whereas the third dimension is much longer, typically a few micrometers. For nanowires to act as actual 1D structures their diameter has to be less than the Fermi wavelength of electrons. If that is the case, electrons can be quantum confined laterally and occupy discrete energy levels in that direction. These quantum confinement effects can be utilized in photonic and electronic applications and for fundamental studies of transport phenomena.

Apart from quantum confinement effects nanowires exhibit two other highly interesting categories of unique properties, namely surface related effects and crystal structure effects. Surface related effects arise due to the large surface-to-volume ratio found in nanowires and can be utilized in nanowire based biosensor applications. The crystal structure of nanowires, depending on production method, can be of very high quality with few defects. Furthermore the crystal structure can be controlled to a large extent by nanowire growth parameter tuning, not equally possible in the production of bulk structures. Finally, defect-free material combinations not possible to achieve in bulk structures, can be utilized in nanowires due to the lateral strain relaxation allowed in nanowires. This control of crystalline quality and the possibility to produce defect free heterostructures makes semiconductor nanowires applicable for industry.

A number of devices based on nanowires have been demonstrated, such as LEDs [10-14], field effect transistors (FETs) [15-18], solar cells [19-21], thermo electronic devices [22] and biosensors [23, 24]. In addition to biosensors, nanowires might also be used for other medical applications in the future. Patterned nanowire arrays have been demonstrated to act as rectifiers and guides of nerve cells on a substrate, which opens up new possibilities for neural network design [25].

Nanowires of a variety of materials have been produced, including metal nanowires, metal chalcogenide nanowires, metal carbide nanowires, oxide nanowires and semiconductor
nanowires. For an extensive review of the materials systems used for nanowire production see for example Rao et al. [26]. In this thesis only semiconductor nanowires will be discussed with the emphasis on III-V semiconductor nanowires, which consists of one element from group III and one from group V of the periodic system. Typical examples are InP, InAs and InSb as well as GaP, GaAs and GaSb. In comparison to a common and widely used semiconductor material such as Si, III-V materials have some beneficial properties. First of all and unlike Si, III-V materials (with the exception of GaP) have a direct bandgap, meaning that electrons and holes can recombine directly with conserved momentum while emitting photons during the process. This property makes III-V materials very useful for optical applications. Secondly, compared to Si, III-V materials exhibit much higher electron mobility, which makes them useful for high-frequency electronic applications.

The fabrication of nanowires can be performed by a number of different techniques, normally divided into top-down and bottom-up methods. Nanowires can be produced by lithographically carving out the structures from the desired bulk material, referred to as top-down production. This method has been used for a long time and is still the method of choice in semiconductor processing. However, when the dimensions of components shrink to the nanometer scale, practical problems arise using the top-down approach. The surfaces of the structures are damaged by the lithographic process, resulting in nanowires of a poor crystal quality. In addition, the lithographic techniques may not be able to produce sufficiently small structures for further down-scaling of devices. To overcome these problems and produce small enough nanowires of high enough crystal quality, the bottom-up approach can instead be used. This means that the nanowires are formed by self-organized “growth” atom by atom in a highly controllable manner.

Among the bottom-up techniques used, the vapor phase epitaxy (VPE) method dominates nanowire growth today [2]. Although VPE is a rather expensive technique it is especially advantageous in two ways. First of all a huge range of vapor phase precursors exist, making it possible to grow nanowires of many different types of materials. Secondly, very high control of the growth process is possible, enabling the production of complex nanowire structures. The VPE technique used throughout this thesis for nanowire growth is the so called metal organic VPE (MOVPE) technique, where metal organic growth precursors are used.

The most widely used method to grow nanowires by MOVPE is the particle-assisted method, where a metal seed particle is used to induce the growth, but reports of particle-free growth exists [27-29]. A variety of different metal particles have been used to seed nanowire growth [30-34], but gold is by far the most used particle material. The reason for this is probably the many early reports on successful nanowire growth from gold, and in addition, the difficulty to achieve and control nanowire growth when using particles of other materials. All nanowires covered by this thesis have been seeded with gold particles.
Chapter 2

2. Nanoparticle Generation and Deposition

In the many reports of gold seeded nanowire growth, the gold seed particles have been generated and deposited by various different methods. Successful and highly controlled nanowire growth has been reported from aerosol-generated gold particles [V], colloidal gold particles [35], electron beam lithography (EBL) defined gold particles [36] and gold particles generated by annealing of thin films [37]. A few reports on nanowire growth from gold particles defined by other methods such as laser ablation [38] and nanoimprint lithography [39] can also be found, but such techniques are less common and will therefore not be considered in this thesis. In this section the different types of gold particles used to seed nanowires during this work, namely aerosol gold particles generated by spark discharge (SDA) and by evaporation/condensation (ECA), colloidal gold particles deposited by direct deposition (DDC) and by electro spray deposition (ESC), gold particles generated by annealing of thin films (TFA) and EBL defined gold particles (EBD), will be described. These acronyms for particles generated and deposited with different methods will be used throughout the thesis to facilitate further reading.

Gold particles generated and deposited with different methods exhibit differences in controllability of size, position, surface density and cleanliness. A certain particle type could be beneficial in one way but less useful from another point of view, and therefore it is not always obvious which particle type or deposition method to use. Throughout this thesis “particle type” is used to indicate gold particles generated and deposited with a specific method. As a general rule of thumb the dimensions of the nanowire (length and diameter), its crystalline structure and the surface density of nanowires needs to be uniform and fully controlled for large scale device production to be possibly. If vertical device design, which means that devices are directly manufactured around the standing wires, are to be realized a complete control of the positioning of the seed particles is also required. Finally, to meet the cleanliness requirements of the semiconductor industry, all possible residues from the particle production step must be fully removed. On the other hand, if the nanowires are to be used for fundamental research about the nanowire growth mechanism, for example, a precise size and position control might not be equally necessary. In the following particle generation subsections, the advantages and disadvantages of each particle type will be briefly discussed. A summary of the differences of the generation and deposition techniques, particularly in control of particle properties, is displayed in Table 2.1.
Table 2.1 Comparison of general particle characteristics between the different gold particle types.

<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>Very Limited</td>
<td>Uncontrolled</td>
<td>Very High</td>
<td>Very Clean</td>
<td>Simple</td>
<td>Medium</td>
</tr>
</tbody>
</table>

2.1 Aerosol Generated Particles (SDA & ECA particles)

Two different generation methods have been used to produce aerosol particles, namely the spark discharge method and the evaporation/condensation method. For the spark discharge method a commercially available aerosol generator (Palas, model GFG 1000), primarily constructed for carbon soot particle production, has been used. The mechanism behind particle formation is based on spark discharge between two conducting cylindrical electrodes positioned in the middle of a polymer chamber with their flat ends separated by a distance of 2 mm (Figure 2.1). The distance between the electrodes is varied automatically by an electric motor, and maintained during particle production to keep the breakdown voltage constant. A 20 nF capacitor is connected to one of the electrodes, and charged by a high voltage supply with adjustable output current [40]. When the breakdown voltage of 2 kV is reached the capacitor discharges instantaneously in a spark across the electrode gap. The local temperature of the spark reaches approximately 20000 to 30000 K [41], resulting in evaporation of electrode material. Primary particles are formed by homogenous nucleation of this supersaturated vapor, and coalesce into larger particles. In the original setup a stream of argon gas and/or air focused between the electrodes transports the as-produced primary particles towards the aerosol outlet about 15 mm downstream of the electrodes. Further growth of primary particles by condensation and coagulation results in the production of highly charged, nanometer-sized agglomerate particles [42]. For the production of gold particles the carrier gas was replaced by ultra-pure nitrogen to comply with cleanliness requirements of the semiconductor industry. Furthermore the graphite electrodes used in the original setup were replaced by high purity gold rods (99.99 %) with diameters of 3 mm mounted to cylindrical stainless steel holders with diameters of 6 mm.
2.1 Aerosol Generated Particles (SDA & ECA particles)

![Figure 2.1 Schematic of the aerosol spark generator used to produce SDA gold particles by spark discharge.](image)

