Alternative Seed Particles for III-V Nanowire Arrays

Towards seed particle engineering for tunable crystal structure and growth direction

Master’s Thesis
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Abstract

In my thesis I explore the engineering of alternative seed-metals for GaAs nanowire growth by electron beam lithography in both molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) systems. This amounted to an investigation into over 60 individual annealing experiments and over 180 nanowire growth samples where I am an active part of an ongoing collaboration between the Center for Quantum Devices and NanoLund. The key findings of my thesis are that by tuning metal-seed composition stable particle arrays are possible and that by using Ag and AgAu alloyed nanoparticles as seeds, state of the art GaAs nanowires are obtained.

Semiconductor III-V nanowires (NWs) are promising components in emerging technologies by scaling the tunability of traditional semiconductors down to the nanoscale. One of the primary techniques to synthesize nanowires is by a bottom-up growth approach using a metal nanoparticle to catalyze growth. Currently, there is effectively a universal preference for Au as the metal of choice due to its consistent success. However, there are circumstances when Au-seeding has yet to succeed, such as certain heterostructures. Au-seeding is also known to cause difficulties in the integration with Si-based technologies. Recently, it has also been shown that the metal-seed material will influence the resulting NWs. Therefore, it is rather conservative to assume that all the current problems with nanowire growth can be solved without investigating alternative seeding materials.

To explore alternative seeds, extensive comparative studies were conducted, using Au as a control, to gain better insight into the role that seeding particles have during growth. We conducted systematic annealing experiments to demonstrate that alternative metals could form the necessary nanoparticles needed for growth. Our studies subsequently benefited our understanding of the resulting GaAs growths in both MBE and MOCVD. Using electron beam lithography, Au, Ag, and AgAu nanoparticle arrays were fabricated with varying diameter and pitches. These arrays were positioned on both GaAs (111)B and (100) substrate orientations and subjected to incremental annealing temperatures in both a MBE and MOCVD. This revealed inherent differences between Au and Ag even during the annealing stage of nanowire growth. Most notable is the tendency for Ag nanoparticles to split into smaller constituent parts at lower annealing temperatures, while at elevated temperatures they behave as predicted by Ostwald ripening. Specifically for the MBE system on GaAs (100) substrates, the Ag particle dynamics seem to be controlled by alloy formation, whereas for Au we propose that the running droplet phenomena plays a critical role. Our experiments show that the AgAu nanoparticle arrays exhibit behaviour simultaneously generally found only in separate Au and Ag arrays. This work finds that the diameter dependence for annealing behaviour is consistent with the liquid drop model. In my thesis, I propose plausible explanations for the pitch dependencies.

A systematic study of MBE GaAs nanowire growth from Ag NPs formed by thin film annealing permits high quality nanowire growth with minimal defects. Control over NW crystal structure is obtained by switching between (111)B and (100) substrate orientations permitting vertically aligned wurtzite and zinc blende stacking sequences, respectively. Our results sug-
gest that (111)B oriented NWs are promising candidates for photo emission devices, due to their single and narrow emission peak centered around 1.52 eV shown by photoluminescence measurements. By separately scaling one flux at a time, the experiments reveal that the nanowires are Ga limited. Investigating film thickness unexpectedly show that NW density and diameters do not behave as predicted by Ostwald ripening.

An analogous study with a MOCVD growth system compares the systems and enhance the research into the nature of seeding material. GaAs nanowires are grown using Ag, Au, and Ag-Au seeding particles formed by thin film annealing. An important finding is that pure Au and Ag seeded GaAs NWs grown in the <111>B direction, using the same growth conditions, have a random polytypic crystal structure, whereas the Ag-Au alloy seeded growth are observed to be pristine wurtzite structure with only rare occurrences of stacking faults. To supplement these results, nanowires were grown from arrays where the majority of vertical nanowires prefer to nucleate from smaller 25 nm nanoparticles. By using arrays, the Ag-Au alloy ratios are controlled, thereby allowing the investigation of the transition from pure Ag to pure Au. Furthermore, by growing on GaAs (100) substrates with thin film and nanoparticle arrays, a near 100% yield of vertically oriented NWs is obtained. At present, I believe this is the highest reported yield of GaAs (100) NWs.
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Electron Beam Lithography</td>
<td>36</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Silver Nanoparticles</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>Pregrowth Conditions</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>Nanoparticle Annealing</td>
<td>39</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Methods and Design</td>
<td>40</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Annealing of Au Nanoparticle Arrays on GaAs</td>
<td>40</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Annealing of Ag Nanoparticle Arrays on GaAs</td>
<td>51</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Annealing of AgAu Nanoparticles Arrays on GaAs</td>
<td>58</td>
</tr>
<tr>
<td>4.1.5</td>
<td>Annealing Experiment Conclusion</td>
<td>61</td>
</tr>
<tr>
<td>4.2</td>
<td>Further Research</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>GaAs Nanowires Grown by Molecular Beam Epitaxy</td>
<td>63</td>
</tr>
<tr>
<td>5.1</td>
<td>Thin Film Growth</td>
<td>63</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Introduction</td>
<td>63</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Methods</td>
<td>64</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Results and Discussion</td>
<td>64</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Conclusion</td>
<td>74</td>
</tr>
<tr>
<td>5.2</td>
<td>GaAs Nanowire Arrays Grown by Molecular Beam Epitaxy</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>GaAs Nanowires Grown by Metal-Organic Chemical Vapor Deposition</td>
<td>77</td>
</tr>
<tr>
<td>6.1</td>
<td>Thin Film Growth</td>
<td>77</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Methods</td>
<td>77</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Introduction</td>
<td>77</td>
</tr>
<tr>
<td>6.1.3</td>
<td>GaAs (111)B Substrates</td>
<td>78</td>
</tr>
<tr>
<td>6.2</td>
<td>GaAs Nanowire Arrays from Alternative Seeds</td>
<td>83</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Results</td>
<td>83</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Discussion</td>
<td>86</td>
</tr>
<tr>
<td>6.3</td>
<td>Vertical Growth on GaAs (100)</td>
<td>90</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusion</td>
<td>92</td>
</tr>
<tr>
<td>A</td>
<td>EBL Recipe</td>
<td>100</td>
</tr>
<tr>
<td>A.0.1</td>
<td>Resist Spinning</td>
<td>100</td>
</tr>
<tr>
<td>A.0.2</td>
<td>Exposure</td>
<td>100</td>
</tr>
<tr>
<td>A.0.3</td>
<td>Development</td>
<td>100</td>
</tr>
<tr>
<td>A.0.4</td>
<td>Metal Deposition</td>
<td>101</td>
</tr>
<tr>
<td>A.0.5</td>
<td>Lift-Off</td>
<td>101</td>
</tr>
<tr>
<td>A.0.6</td>
<td>Before Loading into the MBE</td>
<td>101</td>
</tr>
<tr>
<td>B</td>
<td>Organic Residue Removal and Oxide Removal</td>
<td>102</td>
</tr>
<tr>
<td>C</td>
<td>MBE Thin Film Growth</td>
<td>104</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>D EDS Analysis</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>D.1 Data Acquisition</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>D.1.1 Data Analysis</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>E Additional Annealing Experiments</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>F Experiment List</td>
<td>111</td>
<td></td>
</tr>
</tbody>
</table>
List of Abbreviations

NW …Nanowire
NP …Nanoparticle
MBE …Molecular Beam Epitaxy
MOCVD …Metal-Organic Chemical Vapor Deposition
RHEED …Reflection High-Energy Electron Diffraction
SEM …Scanning Electron Microscope
TEM …Transmission Electron Microscope
EBL …Electron Beam Lithography
EDS …Energy-dispersive X-ray Spectroscopy
UHV …Ultra High Vacuum
ZB …Cubic Zinc Blende
WZ …Hexagonal Wurtzite
TF …Thin Film
TMG …Trimethyl-Gallium
sccm …Standard Cubic Centimeters per Minute
Acknowledgements

I had the pleasure of joining QDev in September 2014 when I started a project for Jessica. I would never have guessed the project would lead me to where I am today. I have had many unforgettable moments and experiences that I will forever keep with me.

First, I’d like to extend a big thank you to my main supervisor Jessica Bolinsson for making this experience possible. Your continued support through this entire thesis is greatly appreciated. It has been a great pleasure to be able to participate in this exciting project and learn so much along the way.