Two parameters can be adjusted in order to optimize particle production namely the spark discharge frequency and the carrier flow rate. The spark discharge frequency, \( f \), is determined by the charging current, \( I \), of the capacitor \([42]\) by

\[
f = \frac{I}{CV_d}
\]

where \( V_d \) is the discharge voltage. It should be noted that the discharge voltage is not exactly equal to the breakdown voltage, \( V_b \), but slightly higher since the discharge conditions require some time to develop \([43]\). An additional overvoltage, \( V_O \), relates the breakdown and discharge voltages by \( V_d = V_b + V_O \). The spark discharge frequency can be varied between 0 and 300 Hz, which corresponds to a charging current increase from 0.13 to 20 mA \([44]\). An increase of spark discharge frequency results in an increase of particle number concentration and a shift to larger particle diameters \([I]\), which is in good agreement with reports on particles of other materials produced by spark discharge \([40, 43, 45]\). In Figure 2.2 the increase of particle number concentration from \( 3 \times 10^5 \) to \( 1.3 \times 10^6 \) cm\(^{-3}\) and particle diameter from approximately 10 to 30 nm on an increase of spark discharge frequency from 30 to 300 Hz is displayed. The higher spark discharge frequency corresponds to an increase in number of sparks per second that evaporates electrode material, which explains the higher number concentration of particles. Furthermore, an increase in evaporated particle material leads to a higher coagulation rate and hence faster growth of particles resulting in particles with larger diameters.

The carrier flow rate can be adjusted between 2 and 8 l/min and is important in order to obtain a reproducible and constant particle generation. The flow rate needs to be large enough to remove all primary particles and ions between the electrodes before the ignition of the next spark. An increase of carrier flow rate from 3.4 to 5.9 l/min results in a slight decrease of
Chapter 2. Nanoparticle Generation and Deposition

Figure 2.2 Size distributions of the agglomerate gold particles generated at a nitrogen gas flow of 5.9 l/min and at spark discharge varying from 30 to 300 Hz, measured by DMA 1.

particle number concentration, but has no effect on particle diameter. However, specific carrier flow rates combined with specific spark discharge frequencies results in a more stable particle production. The highest yield of particles obtained under stable conditions have been observed when combining a carrier flow rate of 5.9 l/min with a spark discharge frequency of 300 Hz [I], and these parameters have been used for production of SDA seed particles throughout this work. It should be noted that replacement of nitrogen with some other gas affect stability and size-distributions of particles [43], and the optimum parameters for stable particle production will most likely differ from the original setting.

The other method to produce agglomerate gold particles, evaporation/condensation, is also based on evaporation of gold, solely by a slightly different technique. For this method a high temperature furnace is used to evaporate material from a solid piece of gold. The evaporated gold is transported away by an ultra-pure carrier gas (nitrogen) and primary particles are formed by homogenous nucleation, which grow by subsequent coagulation into agglomerate particles. The size distribution of particles can be shifted to particles with larger diameters by increasing the temperature of the furnace [46]. During this work temperatures between 1700 and 1950 °C have been used for production of ECA seed particles.

Regardless of one or the other generation method, the as-produced agglomerate gold particles must be reshaped into compact spherical particles if they are to be used as nanowire seed particles. Often monodisperse nanowires of a known diameter need to be produced, which in turn requires monodisperse seed particles of a known diameter [47]. To achieve this, the spark generator or high temperature furnace has been connected to an aerosol nanoparticle system setup [I, 48]. The entire setup, which enables size distribution measurements, reshaping of the agglomerate particles and controlled particle deposition, is shown in Figure 2.3. The agglomerate particles are first send through a neutralizer in order to achieve a reproducible and known charge distribution of primarily uncharged and singly-charged particles by
2.1 Aerosol Generated Particles (SDA & ECA particles)

Figure 2.3 Schematic of the aerosol nanoparticle system setup. Gold particles are produced in the aerosol spark generator and carried by nitrogen gas through the system. Following particle generation differential mobility analyzers (DMAs) are used to size-select and measure size distributions of the particles and a compaction tube furnace is used to reshape them. Finally the particles can be counted by an electrometer or fed into an electrostatic precipitator (ESP) for deposition.

collision of the particles with ions from a $\beta$-emitting $^{63}$Ni source [49]. Once the known charge distribution is achieved the charged particles are size-selected in a differential mobility analyzer (DMA), labeled DMA 1 in Figure 2.3. The DMA, a standard instrument in aerosol science, classifies charged particles according to their mobility inside an electric field [50]. This mobility is roughly inversely proportional to the particle diameter. Following size selection the agglomerate particles can be reshaped into more compact particles inside a compaction tube furnace (route 2 in Figure 2.3). Alternatively, size distribution measurements can be directly performed using an electrometer knowing that each particle that passes the DMA carries one single charge (route 1 in Figure 2.3). To size select and obtain size distribution measurements of the reshaped particles a second DMA, labeled DMA 2 in Figure 2.3, is used. Size distribution measurements are obtained by stepwise scanning the voltage of the DMA and measure the resulting particle concentration with the electrometer. To investigate the compaction temperature of the agglomerate particles the tandem DMA setup is used by scanning the reshaping temperature and measuring the peak value of the size distributions for each temperature [51]. The final part of the aerosol nanoparticle system setup includes an electrostatic precipitator (ESP) for controlled deposition of particles. The ESP focuses charged particles onto a collector electrode [52], where the substrate is placed, and allows for a high efficiency deposition of particles with diameters up to 100 nm.

Both SDA and ECA particles are fully compacted, meaning that no more shrinkage of particle diameter occurs, already below 300 °C [I, 48]. However, although no further shrinkage of particle diameter occurs above approximately 300 °C the reshaping continues at higher temperatures with internal rearrangement of the particle structure. With increasing temperature the particles become more spherical and less polycrystalline. In Figure 2.4 the transformation of crystal structure with increasing reshaping temperature for SDA particles is displayed, starting with the collection of primary particles that constitute the not reshaped
agglomerate particle (Figure 2.4 a). After reshaping at 600 °C (Figure 2.4 c) the particles exhibit a reasonable spherical structure, which is very similar for both ECA and SDA particles. At this temperature the highest yield of particles with a sufficient seed particle structure is obtained, and has therefore been used for production of all aerosol-generated nanowire seed particles throughout this thesis.

The disadvantages of aerosol-generated particles include the less simple and expensive setup and the somewhat limited size distribution of particles. The SDA particles are limited to a maximum diameter of around 35 nm, while the upper limit is around 100 nm for ECA particles, due in both cases to limitations of the setup used. However, the main disadvantage, as for most particle types, is the random positioning of particles on the substrate. On the other hand, aerosol-generated particles provide several advantages. Extremely pure particles with a monodisperse tunable diameter can be produced and deposited with a very controlled surface density at a reasonable throughput. Moreover, an additional advantage of the aerosol deposition method involves substrate flexibility. Particles can be deposited onto more or less any type of substrate having a diameter up to several centimeters.

Figure 2.4 TEM micrographs of (a) an agglomerate gold particle and gold particles reshaped at (b) 300 °C (c) 600 °C (d) 1200 °C in a compaction tube furnace.
2.2 Colloidal Particles (DDC & ESC particles)

Colloidal gold particles are synthesized by a chemical reaction, where chloroauric acid (HAuCl₄) is reduced by citric acid (C₆H₈O₇) or trisodium citrate (Na₃C₆H₅O₇) in an aqueous solution [53]. Normally ligands such as sodium citrate (C₆H₅Na₃O₇), phosphines (PH₃) or thiols (-SH) are attached to the particles in order to keep them suspended in the solution and prevent them from agglomeration [54]. Gold colloid particles are commercially available in a wide range of different diameters with a diameter dispersion of less than 10%. All colloidal particles used as nanowire seed particles in this thesis have been commercially produced (British Biocell International).

Two different methods have been used to deposit colloid particles: The direct deposition method and the electrospray method. For the direct deposition method, a droplet of colloidal solution is placed on the substrate that is subsequently rotated. By rotation of the substrate, typically performed between 500 and 3000 rpm, excess liquid is removed and a more even surface distribution of particles can be obtained. By varying the concentration of the colloid solution the surface density of particles can be controlled to some extent. One problem with direct deposition of colloids onto a substrate is the surface properties of the substrate relative to the surface properties of the colloids, since both are negatively charged. To solve this problem an intermediate layer formed by the surfactant poly-L-lysine (PLL), containing one positively charged end has been added, a method often used to ensure adhesion of the particles to the substrate by electrostatic interactions [35].

For the electrospray deposition method a commercially available electrospray setup (TSI, model 3480) has been used. The colloid solution is soaked through a capillary in a high electric field. Due to electrohydrodynamic breakup at the tip of the capillary the colloid solution is atomized, resulting in highly charged small droplets carrying approximately one particle each [55]. Directly after formation, the droplets are neutralized by a Polonium-210 radioactive α-emitter leading to mainly singly and doubly charged droplets. Following neutralization an ultra-pure carrier gas (nitrogen) is used to dry the particles, by evaporation of the liquid, and transport them to an ESP (TSI, model 3089) for deposition. The deposition is similar to the deposition of aerosol-generated particles, and hence no PLL is needed for the particles to adhere to the substrate.

The main advantage of colloid particles is the availability of particles of a variety of different diameters with a narrow diameter distribution. Some of the other advantages and disadvantages of colloid particles differ slightly depending on deposition method used. If the direct deposition method is used an inhomogeneous particle surface coverage is often achieved and it is difficult to produce samples with precisely controlled particle densities. Moreover, since mechanical rotation of the samples is required, the samples cannot be too thin/fragile, too small or too large. These disadvantages could be overcome by using the electrospray method where samples with a homogenous distribution of a given particle surface density are generated. In addition, by using electrospray deposition, particles can be
Chapter 2. Nanoparticle Generation and Deposition

deposited onto more or less any type of substrate having a diameter of up to a few centimeters. Such a setup is however rather expensive and more complicated to use than the direct deposition method. Furthermore, regardless of deposition method used position control of colloid particles is generally not possible. The major disadvantage for either method is nevertheless contamination problems. Organic remnants from the synthesis and stabilization processes, as well as PLL if the direct deposition method is used, contaminate the particle and substrate surfaces.

2.3 Particles Produced by Annealing of Thin Films (TFA particles)

The common procedure for generation of gold particles from thin films is thermal evaporation of a gold film directly onto the substrates. The deposition rate is typically around 0.1 nm/s and can be measured by a quartz crystal monitor. Normally the thickness of the film can vary between 0.1 nm and a few nanometers. Following film deposition, the substrates are heated up to elevated temperatures in order for the film to split up into particles. When the particles are to be used as nanowire seed particles the heating step often occurs inside the nanowire growth reactor. In addition, *in situ* deposition of the gold film inside the nanowire growth apparatus prior to heating has also been reported [56].

A few parameters can be adjusted in order to affect particle size and particle surface density to some extent. The temperature used during the heating step affects particle distribution slightly with higher temperatures yielding larger particles and lower particle surface densities [57]. In addition, the use of thicker films also results in larger particles and lower particle surface densities [58]. However, regardless of film thickness or temperature it is extremely difficult to achieve a low surface density and to independently control particle diameter and surface density.

Although the TFA particles suffer from extremely poor controllability with respect to particle diameter, particle surface density and particle positioning, this method of producing particles also has advantages. It is a fairly simple, reasonably cheap and very clean method, especially if the film is deposited *in situ* (something that is not possible for most of the other particle types). TFA particles can be prepared on most types of substrates regardless of size, so long as the substrate material allows for diffusion and agglomeration of gold at temperatures that are not destructive to the substrate.

2.4 Electron Beam Lithography Defined Particles (EBD particles)

The production of gold particles by EBL can be seen as a development of the thin film method, since generation of EBD particles also requires evaporation of a thin gold film. However, prior to gold film evaporation a pattern has been defined onto the substrate that determine size, surface density and position of the particles to be produced. In Figure 2.5 a schematic of the EBD particle production process is displayed. In the first step the substrate (Figure 2.5 a) is coated with an electron beam sensitive resist (Figure 2.5 b) that is exposed by
the electron beam to define the desired pattern. If a positive resist is used the exposed areas will be chemically altered to disappear upon development, and if a negative resist is used the exposed areas will be chemically altered to remain upon development. Following development (Figure 2.5 c) a thin gold film is thermally evaporated onto the substrate (Figure 2.5 d). To remove the remaining resist and the excess gold a liftoff step, where the remaining resist is dissolved and hence the gold on top of it removed, is used. This entire procedure results in well-defined gold disks precisely positioned on the substrate (Figure 2.5 e). As for the TFA particles a heating step, often performed inside the nanowire growth reactor, is required to transform the gold disks into particles (Figure 2.5 f).

The major advantage of EBD particles is the highly controlled generation process. Not only can EBD particles be homogenously prepared with a given tunable diameter and surface density, but the exact position on the substrate can also be controlled. A precise limitation of particle diameter and density is difficult to define, but the EBL process becomes increasingly problematic for decreasing particle diameters and increasing surface densities. As for colloidal particles, the main problem with EBD particles concerns contamination of the substrate surface by organic residues from the chemical preparation process. In addition, EBD particles cannot be prepared on substrates that are too thin, brittle, or otherwise unable to withstand a lot of handling and processing steps. As well, the process needs to be modified slightly depending on substrate material used. Finally the preparation method itself is rather expensive and more complicated and time-consuming compared to the other methods resulting in a low throughput of samples.

Figure 2.5 Schematic of the EBL process. (a) The substrate (b) is coated with an electron beam sensitive resist that is exposed by the electron beam to define the desired pattern. (c) Following development (d) a thin gold film is thermally evaporated onto the substrate. (e) Liftoff is used to remove the remaining resist and excess gold resulting in a well defined gold disk. (f) Upon heating the gold disk is transformed to a particle.
Chapter 3

3. Nanowire Growth

Nanowires are normally crystalline which means that they exhibit a specific crystal structure. In crystalline materials the atoms have a certain order, known as their crystal structure. The opposite case is amorphous materials, where the atoms are randomly positioned throughout the structure. To obtain nanowires of a high crystalline quality (highly ordered atoms) epitaxial growth is most often used. Epitaxial crystal (nanowire) growth means that a substrate with a specific crystal structure is used to orient the growth of the crystal (nanowire) in an ordered manner so that the crystal (nanowire) adopts the same crystalline structure as the substrate. If the substrate is of the same material as the nanowire, the growth is known as homoepitaxy (used throughout this thesis) and if the substrate is of a different type of semiconductor material, the growth is known as heteroepitaxy.

3.1 Metal Organic Vapor Phase Epitaxy

Several different epitaxial growth techniques are used for nanowire growth, including molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), and metal organic vapor phase epitaxy (MOVPE). Variations between these techniques include the use of different precursors, growth performed under different pressures and different ways of distributing the precursors, among other things. MOVPE is the main technique used in semiconductor industry today because it is reasonably fast, reliable, a wide range of precursors are available and the cost is relatively low.

MOVPE operates under atmospheric or at reduced pressures, normally 100 mbar. In MOVPE at least one of the precursor species, usually the group III precursor in the case of III-V material growth, needs to be a metal organic compound. Commonly trimethylindium (TMI) and trimethylgallium (TMGa) are used as group III precursors and the hydrides arsine (AsH₃) and phosphine (PH₃) are used as group V precursors. Crystal growth occurs due to surface reactions of the decomposed metal organic compounds and hydrides at the substrate with carbon hydrogen compounds as a rest product. Epitaxial layer growth of GaAs, as an example, occurs between 600 and 700 °C to ensure decomposition of the precursors into elemental Ga and As that incorporates into the GaAs crystal, forming the layer. The detailed chemical processes involved are highly complicated, but the overall chemical reaction for epitaxial GaAs growth can be expressed as:
Figure 3.1 Schematic of the MOVPE system. Hydrogen is used as carrier gas to transport the growth precursors to the reaction chamber. Inside the reaction chamber substrates are placed onto a susceptor and heat is applied. Excess gases and waste material are transported away and rendered harmless by burning.

\[ \text{Ga(CH}_3\text{)}_3(g) + \text{AsH}_3(g) \rightarrow \text{GaAs(s)} + 3\text{CH}_4(g) \] (3.1)

Ultimately all methyl groups are desorbed from the surface, otherwise residual carbon levels may contaminate the GaAs crystal. Depending on growth temperature used carbon contamination can be controlled to some extent [59].