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I owe a thanks to the great technical staff at QDev for making all of our lives a lot easier. A big shout out to Shiv for always being there at any time of the day or night and making sure our tools are always in tip-top shape. Further, I would like to thank Jesper Nygård and and Charles Marcus for making the lab run as smoothly as it does. I have come to realize that we are highly privileged to have such amazing tools, yet such few users.

A special thanks to my parents, family and friends back in Canada for their understanding in the need for me to live so far away.

Lastly, I would like to thank the rest of the amazing people at QDev and the nanowire growth team for making everyday better. This is especially true for all my go-to HF buddies for always keeping their watchful eyes over me. Thanks to the inhabitants of D204: Joachim, Thomas, Aske, August, and Erik along with Anders, and Filip for the valuable discussions and always reminding me what is important in life.
0.1 Introduction

The advancements in technology bring an increased demand to reduce semiconductor device sizes and their facilitating materials. This demand for nanoscale devices introduces many challenges for modern manufacturing processes. Complementary metal oxide semiconductor (CMOS) technology is anticipated to reach size limitations resulting from this continual drive to miniaturize. This is due to problems such as those associated with heat/power dissipation, current leakage, and oxide thickness. To overcome these challenges, while still meeting the high degree of functionality required by devices, new material systems must be developed. One promising candidate for such material systems are III-V semiconductor nanowires (NWs), i.e., one-dimensional nanoscale crystals.

The suitability of NWs for this wide range of architectures stems from their high degree of possible customization. However, at present, NW growth is intrinsically dynamic, largely due to the thermodynamic and kinetic nature of the growth process. The mechanisms to describe NW growth remain incomplete. This is hampered by attempts to generate an atomistic description for NW growth. At the core of NW growth a seeding particle is needed to break crystal symmetry of the surface and allow for unidirectional growth. This particle needs to be supersaturated with growth species, to permit nucleation, and to drive out a solid crystalline NW at the interface between the substrate and the particle. Fig. 1(f-h) are examples of GaAs NWs.

Developments in NW growth has enabled the potential for future advanced functional NW devices. This is due to the control of band gaps and crystal phases, both requirements for high carrier mobility and photoluminescence efficiency. More specifically GaAs NWs show promise in applications such as solar cells. Recently, NWs received attention as prime candidates as solid state hosts for Majorana bound states. This is related to their strong intrinsic spin orbit coupling, large g factor and one dimensionality in hybrid superconductor-semiconductor NW devices.

0.1.1 Motivation for alternative seed materials

Progress in III-V NW growth optimization has led to precise control of NW crystal quality and morphology, which supports the advanced properties required in NWs. However, significant challenges remain for controlled growth. A major problem hampering III-V NWs is that their preferred growth direction is in the <111>B direction. This direction is prone to faults in the stacking sequence of the bilayers structures perpendicular to the growth direction. In addition, III-V NWs in contrast to their bulk form, permit stable polytypes, which allows for a variety of crystal structure to in a single NW. It is generally preferable to achieve pure crystal structures allowing for high quality properties. Indeed, it has been shown that the polytypic formation can be controlled, enabling advantageous use of the defects resulting from the difference band structures of the different stacking segments.

Defect reduction can be attained by forcing NWs to grow in directions where defects are less energetically favourable to form. For instance, if NWs are instead grown in the <100>
Figure 1 – (a-c) Cross sectional SEM images with superimposed schematics illustrating the vapor-liquid-solid growth of NWs. (a) Ag is annealed to form liquid droplets. (b) Vapor growth species (Ga and As) are emitted into the growth chamber and alloy with the Ag droplet. (c) The droplet becomes supersaturated with growth species and NW growth occurs at interface between droplet and substrate at the triple-phase-boundary (TPB). An illustrative example of a Ag seeded GaAs NW can be seen in (h). (d,e) SEM images titled 85° showing the preparation Ag droplets shown in (a) by thin film annealing (d) and annealing of EBL defined arrays in (e). These are the two techniques used in this thesis. SEM images titled by 45° of the corresponding GaAs NWs grown from thin film annealing in (f) and arrays in (g).

direction, in place of the <111>B, then stacking faults would only be possible by inducing dislocations. Bjork et al. (2002),\(^\text{16}\) show that InAs NWs grown in the <111>B direction are highly
populated with stacking faults resulting from switching between cubic zinc blende (ZB) and hexagonal wurtzite (WZ), while growth in the \( <001 \) direction produced heterostructured NWs with perfect ZB structure. InP NWs have also been shown to be defect free when grown in the \([001]\) direction while the \( <111>B\) direction mirror plane stacking faults from WZ segments.\(^{17}\) Alternatively, switching the growth polarity from B to A termination has been shown to reduce the amount of defects.\(^4,18\)

The growth process for NWs usually occurs with a vapor-liquid-solid (VLS) mechanism first proposed by Wager and Ellis in 1964.\(^{19}\) In Fig. 1(a-c) the VLS mechanism is depicted. Metal catalyst NP are heated to form liquid droplets shown in (a). The sources are supplied in the vapor phase and upon reaching the metallic catalyst particle, are incorporated and form an alloy shown in (b). This process continues until the droplet reaches supersaturation, followed by one dimensional crystallization growth of the NW semiconductor at the particle-semiconductor interface schematically shown in (c) and from a SEM image of a GaAs NW in (h).

Recently, there has been a focus towards gaining a better understanding of the various mechanisms governing NW growth.\(^{20–22}\) Direct in-situ observation of NW growth in an environmental transmission electron microscopy is a promising method, where the formation of each bilayer can be monitored.\(^{18,21–25}\) This technique reveals that NW growth is intimately connected to the physical state of the seed particle, the particle-NW interface at the triple-phase boundary (shown in Fig. 1(c)), and more specifically the contact angle between particle and NW\(^i\). Jacobsson et al. (2016)\(^{22}\) further propose that the droplet geometry plays a key part in not only the NW morphology, but the particle size can be tuned by varying V/III ratio, thus switching between ZB and WZ segments.

From these studies it is evident that the seeding particle plays a critical role in NW growth. The choice of seeding material will also have a large influence. In a recent review by Dick et al. (2014)\(^{26}\) the use of alternative seeds for III-V NW growth is detailed. By switching from one metal to another the alloying composition and eutectic points, and therefore the supersaturation of the droplet will all change. For example, comparing the Ag-Ga\(^{27}\) and the Au-Ga\(^{28}\) binary phase diagrams we see a large shift in the liquidus curves and eutectic points. Shifting these critical points by switching seeding material will alter the concentration of sources in the catalyst during growth. This, in turn affects the crystal quality, the morphology, crystal phase, and growth direction of the NWs.\(^{18,29–31}\) The metal choice will adjust the corresponding surface energies and the response to changing V/III ratio.\(^{18,31}\) This has been shown to play a major role in crystal phase.\(^{22}\) Furthermore, the chemical potential of the droplet and its wetting angle is tuned by the potential of the vapor species\(^{32}\) (V/III ratio) and by the influence of the Gibbs-Thomson effect on droplet size.\(^{30}\)

In this thesis we explore the growth of GaAs NWs and GaAs NW arrays. The NWs were primarily synthesized by MBE, however to further our understanding we investigated growth by MOCVD. The growth of GaAs NWs is not a new concept as it is a large field that has many

\(^{1}\)The triple-phase boundary is the boundary between three phase in the VLS mechanism shown in blue in Fig. 1(c). The angle that the droplet makes with the substrate is called the contact angle which will be discussed in detail in the following chapter.
publications based on understanding and controlling the growth process and their applications. GaAs NW arrays have also been realized in the past, though many complications are still prevalent today.33,34

For the majority of research in this field the seeding material is limited to Au. Indeed, it has been shown that crystal structure purity and control is possible with Au by tuning growth parameters.5,35,36 This control has been shown to be pertinent for GaAs NWs optical properties with the crystal structure (ZB, WZ or ZB/WZ mixture) having a major effect by shifting the emission energy when measured by photoluminescence spectroscopy.37,38 However, Au seeding has also been shown to adversely effect the optical properties of GaAs NWs,39 which further enforces the use of alternative seed materials. GaAs NWs have been shown to have many applications. For example if the NWs are doped during growth to form a p-n junction then they are effective for photovoltaic (solar cell) applications.7,40

To form the seeding particles necessary to catalyze the NW growth two different techniques are employed. In Fig. 1(d) and (e) the seeding particles are formed by annealing of thin films and by electron beam lithography (EBL) techniques respectively. The corresponding GaAs NW growth for each technique can be seen below in (f) and (g). Thin film annealing is a cost and time effective method for generating a wide range of particle sizes as seen in (d). Alternatively, using EBL allows for precise control over particle size and interparticle distances (pitch) as shown in (e). This additional control is transferred to the growth process, where the NWs tend to grow more uniformly as shown by comparing (g) and (f). The downside of using EBL results from the high cost of purchasing and maintaining an EBL system and additional processing equipment.