In Figure 3.1 a schematic of the MOVPE setup used throughout this thesis to grow nanowires is displayed. Substrates are placed inside the reactor cell on a graphite susceptor that is heated either by a radio frequency coil outside the reactor chamber or by halogen lamps, depending on MOVPE system used. To ensure that the chemical reactions only take place near the substrate, the walls of the reactor cell are kept cold. The growth precursors are transported via the run line to the reactor chamber by an ultra-pure carrier gas, often hydrogen (H₂), where they form a laminar gas flow across the substrate surface [59]. The gas flows of the different sources are regulated by mass flow controllers (MFCs). Waste material, including unreacted precursors, are transported away either from the reactor cell or directly via the vent line, and rendered harmless by burning.

3.2 Gold Particle Assisted Nanowire Growth

Gold particle assisted epitaxial growth of semiconductor nanowires typically starts with the deposition of gold particles onto a clean semiconductor substrate. Particles with a specific diameter and known surface density are desirable since the diameter and surface density of
3.2 Gold Particle Assisted Nanowire Growth

Figure 3.2 Schematic demonstrating particle-assisted nanowire growth. (a) The seed particles are formed/deposited on the substrate and (b) by heating the substrate to a desired temperature and introducing growth materials an alloy is formed. (c) When a supersaturation of the alloy particle with growth material is achieved, nucleation occurs at the particle-substrate interface. (d) Nanowire growth occurs at the particle-wire interface as long as growth material is provided. (e) By switching to growth conditions favoring planar growth radial heterostructures, known as core-shell nanowires, can be grown. (f) Nanowires containing axial heterostructures with very sharp interfaces can be formed by switching between different growth materials. (g) If a second generation of gold particles is deposited onto the as-grown nanowires and (h) the growth process is repeated, branched nanowires for formation of nanowire networks can be grown.

Particles determine the diameter and surface density of nanowires. The substrates containing the deposited particles are then, in the case of MOVPE, placed inside the reactor cell (Figure 3.2 a). During the first step the substrate is heated to a desired growth temperature, or to a temperature slightly above the growth temperature for an annealing step. The annealing step is used mainly in order to decompose the native surface oxide. Heating occurs under a constant group V partial pressure to prevent decomposition of the substrate at elevated temperatures. Once the growth temperature is reached the group III precursor is also turned on and the actual growth is initiated (Figure 3.2 b). When the precursor materials come into contact with the gold particle at the elevated temperatures an alloy is typically formed. This alloy particle could be either liquid or solid, depending on its melting temperature compared to the growth temperature. When a certain amount of precursor material has been incorporated into the particle it will become supersaturated, and precipitation of material will occur at the particle/substrate interface, referred to as nucleation (Figure 3.2 c). As long as a continuous supply of precursor material is available nanowire growth at the particle/nanowire interface takes place (Figure 3.2 d). By turning off the group III precursor the growth is terminated.

The growth rate of nanowires is determined to a large extent by the supersaturation, which in turn is controlled by the precursor concentration and the temperature. Typically nanowires are grown between approximately 380 and 550 °C, which is significantly lower than the temperatures used for layer growth. In addition, highly complex nanowire structures could be grown by adjustments of the growth parameters. Nanowires containing radial
heterostructures, so called core-shell nanowires (Figure 3.2 e), are grown by switching to conditions that favors layer growth [60]. Axial heterostructured nanowires (Figure 3.2 f) containing very sharp interfaces are grown by abrupt switching between different precursor gas flows [61]. Finally complex nanowire networks consisting of branched nanowires are grown by deposition of a new generation of gold particles onto the already grown wires (Figure 3.2 g) and then repeating the growth process (Figure 3.2 h) [62].

Particle assisted nanowire growth is most often described by the vapor liquid solid (VLS) model developed already in the 1960’s by Wagner and Ellis [63]. In this model vapor denotes the phase of the precursors, liquid the phase of the particles and solid the phase of the nanowires. As mentioned above the particle can also be in a solid state during growth and therefore the vapor solid solid (VSS) model [64] is also used to describe particle assisted nanowire growth. However, none of these models fully explains the mechanism of nanowire growth and the actual role of the particle is still under discussion. Moreover it is not completely understood why gold particles are superior to particles of other materials in most cases of nanowire growth.
Chapter 4

4. Transmission Electron Microscopy

The use of microscopy constitutes an important part when working with small structures, in order to enable careful investigations of the structures. Conventional visible-light microscopy (VLM) can be used to some extent when working with nanostructures but is limited in resolution. The smallest feature that can be resolved with a VLM, $\delta$, according to the Rayleigh criterion is given approximately by

$$\delta = \frac{0.61\lambda}{\mu \sin \beta}$$

(4.1)

where $\lambda$ is the wavelength of the light, $\mu$ the refractive index of the viewing medium and $\beta$ the semi-angle of collection of the magnifying lens. For simplicity $\mu$ and $\beta$ can be approximated to unity which results in a resolution of about half the wavelength of the light. Since visible light has a wavelength between approximately 400 and 700 nm, the investigation of nanowires and nanoparticles with diameters smaller than 150 nm, as in this thesis, requires the use of more powerful microscopes with a better resolution than the VLM.

In electron microscopes visible light has been replaced by electrons, and the resolution hence depends on the wavelength of the electrons (although the Rayleigh criterion is no longer valid since it is based on incoherent illumination). Since the de Broglie wavelength of electrons is much smaller (in the order of pm) than the wavelength of visible light, much smaller features can be resolved in an electron microscope compared to in a VLM. Therefore the use of electron microscopy is invaluable when working with nanostructures. It should be noted, however, that the resolution of an electron microscope is not limited by the wavelength of the electrons but by the quality of the electromagnetic lenses used, which will be discussed later.

Two different types of electron microscopes have been used during this work: The scanning electron microscope (SEM) and the transmission electron microscope (TEM). Note that the abbreviations commonly also refer to the method of microscopy and not only the instrument. SEM provides a good over-view of the samples containing nanowires and nanoparticles and is reasonably fast and easy to operate. TEM on the other hand provides detailed information of the atomic structure of each nanowire or nanoparticle but is more time-consuming and rather difficult to operate. In the remaining part of this chapter, the TEM will be discussed in more detail.
4.1 The Instrument

The basic structure of the TEM (Figure 4.1) is not that different from the basic structure of a VLM and can be divided into three components: The illumination system, the objective lens/stage and the imaging system [65]. The role of the illumination system is to create electrons and transfer them to the sample, and the illumination system consist of an electron gun and condenser lenses. An electron gun comprises an electron source, to create electrons, and a gun assembly, to accelerate and direct the electrons into the rest of the illumination system. Two different types of electron sources are used in a TEM, thermionic sources and field-emission sources. Thermionic sources are either fine tungsten (W) tips or lanthanum hexaboride (LaB₆) crystals which emit electrons when enough heat is applied to overcome the work function, $\Phi$, of the material. Field-emission sources (FEGs) consist of a fine W needle that emits electrons when a high electric field is applied close to the tip. Compared to the thermionic source the FEG has a longer life-time, emit electrons with a more narrow energy spread and is the brightest electron source known (brightness is the current density per unit solid angle of the source). The TEM used in this work (JEOL, model 3000F) uses a FEG.

Once the electrons have been created by the electron gun, the condenser lenses focus the electron beam onto the specimen. Since electrons instead of light are used for illumination, electromagnetic lenses instead of glass lenses are used to direct the electron beam. An

![Figure 4.1 Cross section of a JEOL 3000F TEM column.](image)
The Instrument

Electromagnetic lens is a magnetic field created in the hollow part of a pole piece with a copper coil surrounding it [66]. Unlike the VLM where the positions of the glass lenses are changed to direct the light, the electromagnetic lenses in a TEM are fixed. Instead the strength of the electromagnetic lenses are changed by changing the current through the copper coil in order to affect the electron beam, by means of focus, intensity of illumination or magnification.