0.1.2 My Contribution

In this thesis I was fortunate to work on a variety of different projects with each involving the work of several individuals. This thesis is a reflection on my contribution to these projects.

For the annealing experiments presented in Chapter 4, my role was to design and fabricate more or less all the substrates and contribute to the design of the recipes used for the experiments. I was the primary investigator of the annealing experiments which led to the majority of the results presented. I carried out the primary development of the explanations and theoretical understanding of the results as detailed in the discussions.

I contributed to the Ag seeded GaAs NW growth by MBE presented in Chapter 5 by being the primary SEM investigator for this project and carried out substrate preparation. I contributed to the discussion of results and the development of our paper shown in Chapter 5. In particular, my efforts were focused on the characterization and analysis of growth temperature, growth time, Ga-flux, and thin film series. In addition, I measured the majority of the data presented.

In Chapter 6, the results of NW growth by MOCVD are discussed. I prepared the majority
of the thin film and EBL array substrates for growth. Further, I was the primary SEM investigator of both the thin film and array NW growth. I actively contributed to the discussion of the thin film growth results and I investigated the different dependencies of the NW arrays.

The MBE growths and annealing experiments were performed by J. Bolinsson† and C. Lindberg† at QDev. The MOCVD annealing and growth experiments were carried out at NanoLund in collaboration with E. Mårtensson‡, K. Dick‡, S. Gorji‡. E. Mårtensson‡ was the primary MOCVD operator. I contributed to discussion and development of growth and annealing recipes we used for the MBE and MOCVD experiments. The TEM data presented in this thesis are provided by C. Lindberg†, K. Dick‡ and M. de La Mata Fernandez‡.

I made the figures unless otherwise specified.

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Chapter 1

Thermodynamics of Nanoparticles

This section introduces the general thermodynamic concepts that influence the annealing of nanoparticles (NPs) in addition to the scaling rules associated with downsizing particles to the nanometer scale. The standard thermodynamic formalism\textsuperscript{41,42} will be introduced to provide the framework for the annealing experiments and growth systems that follow later in the thesis. There are many factors effecting the particles that need to be accounted for, such as, semiconductor interfaces, crystal orientation, particle curvature and size.

1.1 Classical Thermodynamics

1.1.1 Free Energy

In traditional physical systems, the constituent parts try to minimize their energies to attain rest in equilibrium. In thermodynamics one approach to visualize the minimization of the processes involved is to examine the Gibbs free energy ($G$) of the system. Analyzing the system free energy is a powerful tool to infer how a system will evolve under various constraints. This will become apparent discussing NP geometries in relation to its environment. Following standard formalism\textsuperscript{41} $G$ can be written as

$$G = U + PV - T\zeta,$$

where $U$, $P$, $V$, $T$, $\zeta$ are the internal energy, pressure, volume, absolute temperature and entropy respectively. This is the maximum amount of work a system can do at constant pressure and temperature. An interpretation of the second law of thermodynamics unveils that by maximizing the entropy, the system will go towards a minimum free energy or equilibrium. This fact can be realized by maximizing the entropy in Eq. 1.1, which minimizes the Gibbs free energy. Alternatively, for systems under constant volume and temperature, then the Helmholtz free energy $F$ is the preferable expression

$$F = U - T\zeta.$$
1.1.2 Chemical Potential

The introduction of Gibbs free energy allows the discussion of chemical potentials of systems or phases. Historically the chemical potential was added to thermodynamics to describe systems where matter exchanges occur. The chemical potential $\mu$ of a certain unary phase $\phi$ is measured by the change in the Gibbs free energy when a particle is either added or removed in this phase at constant temperature $T$ and pressure $P$,

$$\mu_\phi = \left( \frac{\partial G_\phi}{\partial N_\phi} \right)_{T,P},$$

where $\partial N_\phi$ is the infinitesimal change in particle number. If the system is held at constant pressure and temperature then the Gibbs free energy of the system is simply,

$$dG = \sum_i^{n} \mu_i dN_i.$$  \hspace{1cm} (1.4)

In the simplest case for two phases $\alpha, \beta$, the system is said to be in equilibrium when $\mu_\alpha(T, P) = \mu_\beta(T, P)$, i.e., when no particles are being exchanged between the phases. From this it is apparent that the chemical potential will be a key parameter when a system is undergoing a phase transition. For example it is possible to rewrite Eq. 1.1 in terms of $\mu$ as,

$$d\mu = -\zeta dT + V dP.$$ \hspace{1cm} (1.5)

From this it is possible to see how the chemical potential of a component is linked to its phase as depicted by Fig. 1.1 with pressure and temperature coordinates. In this diagram, the lines separate three phases, and along a line, the two phases it separates are in equilibrium and at the triple point $O$ all three phases are in equilibrium.

1.1.3 Supersaturation

Supersaturation is a phenomenon that occurs as the system moves away from thermodynamic equilibrium. For example, assume that a vapor is initially in equilibrium with a crystal at pressure $P_O$. As the pressure of the vapor is increased, the gas becomes unstable with respect to the crystal phase. The crystal phase, in turn, becomes stable which at constant temperature causes the chemical potential of the vapor to be larger than the crystal. Supersaturation and can be written as,

$$\Delta \mu = \mu_v(P) - \mu_c(P)$$ \hspace{1cm} (1.6)
and reflects a thermodynamic driving force governing phase transitions from vapor (v) to crystal (c). This is a key concept behind NW growth. Without loss of generality the supersaturation can be rewritten as \[^{42}\]

\[
\Delta \mu = \int_{P_b}^{P} \frac{\mu_v(P)}{P} \, dP - \int_{P_b}^{P} \frac{\mu_c(P)}{P} \, dP = \int_{P_b}^{P} (V_v - V_c) \, dP. \tag{1.7}
\]

Treating the vapor ideally \((V = \frac{k_BT}{P})\) then we can find the supersaturation to be

\[
\Delta \mu = k_B T \ln \frac{P_v}{P_c}, \tag{1.8}
\]

where \(k_B\) is the Boltzmann constant, and the value \(\frac{P_v}{P_c}\) is generally referred to as the supersaturation ratio. Furthermore, if we consider that only small pressure deviations \(P\) from equilibrium \(P_O\) then there will be practically no change for the crystal phase volume and therefore,

\[
\Delta \mu = \int_{P_b}^{P} V_v \, dP = k_B T \ln \frac{P_v}{P_O}. \tag{1.9}
\]
1.2 Size Dependant Thermodynamics

In general, the thermodynamics of materials can be described by their bulk values. However, in the case of NPs it is observed that the nano-scaling of a system alters the thermodynamic parameters, such as vapor pressure and chemical potential. In chapter 4 the NPs that are fabricated range from 25 to 150 nm in diameter. Therefore, it is a critical to consider size dependant effects to understand the thermodynamics of NP systems.