The objective lens and the specimen stage constitute the part of the TEM where the images and diffraction patterns (DPs) are formed. Since images and DPs are formed by electrons transmitted through the specimen, the specimen needs to be electron transparent, meaning thin enough that electrons can travel through it, for TEM to work. Hence specimen preparation typically is a crucial part of TEM, in order to obtain thin enough specimens to enable high quality imaging. Fortunately the nanoparticles and nanowires investigated in this thesis are already thin enough so that complicated specimen preparation processes can be avoided.

Apart from the quality of the specimen, the quality of the objective lens plays a major role in image/DP formation and the objective lens is clearly the most important lens in the TEM [65]. Unfortunately electromagnetic lenses, such as the objective lens, suffer from severe limitations, such as spherical and chromatic aberrations and astigmatism. Spherical aberration means that the electrons travelling through the electromagnetic lens at different angles from the optical axis will be focused at slightly different focal points. This is due to the different strength of the lens at the edges compared to closer to the optical axis. The consequence of spherical aberration is that a point in the object will be imaged as a disk. Spherical aberration can be corrected for by so called spherical aberration correctors, but they are very expensive and only a small number of TEMs are equipped with such correctors today. Chromatic aberrations arise because the electromagnetic lens focus electrons of different energies at slightly different focal lengths, also resulting in a disk. Monochromators and improved specimen preparation, since thicker specimens may result in a small energy loss of some electrons, can be used to correct for chromatic aberration. Astigmatism is caused by a non-symmetrical electric field in the lenses, but can easily be corrected for by stigmators which induces a compensating electric field. These aberrations of the electromagnetic lenses are what limit the resolution of the TEM, rather than the wavelength of the electrons.

Following image or DP formation by the objective lens, the imaging system uses several lenses to magnify the image or DP and to focus these onto a viewing screen or a charge-coupled device (CCD) camera connected to a computer. A viewing screen or CCD camera is used because human eyes are not sensitive to electron radiation (which most likely would damage the eyes) and hence the electron intensity must be translated into visible light intensity. This is done by coating the viewing screen with a scintillating material, meaning a material that emits light when struck by electrons.
4.2 Imaging

The image created in a TEM is at its best a two-dimensional shadow image of a three-dimensional specimen averaged over the thickness of the specimen. Therefore image interpretation is far from straightforward, and a deep understanding of the interactions between the electrons and the specimen is required in order to correctly interpret TEM images. When describing electron-specimen interactions the electrons can be thought of both as charged particles and as waves having a specific amplitude and phase. From a particle viewpoint, electrons that enter a specimen can be scattered either by a single atom or by an electron cloud. If the electron maintains energy and velocity but changes direction while scattered, the scattering is said to be elastic. The contrast in TEM images are mainly due to elastically scattered electrons. Inelastic scattering means that the electron change both direction and velocity while some of its energy is transferred to the specimen. Inelastic scattering can introduce damage to the specimen and impair resolution but also contain useful chemical information of the sample which will be discussed in section 4.3. The interactions of electrons with the specimen, when using the wave approach, are called diffraction. The diffraction pattern, meaning the distribution of diffracted electrons in reciprocal space, contains information of the crystalline structure of the specimen.

Contrast arise in TEM images due to the electron-specimen interactions, and is defined as the difference in intensity between two adjacent areas [65]. When the electron wave passes through the specimen a change both of amplitude and phase may occur, which give rise to amplitude and phase contrast respectively. Usually a combination of amplitude and phase contrast contributes to the image, but often one type is dominating. Amplitude contrast can be divided into mass-thickness contrast and diffraction contrast, and arise because of thickness and density differences or local diffraction differences in the specimen. Mass-thickness contrast is the most important contrast for imaging of non-crystalline materials, such as biological materials. This contrast arises from Rutherford scattering of electrons and is therefore strongly dependent of the atomic number, Z, the density, ρ, and the thickness, t, of the specimen. Areas of larger mass or larger thickness will have more pronounced scattering and multiple scattering events can occur, reducing the number of electrons transmitted through the specimen in the forward direction. If electrons scattered at large angles (>50 mrad) are used to form the image, the contrast depends almost only on Z.

Diffraction contrast is related to the local variation of diffraction in the specimen. An amorphous region will scatter less than a crystalline region of the same material and will therefore appear brighter. In addition, a crystal (particle) oriented closer to a highly diffracting zone will scatter more than a crystal (particle) oriented further from a highly diffracting zone and hence appear darker.

Phase contrast is the main contrast behind high resolution TEM (HRTEM) images and appears any time more than one beam (the direct beam and one or more diffracted beams) contributes to the image and interference occur. Due to interactions with the sample the phase
of the electron wave can be changed relative to the direct beam and phase contrast arises. The phase contrast mechanism is very sensitive to small changes in orientation, thickness or scattering factor of the specimen and variations in the objective lens, such as focus and astigmatism. Because of this sensitivity phase contrast can be difficult to interpret but is on the other hand sensitive enough to image the atomic structure of the specimen.

HRTEM images contain a lot of information which must be correctly interpreted in order to understand what is actually displayed in the image. Therefore a thorough understanding of the image formation is crucial. As mentioned earlier a point in the specimen, described by \( f(r) \), is transformed into a disk in the image, described by \( g(r) \). Therefore each point in the final image has contributions from many points in the specimen. The point spread function, \( h(r) \), describes this smearing of a point into a disk, and the three terms are related by

\[
g(r) = f(r) \otimes h(r)
\]  

(4.2)

The point spread function describes how certain frequencies (equivalent to lattice distances) are filtered through the lens system [66]. Since frequency in a HRTEM image is related to \( 1/x \), with \( x \) being a distance, high spatial frequencies corresponds to small distances in the specimen. High resolution therefore requires high spatial frequencies. Since \( h(r) \) describes how information in real space is transferred from the specimen to the image, its Fourier transform, \( H(u) \), describes how information (contrast) in the reciprocal (\( u \)) space is transferred to the image. When using the Fourier transform of the terms in equation 4.2 they are related by

\[
G(u) = H(u)F(u)
\]  

(4.3)

\( H(u) \) is known as the contrast transfer function and can be expressed as a product of the aperture function, \( A(u) \), the envelope function, \( E(u) \), and the aberration function, \( B(u) \)

\[
H(u) = A(u)E(u)B(u)
\]  

(4.4)

The aperture function describes which spatial frequencies are cut off by means of the radius of the aperture, the envelope function is a property of the lens related to chromatic aberration and the spatial coherence of the electron beam and the aberration function describes the effects of spherical aberration.

If the specimen is thin enough so that the amplitude contrast can be neglected, meaning that it acts as a weak-phase object, \( B(u) \) can be set to \( 2\sin \chi(u) \), where the term \( \chi(u) \) can be expressed as

\[
\chi(u) = \pi \Delta u^2 + \frac{1}{2} \pi C_s \lambda^4 u^4
\]  

(4.5)
where $\Delta f$ is the defocus value chosen to form the image and $C_s$ is the spherical aberration constant. Furthermore a new quantity, $T(u)$, can be defined which is often also referred to as the contrast transfer function (CTF)

$$T(u) = A(u)E(u)2\sin \chi(u)$$  \hspace{1cm} (4.6)

It is however highly important to note that $T(u)$ can be considered the CTF only if the amplitude contrast is neglected [65]! The CTF is an oscillatory function (Figure 4.2) with maximum contrast transfer for multiple odd values of $\pm \pi/2$ and no contrast transfer for multiple values of $\pm \pi$. For negative values of CTF, positive phase contrast will occur, meaning that electrons appear dark on a bright background. The opposite is true for positive values of CTF. In theory the CTF can transfer information for any spatial frequency meaning that the oscillations can continue forever. In reality, however, the oscillations are damped by the envelope function.