1.2.1 Laplace Equation

The first parameter discussed is pressure and how it is effected by down scaling. Consider a system with a liquid (or solid) NP residing on a solid surface and surrounded by a vapor (v) inside a system with a constant volume. Assume that a NP has an internal pressure $P_{np}$ while the vapor has pressure $P_{v}$ then if we apply a constant temperature the corresponding Helmholz free energy is

$$F = -P_{np}V_{np} - P_{v}V_{v} + \gamma S,$$  \hfill (1.10)

where $S$ is the surface area, and $\gamma$ is the surface energy. Now it is possible to use the fact that the total volume remain constant, $V_{np} + V_{v} = const$ and therefore $dV_{np} = -dV_{v}$. The equilibrium state of the system is the same as minimizing the Helmholz free energy ($dF = 0$) and therefore,

$$dF = (-P_{np} + P_{v})dV_{np} + \gamma dS = 0$$ \hfill (1.11)

and

$$P_{np} - P_{v} = \gamma \frac{dS}{dV_{np}}.$$ \hfill (1.12)

This equation 1.12 is formally known as the Laplace pressure. It shows that the pressure in the NP will always be larger than in the vapor. This pressure difference is caused by the surface tension at the interface between the particle and vapor. Now already it is apparent that there is a strong dependence on the size of the NP from the $\frac{dS}{dV_{np}}$ term. This term scales linearly with inverse radius of the NP. For example, if we assume a spherical NP, then $S = 4\pi r^{2}$ and $V = \frac{4}{3}\pi r^{3}$ and therefore,

$$\frac{dS(r)}{dV(r)} = \frac{dS}{dr} = \frac{2}{r}.$$ \hfill (1.13)

1.2.2 Gibbs-Thomson Effect

The Gibbs - Thomson effect is another important size dependent thermodynamic relation for chemical potential. Consider the same system as presented above, but with constant pressure
CHAPTER 1. THERMODYNAMICS OF NANOPARTICLES

and temperature instead constant volume and temperature. In this scenario, it is preferable to use the Gibbs free energy in terms of chemical potential as in Eq. 1.4,

$$dG = \mu_{np} dN_{np} + \mu_v dN_v + \gamma dS.$$  

(1.14)

Using arguments similar to those for the Laplace pressure ($dG = 0$), but instead having constant particle number $N_i$, a relation between the chemical potentials is revealed as

$$\mu_{np} - \mu_v = \gamma \frac{dS}{dN_{np}}.$$  

(1.15)

This is the famous Gibbs-Thomson relation. To extend the same example to a spherical NP, we can apply the following expression,

$$\mu_{np} - \mu_v = 2\gamma \frac{V_{np}}{r},$$  

(1.16)

where the difference $\mu_{np} - \mu_v$ is similar to the supersaturation introduced in Eq. 1.8. Using supersaturation it is possible to rewrite the Laplace equation as,

$$\gamma \frac{dS}{dN_{np}} = k_B T \ln \frac{P_v}{P_O}$$  

(1.17)

and

$$P_v = P_O e^{\left(\frac{\gamma}{k_B T} \frac{dS}{dN_{np}}\right)_{sphere}} \approx P_O e^{\left(\frac{\gamma}{k_B T} \frac{2V_{np}}{r}\right)},$$  

(1.18)

where $P_O$ denotes the pressure at equilibrium. This illustrates that the chemical potentials of the vapor and particle phase in equilibrium are shifted away from this equilibrium by the decreasing particle size. This is illustrated in Fig. 1.2(a).

1.2.3 Liquid Drop Model

Melting Point Suppression

Over the past decade there has been a plethora of research into understanding how different physical properties of a NP will react to nanoscaling. At the nanometer scale the surface area of system becomes comparable to the volume and therefore the physics of the system should change. Baffat et al. (1976) investigated the size dependence of the melting temperature of gold. A more common approach developed by Nanda et al. (2002,2012) was to investigate the downsizing of the NP system through a simplistic ‘liquid drop model’. Through this model, it has been shown and experimentally verified, that the diameter of a particle correlates with melting point suppression.

Due to the nanoscopic nature of seed particles, the ratio of surface area to volume is non-negligible, inferring that one must consider the cohesive properties of the system. Cohesive energy ($E_c$) can be considered to be the energy that keep a particle together (cohered). This can
1.2. SIZE DEPENDANT THERMODYNAMICS

**Figure 1.2** – (a) Sketch of the effect of NP radius on its vapor pressure in Eq. 1.18 and supersaturation as detailed by the Gibbs-Thomson relation for a sphere in Eq. 1.16 with arbitrary units. (b) Sketch of the size dependent melting point for a NP as described by Eq. 1.21 known as melting point suppression with arbitrary units.

be thought of as if there is some internal pressure inside of a sphere that is being held together by the shell. This is physically is the difference between volume energy or bulk energy \( E_{B,c} \) and surface energy \( E_s \). The cohesive energy per atom of a spherical NP with \( N \) atoms can then be formulated as follows,

\[
E_{np,c} = E_{B,c} - E_s N^{-\frac{1}{3}}. \tag{1.19}
\]

For a spherical NP, \( E_s = 4\pi r_a^2 \gamma \) and \( N = \frac{d^3}{(2r_a)^3} \) where \( r_a \) is the atomic radius \( \gamma \) is the coefficient of surface energy and \( d \) is the diameter of the NP which gives a cohesive energy for a NP to be

\[
E_{np,c} = E_{B,c} - \frac{6V_a \gamma_{np}}{d}. \tag{1.20}
\]

The cohesive energy can also be expressed in terms of the measurable melting temperature \( T_m \),

\[
\frac{T_{np,m}}{T_{B,m}} = 1 - \frac{6V_a \gamma_{np}}{d}. \tag{1.21}
\]

The above expression is usually discussed in terms of melting point suppression. By decreasing the NP size, the melting temperature also decreases compared to bulk values. This effect is shown in **Fig. 1.2(b)**.

From this simple cohesive energy model, we note that with decreasing NP diameter, or increasing substrate temperature, the cohesive energy decreases. Once the cohesive energy becomes less than zero, the NP becomes unstable and is able to split apart.\(^{47}\) It may be argued that the subsequent split particles have a decreased diameter, thus the splitting will continue recursively.
CHAPTER 1. THERMODYNAMICS OF NANOPARTICLES

It is also possible to incorporate the effect that the underlying substrate will have on the NPs. When the NPs are annealed in a growth system the substrate is thermally heated by the sample holders. This energy is transferred to the NPs through the substrate. If the substrate has a coefficient of surface energy $\gamma_{\text{sub}}$ with a lattice matching constant $\alpha_{\text{epitaxy}}$ (valued between 0 for total mismatch and 1 for epitaxial match) then

$$E_{\text{np,c}} = E_{b,c} - \frac{6V_a \gamma_{\text{np}}}{d} - \frac{6V_a \gamma_{\text{sub}}}{d} \alpha_{\text{epitaxy}}.$$  \hspace{1cm} (1.22)

If the NP has a perfect epitaxial match with the substrate then,

$$\frac{T_m}{T_{b,c}} \approx 1 - \frac{6V_a}{d} \left( 1 - \frac{\gamma_{\text{sub}}}{\gamma_{\text{np}}} \right).$$  \hspace{1cm} (1.23)

From this equation we can see that with an increase in substrate temperature, energy is transferred to the NP, and therefore lowers the cohesive energy of the NPs.

Size Dependent Effects on Phase Diagrams: Solidus-Liquidus Lines

The size of NPs also has an effect on the phase diagram for its system. If we consider a binary system of two components A and B described by $A_x B_{1-x}$. For this system we are interested in the solidus - liquidus curves to detail the different phases regions of this system. Consider two equations for the chemical potentials for these curves. The chemical potentials for these curves are as follows:\textsuperscript{48}

$$k_B T \ln(\frac{x_{\text{solidus}}}{x_{\text{liquidus}}}) = C_A \left( 1 - \frac{T}{T_{m,A}} \right).$$  \hspace{1cm} (1.24)

and

$$k_B T \ln(\frac{1 - x_{\text{solidus}}}{1 - x_{\text{liquidus}}}) = C_B \left( 1 - \frac{T}{T_{m,B}} \right).$$  \hspace{1cm} (1.25)

The values of $x_{\text{solidus}}, x_{\text{liquidus}}$ determine the curves at a given temperature $T$ where $C_A, C_B$ are the latent heat of melting for the respective components A and B. If component A in the system is a NP, then the above expression for melting point suppression in Eq. 1.21 can be substituted into obtained expression this binary system particles. Thus, with decreasing diameter we get a suppression of the melting temperature for a NP, and subsequently a reduction of the solidus-liquidus curves.

Recent work by Ghasemi et al. (2015)\textsuperscript{49} show through the calculation of phase diagrams (CALPHAD) method that the InSb phase diagram has a size and shape dependence. Their calculation show that with a decreasing NP size (labels 1 to 4) that there is a decreasing temperature shift in the solidus-liquidus curves.
1.3 Surface Energy

1.3.1 Equilibrium Shape

Crystals reduce their surface free energies \( (G_i) \) through relaxation to equilibrium shapes. This is determined by minimizing the amount of work needed to form the crystal at a given volume. \( G_i \)\(^{50} \) i.e.,

\[
G_i = \gamma_i S_i ,
\]

where \( \gamma_i \) is the surface energy per unit area and \( S_i \) is the surface area of the interface. In chapter 4 on pregrowth condition experiments, NPs are annealed at different temperatures. Upon cooling the NPs will form an equilibrium shape which will be related to the crystallographic orientation of the substrates. These interfaces also depend on the crystallographic orientations.

Consider a crystal NP residing on another crystal face. At this interface \((i)\), a new phase-dividing surface will be created with a corresponding surface free energy associated with this boundary. These interfaces will also depend on the crystallographic orientations, since they have different energies associated with their faces.

In general, \( \gamma \) is the work needed to create a new unit of surface area. When a new surface
is created, chemical bonds are either broken or created and therefore surface energy to first approximation is the sum of the energies of broken bonds per unit area.\textsuperscript{42} The Kossel crystal model can be used to realize how substrate orientations will impose different surface energies, which takes into account the bonding between neighbouring atoms. Following the formalism in Markov (2003)\textsuperscript{42} for the Kossel crystal example, the first, second, and third next nearest neighbour interactions are accounted for in the surface energy $\gamma$ with a unit cell surface area $\Sigma_{hkl}$ in contact a crystal face with miller indices $hkl$,

$$\gamma_{hkl} = \frac{\Psi_{hkl}}{2\Sigma_{hkl}},$$

(1.27)

where $\Psi_{hkl}$ is the energy needed to detach a surface from this $hkl$ face. For example,

$$\gamma_{(100)} = \frac{\psi_1 + 4\psi_2 + 4\psi_3}{2b^2},$$

(1.28)

or

$$\gamma_{(110)} = \frac{2\psi_1 + 6\psi_2 + 4\psi_3}{2\sqrt{2}b^2},$$

(1.29)

where $\psi_i$ is the work required to break the bonds of the next nearest neighbour $i$, and $b$ is the atomic distance. Based on this it is easy to show within this approximation that

$$\gamma_{(100)} < \gamma_{(110)} < \gamma_{(111)}.$$

(1.30)

### 1.3.2 Wulff

Using the approximation that the NP will have a constant volume, then the NP will strive to minimize its surface energy by forming into an equilibrium shape governed by,

$$\Delta G_i = \sum_j \gamma_i S_i,$$

(1.31)

where we have taken Eq. 1.26 and summed over the corresponding surfaces $j$. Following this Wulff (1901)\textsuperscript{51} proposed that it is possible to derive the equilibrium shape by relating the surface energy of a crystal face and the distance to that face. He stated that the length of the vector ($\vec{a}$) which is perpendicular to a given face $i$ will be propositional to its surface energy

$$\frac{\gamma_i}{|\vec{a}_i|} = \text{const},$$

(1.32)
1.3. SURFACE ENERGY

Figure 1.4 – (a) Illustration of how the a crystal’s Wulff construction is formed by the balancing of surface energies where $\gamma_{<11>} > \gamma_{<10>}$. (b) is the resulting Wulff shape or equilibrium shape of the crystal for these surface energies. (c) Surface energy depiction of the wetting of a NP controlled by the three surface energies $\gamma_i$, $\gamma_M$, $\gamma_s$. (a,b) were inspired by [52] and (c) was inspired by [53].

which is known as the Gibbs-Wulff theorem. Therefore, a surface or facet with a smaller surface energy will have a larger area and vice versa. An example of this construction can be seen for a 2D system in Fig. 1.4(a) where $\gamma_{<11>} > \gamma_{<10>}$ and the corresponding equilibrium shape in (b).

1.3.3 Wetting

The previous section detailed how a solid crystal contained in either a vapor or a liquid would relax into its equilibrium shape by minimizing its own surface energies. However, in our case the NPs will be in contact with a crystal substrate which will have its own surface energies that need to be considered. Therefore, it is interesting to discuss how a crystal will react at the substrate interface. This problem was addressed by Winterbottom (1967),\textsuperscript{54} where he investigated the wetting of a particle on a substrate as depicted in Fig 1.4(c). Here the wetting of the NP is
regulated by an interface energy $\gamma_i$,

$$\gamma_i = \gamma_M + \gamma_s,$$  \hspace{1cm} (1.33)

which is determined by the surface energy of the metal NP equilibrium $\gamma_M$, and the substrate $\gamma_s$. If the surface energy of the NP ($\gamma_M$) is large compared to the substrate surface energy $\gamma_s$ then no wetting will occur. As $\gamma_s$ increases and becomes comparable to $\gamma_M$ ($\frac{\gamma_s}{\gamma_M} = 1$) the NP will begin to wet the surface. This causes the NP to increase the interface surface area. Further increasing $\gamma_s$ ($\frac{\gamma_s}{\gamma_M} > 1$) causes an increase in wetting until no Wulff shape remains and the metal completely wets the surface forming a thin film.

### 1.3.4 Gibbs Free Energy of a Liquid Nanoparticle

![Figure 1.5 – Triple phase boundary for a liquid droplet. $\gamma_i$ represents the surface energy of at the interface $i$ where $i$ is either solid-vapor (SV), solid-liquid (SL), or liquid-vapor (LV). $\theta$ represents the wetting angle of the droplet which is controlled by Eq. 1.41. $R$ is the radius of the droplet and $S_o$ is the constant solid substrate area not covered by the droplet.]

The surface energy of a liquid NP in a vapor environment situated on a solid substrate depicted by Fig. 1.5. The curvature of this droplet is shaped by a triple-phase system. The Gibbs free energy for this system can be realized by Eq. 1.26 where $i$ denotes solid-vapor (SV), solid-liquid (SL), or liquid-vapor (LV). Then the total surface energy ($G$) is the sum of the three phase boundaries\(^{43}\)

$$G = \gamma_{LV}\frac{2\pi R^2}{1 + \cos \theta} + \gamma_{SV} \pi R^2 + \gamma_{SL}(S_o - \pi R^2),$$  \hspace{1cm} (1.34)

with $R$, $S_o$, and $\theta$ denoting the NP radius, constant solid substrate surface area, and contact angle respectively. The index $j$ on the solid liquid surface energy denotes the crystal orientation and due to Eq. 1.27 it is apparent that the different directions will have varying energies. Since the volume of the NP is usually held constant, a NP can only minimize its free energy by means of which surfaces it exposes.
1.3. SURFACE ENERGY

1.3.5 Contact Angle

A NP’s volume can be assumed to remain constant. Thus, if it is to contort itself in order to minimize its’ free energies then \( R \) and \( \theta \) must be allowed to evolve. The differential free energy is,

\[
dG = dR \left[ \gamma_{LV} \frac{4\pi R}{1 + \cos \theta} + \gamma_{SL;i}2\pi R - \gamma_{SV}2\pi R \right] + d\theta \left[ \gamma_{LV} \frac{2\pi R^2 \sin \theta}{(1 + \cos \theta)^2} \right]. \tag{1.35}
\]

To find how \( R \) and \( \theta \) vary the constant volume of the particle is used, where the volume of the particle depicted in \textbf{Fig. 1.5} is

\[
V = \frac{\pi R^3}{3} f(\theta), \tag{1.36}
\]

with \( f(\theta) = \frac{(1 - \cos \theta)(2 + \cos \theta)}{(1 + \cos \theta)\sin \theta} \). Taking the differential volume to be zero, a relation between \( R \) and \( \theta \) is found to be

\[
dV = \pi R^2 f(\theta) dR + \frac{\pi R^3}{3} \frac{df(\theta)}{d\theta} d\theta = 0 \tag{1.37}
\]

and

\[
R d\theta = -(2 + \cos \theta) \sin \theta dR. \tag{1.38}
\]

Then by substituting \( d\theta \) into Eq. 1.35 we can find the following expression

\[
dG = 2\pi R dR \left[ \gamma_{SL;i} - \gamma_{SV} \right] + \gamma_{LV} 2\pi R dR \left[ \frac{2}{1 + \cos \theta} - \frac{\sin^2 \theta(2 + \cos \theta)}{(1 + \cos \theta)^2} \right] \tag{1.39}
\]

and

\[
dG = 2\pi R dR \left[ \gamma_{SL;j} - \gamma_{SV} + \gamma_{LV} \cos \theta \right]. \tag{1.40}
\]

If we look for a solution for the minimum energy (\( dG = 0 \)) then Young’s equation is recovered,

\[
\gamma_{SV} = \gamma_{SL;j} + \gamma_{LV} \cos \theta. \tag{1.41}
\]

Young’s equation can be viewed as the interfacial force balance at the triple phase boundary.
Chapter 2

Epitaxy

NWs can be realized from a variety manners such as from top-down selective etching of bulk material, or synthesized in solutions. However, for the purpose of this thesis we will only focus on the bottom-up epitaxial growth of NWs from a vapor phase on crystalline substrates. Epitaxial growth refers to the assembly of growth species as a crystalline layer over a crystalline substrate. This process requires an interfacial matching of similar lattice parameters of the two crystalline materials. The growth of vapor phase crystals can be separated into two main categories, physical vapor deposition (PVD) and chemical vapor deposition (CVD). Herein we investigate both types of systems by use of a molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) systems, respectively, for PVD and CVD. These two growth systems are more or less dominated by kinetic processes rather than thermodynamics ones because they operate far from equilibrium. In this thesis, we primarily focused on the MBE system. The MOCVD system was used to draw comparisons between the different environments.