Of the terms affecting the CTF, the minimum wavelength (determined by the electron acceleration voltage) and $C_s$ are fixed values of the microscope itself but the defocus value, $\Delta f$, can be adjusted. At the optimum value of $\Delta f$, known as Scherzer defocus, all beams will have a nearly constant phase out to the first “cross-over” of the zero axis. This cross-over is known as the resolution limit of the microscope. The value at this point is the point resolution of the microscope and up to this spatial frequency, the contrast in the images can be intuitively interpreted. At higher spatial frequencies the information in the images cannot be intuitively interpreted. Image processing such as image reconstruction is therefore required.

![Figure 4.2 The contrast transfer function (CTF) at Scherzer defocus for a 300 kV FEG TEM with $C_s = 0.6$ nm. The undamped function is shown by the dotted line, the symmetrical envelope function by the dashed lines and the resulting damped CTF by the full line.](image-url)
4.3 Chemical Analysis

Chemical analysis of a specimen can be enabled in TEM due to the transfer of energy from some of the beam electrons (the inelastically scattered) to the specimen. If a high energy beam electron interacts with an inner-shell (core) electron, that electron can be ejected and leave a hole in the inner shell. For the electron to be ejected a specific amount of energy, known as the ionization energy, must be transferred from the beam electron to the inner-shell electron. Due to the ejection of the inner-shell electron the atom is said to be in an excited state. The atom will strive to return to its ground state and can do so by filling the empty inner-shell hole with an electron from an outer shell. The energy released by this transition will result in the emission of either an Auger electron or an X-ray. The entire process is displayed in Figure 4.3. Both the Auger electron and the X-ray have a characteristic energy related to the energy difference between the two involved electron shells. This energy is element specific and hence the detection of Auger electrons or characteristic X-rays provides chemical information of the sample.

Detection of characteristic X-rays is more widely used in TEM compared to detection of Auger electrons, since the Auger signal is weaker. To detect characteristic X-rays an X-ray energy dispersive spectrometer (XEDS), typically a Si(Li) detector is used. Inside the detector the incoming X-ray generates a number of electron-hole pairs and they result in a charge pulse, proportional to the X-ray energy, which can be measured. The detector is connected to a computer via a pulse processor and the output from the detector onto the computer is an XEDS spectrum where the energy versus counts is shown. The detection limit of the XEDS used in this work is around 1 at% and the lightest detectable element is Be. Quantitative information of the elements in a specimen can also be obtained by XEDS [65].

**Figure 4.3** Schematic of the mechanism behind characteristic X-ray formation. An incoming high energy electron interacts with an inner shell electron that gets ejected and the atom is said to be in an excited state. By filling the formed hole by an electron from one of the outer shells, the atom returns to its ground state. The energy difference is released either as a characteristic X-ray or as an Auger electron.
Chapter 5

5. Gold Particle Effect on Nanowire Growth

Gold seed particle assisted nanowire growth can be affected by properties of the gold seed particle such as the diameter, as well as other properties induced by the particle generation or deposition method. In the first section of this chapter, 5.1, the effect of gold particle diameter, and hence nanowire diameter, on the crystal structure of nanowires will be presented. In section 5.2 the general properties of the material gold with respect to nanowire growth will be discussed. Finally, in section 5.3, gold particles generated and deposited with different methods are used to seed nanowire growth and variations with respect to growth, induced by the different particle types will be presented.

5.1 Particle Diameter

The crystal quality of nanowires may play an important role in nanowire based electronic and optoelectronic devices. III-V nanowires exhibit the hexagonal wurtzite (WZ) or cubic zinc-blende (ZB) crystal structure, but are often composed of a mixture of the two structures, known as polytypism. Typically crystal defects such as stacking faults or rotational twin planes are found in III-V nanowires, especially in nanowires with a severe mixing of the two crystal structures. Stacking faults and twin planes can act as scattering centers for electrons [67] and, in addition, affect the optical properties [68] of the nanowires; effects detrimental for electronic or optical devices.

The ZB and WZ crystal structure of III-V nanowires consists of differently stacked layers. Each layer is a bilayer, meaning that it consist of pairs of one group III and one group V atom, and each bilayer is represented by a letter. The WZ and ZB structures are extremely similar, with WZ having an ABABAB stacking and ZB an ABCABC stacking in the close-packed direction. A stacking fault is referred to as an interruption of the WZ structure, such as ABABCBAB, with C being the misplaced bilayer creating the stacking fault. A stacking fault could also be seen as a short switching of crystal structure from WZ to ZB. A rotational twin plane on the other hand is found in the ZB structure when the stacking sequence switches from ABCABC to ABCACBACB, with A being the misplaced bilayer referred to as the twin plane.
Chapter 5. Gold Particle Effect on Nanowire Growth

Figure 5.1 Dependence of InAs nanowire crystal structure on diameter from wurtzite (WZ) to zinc-blende (ZB). a – d, TEM images viewed along the <-110> zone axis (zinc-blende notation), showing the influence of nanowire diameter on the InAs nanowire crystal structure, with diameter increasing from a to d. With increased diameter, the crystal structure changes progressively from pure WZ (a), to WZ with single stacking faults (b, see arrows), to a mixed WZ–ZB structure (c) and finally to pure ZB (d).

From attempts to control the crystal structure of III-V nanowires it is known that temperature and V/III ratio can modify the crystal structure to some extent [69, 70]. Addition of dopant species has also been shown to affect crystal structure [71], at the expense of changing the electronic and optical properties of the nanowires by the dopant species themselves. Finally, nanowires grown in other directions than the typically used <111>B direction could be more or less free from twin planes [72]. However, growth of nanowires in other directions is extremely difficult and often results in a very low yield of nanowires.

Another option to alter the nanowire crystal structure is by changing the diameter of the wire by changing the diameter of the seed particle [II]. In Figure 5.1 TEM images of InAs nanowires of different diameters, determined by their ECA seed particle diameter, grown at 460 °C at a V/III ratio of 130, is displayed. For small diameters the nanowires exhibit WZ structure, almost completely free of stacking faults (Figure 5.1 a). By slightly increasing the diameter, the number of stacking faults increases, but the structure is still mainly WZ. At a diameter of 43 nm (figure 5.1 b), the number of stacking faults is roughly 30-35 per micrometer length (measured from 10 nanowires with this diameter). Further increase of
diameter leads to an even further increase of stacking faults, and ZB segments of a few nanometers can be found. At larger diameters the nanowires exhibit a complete mixture of ZB and WZ structure. For a diameter of 84 nm (Figure 5.1 c) the composition is approximately 75 % ZB and 25 % WZ. At even larger diameters (Figure 5.1 d) a switch to pure ZB is observed, defined as less than 1 WZ segment per micrometer length. The pure ZB structure in these large nanowires exhibit periodic twinning, meaning that the nanofacets (the exposed surfaces) are altering (111)A and (111)B surfaces of the same area. Furthermore, by decreasing the nanowire growth temperature the proportion of WZ in the nanowires increases for all diameters. Therefore, a good control of nanowire crystal structure can be obtained by combining the two parameters temperature and seed particle diameter.

One way to predict WZ or ZB crystal structure in III-V nanowires is to consider the ionicity of chemical bonds, with high ionicity favoring WZ structure and low ionicity favoring ZB structure. This holds for materials with extreme ionicity values, such as nitride nanowires with a very high ionicity that exhibit WZ structure [73] and antimonide nanowires with a low ionicity that exhibit ZB structure [74, 75]. However, the standard III-V nanowires (GaP, GaAs, InP and InAs) all have ionicity values in between the extremes and all show polytypism. Therefore other concepts might be more useful when trying to understand the polytypism in these standard III-V nanowires.

Akyiama and colleagues [76] suggest that the energy of the side facets in a small structure dominate the total energy of that structure. Since WZ is assumed to have lower side facet energies than ZB this would explain why small nanowires exhibit WZ structure. However their predicted diameter cross-over from ZB to WZ is much smaller than the cross-over obtained above for InAs nanowires. Johansson et al. [VII] and Dubrovskii et al. [77] instead use classical nucleation theory with the Gibbs-Thomson effect included in the chemical potential to account for the diameter dependence, to explain the cross-over. This approach leads to larger and more realistic cross-over diameters, and seem to be a reasonable explanation for the effects of diameter on nanowire crystal structure.

5.2 The Material Gold

Gold is by far the most widely used material for nanowire seed particles, since it is superior to other materials in most cases of nanowire growth. The major advantage of gold is that regardless of growth parameters it is reasonably easy to achieve a high quality nanowire growth from gold seed particles. High quality growth is defined as growth that provides a high yield of straight crystalline nanowires epitaxially grown in a certain crystal direction [III]. When a <111> oriented substrate is used, which is often the case, the nanowires grow perpendicular to the substrate due to the preferred <111> growth direction of nanowires. To illustrate high versus low quality nanowire growth, nanowires seeded with gold and palladium particles grown under similar conditions are displayed in Figure 5.2 a and b respectively. Even though nanowires form from the palladium particles, the nanowires do not grow straight and are not epitaxial, clearly demonstrating the advantage of gold particles.
Although gold particle-assisted nanowire growth dominates the reports of successful nanowire growth today, no clear understanding of why gold is such a suitable seed particle material exists. The typically used models for particle-assisted nanowire growth, such as the VLS [63] and VSS [64] models, and the recently suggested more general preferential interface nucleation model [78], all explain the involvement of the particle during growth to some extent, but are applicable to particles of any material. To date, the only attempt to theoretically predict which metals that might be appropriate for seeding of nanowires is the model by Nebol’sin and Shchetinin [79]. Their model is developed for growth of Si nanowires, and is based on the wetting angle of liquid metal drops on Si. However, the predictions by the model do not generally agree well with experimental data. Since no applicable theoretical model exists several experimental attempts to find other suitable nanowire seed particle materials than gold have been performed [30-34]. Apart from improving the understanding of the mechanism behind nanowire growth, finding other particle materials than gold is useful from a device perspective since gold is not really compatible with the silicon semiconductor industry of today [80].

One of the most common explanations for why gold is such a suitable nanowire seed particle material is that many of the precursor materials used for nanowire growth are soluble in gold. Liquid alloys of gold-indium and gold-gallium exists at temperatures below the commonly used growth temperatures. However, no stable gold-phosphorous or gold-arsenic phases have been reported, raising the question of how the group V species gets incorporated into the nanowire. A possible explanation could be that the group V precursor travel along the growth interface or along grain boundaries if the particle is in a solid state [2].

As mentioned in section 3.2, the seed particle might not necessarily be in a liquid state for nanowire growth to occur, but it might be an advantage if it is, at least for other materials than gold. Controlled nanowire growths at temperatures below the melting point of an existing liquid gold-based alloy have been reported [64, 70, 81]. In addition, when other materials than gold have been used for seeding, the particles are often in a solid phase. Although growth is
enabled from these solid seed particles the direction of the nanowires are often much less controlled, probably due to the difficulty of a solid seed particle to epitaxially orient with the substrate. GaAs nanowires seeded with iron particles [33] and manganese particles [82], and Si nanowires seeded with copper particles [34] are all demonstrated to grow in several different directions. As an exception, controlled growth in the \( <111> \) direction of Si nanowires seeded with solid aluminum particles has been reported [32].

A further advantage of liquid seed particles might be that they are likely to have a more uniform shape than solid seed particles that are often faceted, hence forming nanowires of a more uniform shape. However, gold is a very soft material, meaning that it most likely forms reasonably uniformly shaped particles also in a solid state, yet another advantage of gold. The final advantage of a liquid seed particle, is the often much higher diffusion of precursor material, such as Ga or In, through a liquid compared to a solid material. For many solid materials the diffusion rate is very slow, resulting in an impractically low nanowire growth rate. Again gold is an exception, since the diffusivities of both In and Ga are very high also through a solid gold particle. Moreover, gold has a high self-diffusivity coefficient that allows for a quick formation of equilibrium shapes, perhaps one more small advantage of gold compared to other materials.

The catalytic property of gold seed particles with respect to precursor decomposition is largely debated. The common method to determine if a catalytic effect exists has been to compare the activation energies of the decomposition with and without the catalyst particles present. Reports of unchanged activation energies [63, 83-85] as well as reports of enhanced activation energies [86, 87] in the presence of gold can be found, indicating that gold can act as a catalyst in some system but that catalytic activity is not a requirement for growth to occur. If a catalytic activity would be crucial in order to achieve nanowire growth other particle materials normally known to have a much higher catalytic activity than gold such as platinum or rhodium, would be a more suitable choice. Instead, the property of gold as a highly un-reactive material, better explain why gold particles are extremely suitable as nanowire seed particles. Unlike many materials that easily form oxide shells when exposed to air, nanowires larger than 5 nm are known not to spontaneously oxidize in air [88]. An oxide shell surrounding the particle most likely prevents the epitaxial orientation of the particle with the substrate resulting in un-controlled growth or no growth at all. In addition, gold particles do not react with the commonly used carrier gasses hydrogen and nitrogen, simplifying a continuous alloy formation between the growth precursors and the gold particle.

Comparing gold to other materials capable of seeding nanowires, the major difference is that gold has been reported to successfully seed growth of all different types of nanowires at a wide range of growth conditions whereas other materials might seed growth of one type of nanowire at a specific set of growth conditions. Of all the advantageous properties of gold discussed in this section, such as its inertness to oxygen, its high diffusivities and its ability to form alloys with the growth precursors, it seems unlikely that one specific property is what makes gold superior to other nanowire seed particle materials. Particles of other materials used as seeds for nanowires may have some of these advantageous properties, but not all of
them for all materials and growth conditions. Therefore it is likely to believe that all the
advantageous properties together, instead of one specific property, are what make gold the
most universal material for nanowire seed particles [III].

5.3 Gold Particles of Different Origin

Highly controlled nanowire growth has been reported from several different types of gold
particles, meaning gold particles generated and deposited by different methods, as mentioned
in chapter 2. However, no reports in literature of a direct comparison of the effects of gold
particle generation and deposition method on nanowire growth have existed up to now.
Therefore it has been unclear whether nanowire growth studies performed in similar systems
can be directly compared, when different types of gold particles have been used to seed the
growth.

From a direct comparison between different gold particle types it is observed that particle type
has little effect on general nanowire growth characteristics such as overall growth rate,
tapering and side faceting [IV]. ECA, SDA, ESC, DDC and EBD particles with a diameter of
30 nm and an approximate particle surface density of 1 particle/µm² and TFA particles with a
broad diameter distribution and a surface density of above 70 particles/µm² all seed straight
epitaxial growth of GaAs nanowires at 430 (Figure 5.3) and 480 ºC at a V/III ratio of 60. Also
for particles with a diameter of 80 nm straight epitaxial growth is achieved at these
temperatures and V/III ratio. However, at a growth temperature of 380 ºC a small fraction of
the 30 nm sized nanowires kinks during growth and growth of free-standing straight
nanowires from 80 nm seeds is not at all possible. This is true for all particle types used and is
not surprising since 380 ºC is a rather low temperature for growth of GaAs nanowires [83]
and since nanowires with diameters as large as 80 nm are known to be more sensitive to
growth conditions than slightly thinner nanowires.

All nanowires, in the case of straight epitaxial growth, have {112}-oriented sidewalls
consisting of alternating {111}A and B microfacets, regardless of seed particle type.
Moreover, for all types of seed particles of both 30 and 80 nm the overall nanowire growth
rate increases with growth temperature as expected [83]. The overall growth rate is defined as
the measured nanowire length divided by the nanowire growth time for the different growth
durations – in other words the average growth rate without accounting for variations with time
or length. No clear difference in nanowire length is observed after growth times of 4 min and
longer between nanowires seeded with the different particle types (except for nanowires
seeded with TFA particles) indicating a similar overall nanowire growth rate for all particle
types. The TFA seeded nanowires are much shorter than the other nanowires at all growth
temperatures, which is attributed to the much higher particle density on these samples
(induced by the limited preparation technique) resulting in a lower local supply of growth
species. Nanowire growth from ECA samples with a similar particle surface density as the
TFA particle samples were used to verify the hypothesis that the higher surface density of
particles, rather than particle type, is responsible for the shorter nanowires. As expected
nanowires seeded from these high density samples decorated with ECA particles also exhibit a reduced growth rate compared to the ECA samples with a density of 1 particle/µm².