2.1 Growth Systems

2.1.1 Molecular Beam Epitaxy

A schematic drawing of a MBE system is illustrated in Fig. 2.1(a). This growth system was developed to enable a high-level of control over the growth process and purity that is needed in the manufacturing of high quality semiconductors. In comparison to other growth systems that attach chemical precursors to their species, a MBE only uses pure growth species. This, in conjunction with the ultra high vacuum (UHV) conditions, allow for high purity semiconductors to be synthesized. The growth process can be tuned to allow for atomic layer by layer growth, as well as atomically abrupt heterostructures interfaces. This offers precise control over the semiconductor band-gaps as seen in MBE grown two-dimensional electron gases with mobilities exceeding $35 \times 10^6 \text{ cm}^2 \text{Vs}^{-1}$.

The MBE used in our experiments is a Varian GEN II MBE system equipped with a solid
As source installed with a cracker to separate $\text{As}_4$ into $\text{As}_2$. The system has Ga, In, Sb, Be and Si sources. Additionally, it has an in-situ Au cell for catalyzing NW growth. The source fluxes are controlled by heating the cells to a given temperature, expect for As which is controlled by a needle valve. This is a UHV system with two 8” cryo-pumps and one 400 $L_s$ ion pump allowing for a base pressure of around $10^{-11}$ torr. In-situ monitoring is possible by reflection high-energy electron diffraction (RHEED). To read more about all the MBE components and their intricacies see [59].

**Figure 2.1** – Schematics depicting the two growth systems used in this thesis. (a) A MBE UHV growth chamber with the key components. Samples are loaded onto the heated rotating substrate holder and subjected to effusion cells controlled by a shutter. (b) A MOCVD growth chamber with black lines representing flow lines inside the system. The sources are chosen based on the sources used in this thesis. Samples are loaded in a N$_2$ environment onto a susceptor. During growth the chamber is flooded with H$_2$ which carriers the AsH$_3$ and the TMG to the heated susceptor. (a) is adapted from [60].

### 2.1.2 Metal Organic Chemical Vapor Deposition

A typical MOCVD system is depicted in **Fig. 2.1(b)** where a carrier gas is used to transport the source material to the growth chamber. Here H$_2$ is used to transport the metal-organic precursors such as trimethyl-gallium (TMG) and the Group V hydrides, for instance, AsH$_3$.

There are two key distinctions between MOCVD and MBE systems. First, the growth chamber in the MOCVD is an environment due to the H$_2$ supply. Therefore, there is a large pressure difference between the two systems. Secondly, the source material is carried by precursors that need to be cracked to become available. The precursors can also effect the purity of the resulting growths since they may be able to also absorb into the semiconductor. MOCVDs have a much
lower operating cost than MBEs and therefore are employed much more readily for industrial applications. A good textbook on all things in reference to MOCVD see \[61\].

The MOCVD used in this thesis is an AIXTRON Close Coupled Showerhead\textsuperscript{®} (CSS) 3x2 inch MOCVD reactor. The advantage of this new design of MOCVD stems from the precise control possible over the precursor flows with improved flow controllers. Also, the precursors are injected directly over the sample resulting in a more uniform and homogeneous mixture of source material. The sample holder (susceptor) is horizontal with an area of 3x2 inches. This allows for a large amount of samples to be loaded at once. Due to the reactor being in an environment, the growth time is greatly diminished (\(\sim 1\text{h 30 min for loading, growth, and unloading}\)).

### 2.2 Nanowire Growth

The growth of NWs can be boiled down to four basic ingredients. First, the substrate. This acts as the foundation from which NWs will grow and is a pure crystal cleaved in a specific direction usually with the similar lattice spacing as the growth species to allow for epitaxial growth. Secondly, the growth species, which are the building blocks the NW will be constructed out of. The choice of these species is critical for desired properties the NWs possess such as which band-gaps will be present in the resulting NW. The sources are tuned by controlling the amount of flux of a certain element is introduced into the growth chamber. The third ingredient is growth temperature. This parameter that controls how much energy is supplied to the system, and therefore controls the corresponding chemical potentials making it the largest proponent for change. The final ingredient is the seed material which are crucial since they break the isotropic crystal surface symmetry and allow anisotropic unidirectional growth to occur. With these four basic ingredients and some fine tuning, NW growth is possible. All of these parameters are dependent on each other and therefore changing one will have an impact on the others.

#### 2.2.1 VLS

The most common mechanism used to describe the growth of NWs is the the vapor-liquid-solid mechanism first proposed by Wagner and Ellis (1964).\textsuperscript{19} Since this first report, the theory has seen a large development of this mechanism.\textsuperscript{62–70} In Fig. 2.2 the VLS mechanism is systemically presented in relation to a mock phase diagram in resemblance of the Au-Ga binary phase diagram.\textsuperscript{28,71} In this mechanism, vapor growth species are incident to a substrate containing solid seeding particles (1) that when heated transition to liquid droplets (2). The supplied vapor is able to then dissolve into the droplet and form an alloy (3), shifting the position on the phase diagram. This process continues until the the particle becomes supersaturated as described by Eq. 1.8 in chapter 1.1

\[
\Delta \mu = k_B T \ln \frac{P_v}{P_c},
\]  

(2.1)
2.2. NANOWIRE GROWTH

and crosses the liquidus line (4). The growth species are then expelled from the particle at the triple-phase boundary between the particle and the substrate causing a nucleation event and precipitating NW growth (5). The supersaturation process for NW growth can be equated by

\[ \mu_{\text{species}} \geq \mu_{\text{particle}} \geq \mu_{\text{nanowire}}. \]  \hspace{1cm} (2.2)

If this condition is met then vapor growth species are able to accumulate in the particle and be further transported to the NW since the NW has a lower chemical potential.

Many alternative mechanisms have been introduced and backed-up with experimental evidence since the proposal of the VLS mechanism. For example, NWs have been shown to be grown with solid NPs with vapor-solid-solid mechanism. For further expansions on the VLS mechanism see Wacaser et al. (2009)\textsuperscript{2} and for alternative mechanisms such as vapor-solid-solid and self seeded growth see [72, 73]. For a good review of the III-V NW growth process and how the different growth parameters can be used to control NW growth see Joyce et al. (2001).\textsuperscript{38}

**Figure 2.2** – Binary phase diagram representing the stages in NW growth in the VLS mechanism. Stage (1) is where solid seed particles reside the substrate, and then are heated (2) causing a transition to the liquid phase. The supplied vapor is then incorporated into the droplet forming an alloy (3), until supersaturation (4), allowing for solid crystalline NW growth to occur (5). This figure is adapted from [71].
2.2.2 III-V Nanowire Crystal Structure

One of the defining characteristics of a crystal is its underlying structure. This structure details how the atoms in the crystal lattice are arranged with respect to one another, which dictates the properties the material will possess such as the electronic band-structure. This makes each crystal material unique and have its own set of applications. For most semiconductors, the electronic band-structure has a gap at the fermi energy, separating the conduction bands and the valence bands. This allows the tuning of electrical properties of the semiconductor materials which is not possible with metals.

In general, bulk III-V semiconductors have a cubic zinc blende (ZB) crystal structure. The atoms are held together by covalent tetrahedral bonds with small amount of ionic bonds resulting from the different charges of atomic species. High ionic bonding materials such as II-VI have an increase in interelemental attractive Coulomb force which decreases the effective distance between elements giving rise to a stable hexagonal wurtzite (WZ) phase.

The two dominate crystal structures found in <111>B oriented III-V NWs are ZB and WZ, although, higher order polytypes do exist. These two structures are illustrated in Fig. 2.3 viewed from the <110> direction. For ZB, the atoms are arranged in an interconnected face-center cubic lattice unit cell following an ABCABC...periodic stacking sequence. Notice that each bilayer A and B consists of two atoms denoted either Aa or Bb respectively which constitutes the Group III or V atomic layer. Similarly, for WZ, the unit cell is two hexagonal close-packed lattices following an ABAB... periodic stacking sequence. Individual NWs can posses both crystal structures along with the higher order polytypes.
2.2.3 Nanowire Arrays

In this section we will motivate the growth of NWs from patterned arrays. There are many techniques employed to fabricate NP arrays in conjunction with NW growth such as nano-imprint and nano-sphere lithography. In this thesis electron beam lithography (EBL) techniques were used to fabricate NP arrays with diameters ranging from 25 to 150 nm. As detailed in Section 3.2, even though EBL lithography is a costly process, it is an important control tool for NW growth. By defining the seed particle array’s pitch and diameter the resulting NWs should experience the same growth conditions. This allows for more uniformity in NW growth which is important for device fabrication. NW arrays can be used as an investigation tool, where the fundamental NW properties can be probed. This will be discussed in chapter 6.

Fig. 2.4 details the influence that NW arrays have on the resulting NWs. In Fig. 2.4(c) an individual NW is grown from two primary fluxes. The first being the direct flux, which is incident to the NP. Second, the substrate flux, which contributes by diffusing across the substrate, along the NW and into the droplet. In Fig. 2.4(a) the pitch dependence is shown where an individual NW has a circular collection area. The collection area of a NW is defined by the length (radius) the surface adatoms are able to diffuse to the base of the NW. If two NWs are placed closer together then their total substrate flux will is partly shared and therefore the net flux one NW receives decreases.

To overcome the challenge of completing substrate contributions, NWs can be grown from hexagonal arrays as shown in (b). Here each NW will receive the same total flux. This phenomenon is illustrated in (d-f), where the NWs pitch distance is increased. The resulting NWs are all uniform, and as the pitch distance is increased, the NW length increases due to the increase in total flux each individual NW receives. To read more about NW arrays and their dependencies see [76–78].

\[^{1}\text{For a detailed review of the different lithography techniques for NW arrays see [75]}\]
Figure 2.4 – (a) Schematic detailing the collection area and the two relevant diffusion length $\lambda_s$ and $\lambda_w$ for the substrate flux contribution. (c) Schematic of direct flux and substrate flux, which contributing to NW growth. (b) SEM image of a hexagonal array pattern. (d-f) SEM image of InAs NW arrays with varying pitch (increasing left to right). (a) is adapted from [77] and (b-f) are adapted from [76]. All scale bars are 1 $\mu$m.
Chapter 3

Experimental Techniques

3.1 Scanning Electron Microscopy

The objects investigated in this thesis are dimensioned on the nanometer scale. Therefore, the required investigation and characterization techniques are of a sophisticated nature. As our objects are on the same order as the wavelength of visible light, optical microscopes are inappropriate for the job\(^1\).

In this thesis, the primary investigation technique is scanning electron microscopy (SEM). The wavelength of electrons is much smaller than that of visible light. For example, a SEM operating at 10 keV will have wavelength of 0.012 nm which can be found by the de Broglie wave equation. Another technique that is used to characterize our samples is a transmission electron microscope, which generally operates at 200 keV has an electron wavelength of 0.0025 nm.

The electrons needed for imaging in a SEM are produced by heating a filament similar to the process for photon generation in a light bulb. Electrons are then stripped from the filament by application of the user set acceleration voltage usually between 1 to 30 keV. These electrons are focuses by a series of lenses shown in Fig. 3.1(a). A specimen held by the stage is placed incident to the electron beam. A series of coils controls the direction of the electron beam, which scans the electrons over the surface of the specimen. The electron beam interacts with the specimen, by dissipating its energy in a series of ways as detailed by Fig. 3.1(b) and produces three distinct signals depending on the excitation volume. A SEM usually operates by detecting secondary electrons, which are produced a few nm under the specimens surface by inelastic scattering. This signal gives important information on the surface morphology and topography of the specimen. Additionally, a SEM can usually detect backscattered electrons which are generated deeper into the sample. These electrons give useful information about the contrast of elements present in the sample.\(^79\) This signal is based on that the scattering events

\(^{1}\)The wavelength of visible light is \(\sim 390\) to \(700\) nm and the theoretical resolution limit for an optical microscope (defined by the Rayleigh criterion) is \(\sim 200\) nm.
CHAPTER 3. EXPERIMENTAL TECHNIQUES

dependent on the difference in atomic weight between atoms. The third signal generated by the electron beam is characteristic x-rays which gives useful information on the elements in a sample will be discussed below.

The SEMs used in this thesis are a Jeol 7800F, Raith eLine 100, and a JEOL JSM-6320F systems.

3.1.1 Energy-dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is a technique used to characterize the elements in a sample or region. This technique depends on the generation of X-ray from the incident electron beam. The X-rays that are generated will have specific energies which depend on the material in which the electron beam is incident on. When an incident beam excites an electron to a higher orbital, the electron can relax by emitting a X-ray. Since each element has a unique atomic structure, the X-rays energy can be used to determine which elements are present in the sample. An example of a EDS spectrum can be seen in Fig. 3.2 which is the cross sectional analysis of a NP with Fig. 3.2(b) being a zoom in of Fig. 3.2(a). What’s significant is the four characteristic peaks. These peaks denote individual elements which can be found by

![Figure 3.1](image_url) - Schematic detailing the generation of an image by a scanning electron microscope (SEM). (a) The key components in a SEM. The electrons are generated in an electron gun. The electron beam is focused and scanned over a specimen which generates a signal. The three key signals generated can be seen by the excitation volume shown in (b). The signal depends on the type of scattering the electrons have within the sample and where the interaction takes place. This figure is inspired by my previous report [80].

34
3.1. SCANNING ELECTRON MICROSCOPY

Figure 3.2 – EDS scan data collected for a Au NP annealing on a GaAs substrate. Peak evolution shows a change in substrate composition. (b) is a zoom in on the data in (a) showing the Ga, As and Au peaks. The scan location moves closer to the NP and vacuum with increasing number.

referencing a table with the characteristic X-ray energies for each element. In these spectra the peaks specify that there is Ga, As and Au in the sample. Each spectrum is taken at a different location therefore the elemental composition is varying. This causes the evolution in the peak height seen in Fig. 3.2(b). Data acquisition and analysis techniques can be found in appendix D.
3.2 Electron Beam Lithography

Lithography is a process to transfer a pattern or design onto a surface. This technique has been shown to be exceedingly useful in the nanoscience field due to the versatility and control it offers the user. Nanolithography allows for nanoscale designs to be transferred on to desired substrate. Numerous methods of nanolithography techniques exist, for example, photolithography, nanosphere lithography, and electron beam lithography (EBL). With photolithography and nanosphere lithography patterns are transferred onto a target by the use of a mask, and therefore are limited to the mask’s pattern design and the resolution in making a mask. Electron beam lithography’s ability to have precise control over the electron beam’s position resulting in the desired pattern to be exposed makes it more desirable than other forms of lithography. In this thesis we will focus on the use of EBL. For a detailed review of the different nanolithography techniques in relation to NW growth see [75]. The downfall of this technique comes from the high cost in purchasing and maintaining these delicate systems and the long writing times needed to transfer complex patterns compared to other lithography techniques. This severely limits the scale-ability for this technique for industrial applications.

The wavelength of an electron is on the order of nm as discussed in the SEM section above. Due to this, features as small as 20 nm can be written on substrates with great precision. EBL uses the electron beam from a scanning electron microscope to write patterns into either a positive or negative resist. For positive resist, such as PMMA (polymethyl-methacrylate), when the beam interacts with the resist chemical bonds are cracked and this region becomes soluble to a developer. With negative resists, the electrons cause cross-linking of the resist molecules with the consequence of having a reduction in solubility. Challenges arise when fine features (<1 µm) are to be exposed, because extensive dose testing is required to generate the desired pattern.