Little difference between nanowires seeded with different particle types regarding tapering, i.e. non-seeded lateral growth on the nanowire side walls that often results in conically-shaped nanowires, is observed. Tapering is observed to increase with temperature as expected, since layer growth conditions are approached. However, the exception is again the TFA particles and the high density ECA particles. For these samples no tapering is observed at any growth temperature, again attributed to the higher particle density rather than particle type.

The major difference between particle types with respect to nanowire growth is found in their behavior during annealing. Annealing has typically been performed under group V pressure at a rather high annealing temperature of 650 °C in order to achieve TFA particles with the lowest possible surface coverage. At this annealing temperature, a small fraction of the 80 nm particles splits up into larger and smaller particles. Moreover, movement of particles onto the substrate is apparent for EBD particles in some cases since wire positions is observed to deviate from the defined pattern (Figure 5.4 a). This is most likely true for the other particle types as well, but cannot be identified due to the random distribution of particles following deposition. 30 nm sized particles seems to be unaffected by this annealing temperature.

When growth is performed without the annealing step, by directly heating to the growth temperature, nanowires seeded with colloidal and aerosol-generated particles are slightly shorter than at the same growth conditions with the annealing step prior to growth. However, they still grow straight and perpendicular to the substrate, which is not always the case for
Chapter 5. Gold Particle Effect on Nanowire Growth

Figure 5.4 SEM images (30° tilting angle) displaying annealing effects for 80 nm sized EBD particles grown for 4 min at (a) 480 °C with annealing (b) 480 °C without annealing and (c) 430 °C without annealing.

TFA and EBD seeded nanowires grown without annealing. Regardless of growth temperature, a larger amount of “crawling” and kinked TFA seeded nanowires is observed when excluding the annealing step. Apparently a certain temperature is needed for appropriate particle formation to take place before the growth precursors can be turned on. For the EBD particles, no annealing seems necessary if a growth temperature as high as of 480 °C is used. For 80 nm particles, excluding the annealing step is even observed to improve the growth since no particle movement is observed and the particle pattern remains (Figure 5.4 b). On the other hand, at the lower growth temperatures a majority of the nanowires are short, kinked, not nucleated at all or “crawling” without annealing (Figure 5.4 c). Hence a certain temperature is needed to provide controlled nanowire growth from EBD particles, in order for the particles to form and remaining residues from the particle processing to be evaporated.

Another pronounced difference between nanowires seeded with different particle types is apparent at the very first stage of the growth process. Clear differences in nanowire incubation time is found, meaning the time from when the growth precursors are turned on until the nanowires are observed to grow (Figure 5.5). However, the observed differences are too small to affect the final length of nanowires and hence the overall nanowire growth rate. Typically nanowires seeded with aerosol-generated particles have the shortest incubation time with a slightly longer time for the ECA compared to the SDA seeded nanowires. They are followed by the ESC seeded nanowires that have an almost equally short incubation time as the ECA particles. Nanowires seeded with DDC and EBD particles prove to have longer incubation times, with EBD seeded nanowires normally demonstrating the longest incubation time. Incubation times of TFA seeded nanowires are difficult to quantitatively compare to the other particle types, due to their broad diameter distribution and high particle density, but are almost the same as for nanowires seeded with EBD particles.

An important particle characteristic that seems to be related to the incubation differences may be the carbon content in and/or surrounding the particles, which may interfere with the gold-substrate-precursor interaction, hence increasing the incubation time. Carbon-containing chemicals are involved in the preparation processes of both colloidal particles and EBD particles, but not in the aerosol particle process. Moreover, larger amounts of chemical
residues are observed to surround the DDC particles compared to the ESD particles. This, in addition to the PLL layer used for deposition of DDC particles indicates that DDC particles are probably surrounded by more carbon, which hence explains the longer incubation time for DDC compared to ESC particles. Finally, ECA particles might be exposed to higher amounts of carbon than SDA particles since part of the ECA particle generation is performed in a graphite tube. This further strengthens the hypothesis that the carbon content in and/or surrounding the particles may play an important role during incubation since SDA particle seeded nanowires have the shortest incubation times of all particle types.

From investigations of nanowire crystal structure it is clear that no pronounced difference between nanowires seeded with different particle types is apparent. The only deviation occurs for the TFA seeded nanowires. At a growth temperature of 430 °C nanowires seeded from the other particle types exhibit cubic ZB structure with a number of randomly distributed twin planes. Nanowires seeded with TFA particles also exhibit cubic ZB structure but contain a significantly lower density of twin planes. Also this observation is attributed to the much higher surface density of particles compared to the other samples resulting in a very different local supersaturation which is known to affect crystal structure [89]. This was confirmed since nanowires seeded from the high density ECA particle sample, with a similar particle surface coverage as the TFA particle samples, also exhibits a reduction of twin planes to a level
roughly the same as for the TFA particle samples (Figure 5.6).

It can be concluded from the above discussion that very small differences in general nanowire growth characteristics appear between nanowires seeded with the various particle types. The overall growth rate, microfaceting, tapering behavior and crystal structure are extremely similar. Although differences with respect to incubation time and sensitivity to annealing is apparent, these can be made less important by using an appropriate annealing temperature and a sufficiently long growth times for the incubation not to affect overall growth rate. It is however important to be aware of the number density and size of particles, since both seem to have a larger effect than particle type itself, on characteristics such as overall growth rate, tapering and crystal structure. These results strongly indicate that direct comparisons of nanowire growth studies done in similar systems can be performed, even when different types of gold particles have been used as seeds for the wires.

Figure 5.6 TEM images of nanowire crystal structure for nanowires grown at 430°C seeded with (a) ECA particles with density 1/µm² (b) TFA particles with density 70/µm² and (c) ECA particles with density 70/µm².
Chapter 6

6. Conclusions and Outlook

Nanowire growth induced by gold seed particles is by far the most common method reported for generation of epitaxial semiconductor nanowires. The major advantage of gold particles compared to particles of other materials is that gold particles successfully seed the growth of nanowires of all types of materials at a wide range of growth conditions. Although several nanowire growth models have been reported no clear understanding of why gold is such a suitable seed particle material exists today. Commonly this is explained by one specific property of gold, including its ability to form liquid alloys with the growth precursors, its high diffusivities or its inertness to oxygen. It is more likely to assume that it is not one specific property, since some particular properties can be found in other materials as well, but all advantageous properties added together that makes gold superior to other materials for seeding of nanowire growth.

Gold seed particle assisted nanowire growth can, in addition, be affected by properties of the gold particle itself. At specific growth conditions the diameter of the gold particle, and hence the diameter of the nanowire, can be used to tune the nanowire crystal structure. Moreover the use of different generation and deposition methods for fabrication of gold seed particles can affect nanowire growth. General growth characteristics such as overall growth rate, crystal structure and tapering is highly similar regardless of gold particle fabrication method, but differences are seen in incubation time and sensitivity to annealing. However, it is important to note that the various particle generation and deposition methods themselves suffer from different limitations which sometimes make it hard to precisely control important particle parameters such as density and diameter which in turn can affect nanowire growth rate, tapering and crystal structure.

For the future, investigations of optical and electronic properties of nanowires seeded with gold particles fabricated by different methods could be extremely interesting. In addition, in situ TEM investigations of the particle nucleation event might be useful in order to explain the differences seen in incubation behavior between the different particles and moreover add to the understanding of the mechanism behind nanowire growth. Finally, to gain more knowledge about the particle involvement in nanowire growth, the search for other particle materials than gold with the ability to successfully seed nanowire growth is crucial.
References


References


References


[34] J. Arbiol, B. Kalache, P. Roca i Cabarrocas, J. R. Morante and A. Fontcuberta i Morral, Nanotechn., 2007, 18, 305606


References


References