The pattern transfer method used in this thesis will now be discussed. First a substrate is spin-coated with resist ensuring a uniform thickness. The substrate is loaded into an EBL system and the desired pattern is exposed into the resist. Once the resist (PMMA) has been exposed, the chip is submerged in a developer solution (MIBK). The resist that has been exposed to the electron beam is removed by the developer solution. To ensure that there is direct contact with the substrate It is usually recommended to plasma ash the sample to remove ~ 10 nm of resist. The chip is dipped in HF to remove any oxide residing on the surface to further improve contact with the substrate surface. This also removes unwanted oxides that ashing will produce. This step is discussed further in appendix B. Immediately after the HF dip, the substrate is transferred into the electron beam evaporator, which deposits the desired amount of seed material. The seed material will cover the entire substrate, but once the sample is placed in the lift off solution (NMP/acetone), the resist will be stripped away. This leaves behind the metal where the pattern had been exposed and removes all other metal and resist.

The benefits of using electron beam lithography in comparison to other fabricating methods comes from the ability to have precise control over the desired patterns since the electron beam can be exactly positioned. Many of the other fabrication techniques have limited control of
3.2. ELECTRON BEAM LITHOGRAPHY

the size, shape, or overall design of the end product. In this thesis EBL defined NP arrays are fabricated. This allowed for NP arrays with diameter between 25 to 150 nm and pitches of 0.2 to 5 µm to be fabricated. A detailed fabrication plan can be found in appendix A.

The EBL system used in this thesis is a Elionix ELS-7000 100keV system.

3.2.1 Silver Nanoparticles

The use of alternative seeding materials is still in its infancy. Therefore, there are a lot of unforeseen complications based on using these new metals. This became apparent in due course through our experiments, especially for our Ag NPs. When Ag is exposed to atmospheric conditions, it tends to degrade through sulfidation to form Ag₂S when it reacts with hydrogen sulfide or with carbonyl sulfide. Graedel et al. (1985) also noticed that if the Ag was stored in a high humidity atmosphere then this led to an enhancement of the sulfidation.

In the context of NPs, the rate at which sulfidation occurs is increased since of the large surface area to volume ratio. This phenomenon has now been well documented by Cao et al. (2009), where Ag NPs were fabricated by EBL and were observed over a 12 week period. It is observed that by week 7, the NPs developed hillocks and by week 12 voids were forming within the NPs. EDS analysis shows that the NP contained S while samples stored in a vacuum were absent of S. Furthermore it was determined that the ratio of Ag to S was 3:2, suggesting that Ag₂S is forming. Cao et al. (2009) went on to show that the degeneration of the Ag NPs caused a large blue-shift in the LSPR spectra, and determined that dark field optical microscopy and spectroscopy to be the best method of observing the degradation of the NPs without altering them.

It is therefore deemed crucial to use the Ag NPs as soon as possible after evaporation, or to store them in a nitrogen environment.

Ag nanostructures are not limited to environmental interactions by sulfidation, but can also emit Ag⁺ ions which are toxic, limiting its use in biological systems. This is also a problem when dealing with Cu nanostructures. In stark contrast to these two seed materials, Au does not exhibit any of this instability issues, and is not known to oxidize.

Another curious feature of Ag NPs is observed during this project. For a large duration of this project, many complications hindered the use of Ag NP arrays. After lift-off in 60 to 80 °C NMP the NPs would transform from their planned disk morphology to one that resembles popcorn that are many times the planned size shown in Fig.3.3a. The source of this problem eluded us for a long time. We now believe that this is caused by an oxidation process instead of sulphurization one. When the Ag NPs are subjected to the warm NMP lift-off solution this reaction occurs forming dendrite structures. When these samples are annealed, the NPs melt and form compact spherical particles, but as shown in Figure 3.3b they do not collapse down to their designed size. A similar solid-solid transformation is documented by Lee et al. (2012) who noticed that Ag NPs exposed to reactive ion etching would also take on a popcorn morphology.

A solution to this problem came when we switched the lift-off solution from warm NMP to cold acetone for an overnight liftoff. We believe that the heat added to the Ag NPs in the
heat-bath acted as a catalyst for an oxidation process.

**Figure 3.3** – SEM images showing the formation of Ag dendrites (a) after lift off and (b) after annealing at 550 °C by MOCVD.
Chapter 4

Pregrowth Conditions

This section is in the process of being rewritten into a manuscript

There are many processes to prepare catalyst particles for nanowire (NW) growth. In our studies we use thin film annealing and electron-beam lithographically (EBL) defined nanoparticles (NPs) to form the catalyst particles. The focus of this thesis is the use of alternative seeding materials for NW growth. Presently, there is little documentation on the effects that these NPs will have in relation to the substrates, in the growth systems, and to the annealing temperatures. Therefore, this warrants an investigation into how the alternative metals will react to these factors in order to verify their suitability as seed particles and to better understand the resulting NW growth.

4.1 Nanoparticle Annealing

The evolution of NPs subjected to thermal annealing is complex, resulting from the impact of a variety of factors including, but not limited to, seed material, substrate composition, crystal orientation, annealing temperature, and growth system. In this study, we examine and compare these factors to gain insights into the nature of alternative seed materials. Certain growth parameters affect the evolution of NPs. For example, annealing temperature is the dominant precursor for change and therefore when comparing individual samples the annealing temperature should be held constant. For our annealing studies, we fabricated NPs by EBL. The ingenuity of using EBL defined NP arrays arises from the added level of control over particle size and inter-particle distances compared to regular thin film annealing.

To better understand how catalyst materials react to substrate orientation and elemental composition, the experiments were designed with Silver (Ag), Gold (Au), and Silver-Gold (AgAu)\(^1\). The experiments were setup to test a) the difference between seeding materials b) the stability

\(^1\)In appendix E additional annealing experiments with Cu and on InAs(111)B are presented.
CHAPTER 4. PREGROWTH CONDITIONS

and evolution of the NPs, and c) the diameter and pitch effects.

This work aims to expose the main challenges that effect the annealing of lithographically defined seed particles which are needed for NW growth. Since Au is the most common metal seed used for NW growth, a large research effort has been invested into understand how it reacts to certain influences. Therefore, the Au annealing experiments will be presented first to act as a control and reference to previous work. Owing to the novelty of using Ag, it has not been investigated as thoroughly as Au. Consequently, certain similarities between the results from Au and Ag will need to be drawn, but as will become apparent in the following sections there are distinct differences as well.

4.1.1 Methods and Design

To study the effects that annealing has on catalyst particles, EBL defined arrays were prepared on Epi-ready GaAs (111)B and (100) wafers. The EBL procedure can be found in appendix A. Arrays were fabricated with particle diameters 25, 50, 75, 100, and 150 nm, with pitches 0.5, 0.75, 1, 1.5, 2, and 5 µm and with areas 100 - 200 µm² as shown in Fig. 4.1. The thickness of deposition (h in Fig. 4.1(d)) was kept constant at 15 nm. For the AgAu NPs, 7.5 nm of Au was under 7.5 nm of Ag. Annealing was preformed in both a MBE and MOCVD. For both systems, the annealing temperature was incrementally increased instead of a direct ramp to the annealing temperature, to help have a more stable temperature. For the MBE experiments, the temperature was increased until it reached the annealing temperature as measured by a pyrometer then directly cooled. In the MOCVD experiments, the temperature was set by a temperature standard and annealing was carried out for 7 minutes after the annealing temperature was reached. A constant As overpressure was used in both systems with a As₂ flux of 6E-06 torr and 20 sccm AsH₃ for the MBE and MOCVD, respectively.

To compare between different samples it was necessary to hold certain parameters constant. Therefore, arrays of 100 nm particles with a 0.5 µm pitch are used as a standard to compare between different metals, orientations, and systems. Any additional pitch or diameter dependencies is presented separately.

4.1.2 Annealing of Au Nanoparticle Arrays on GaAs

Results

In Fig. 4.2 the SEM images show the annealing evolution of Au 100 nm arrays in a MBE from plan view and with 85 °tilted insets. First, it is clear that the 100 nm Au NPs are stable on both GaAs orientations, evident due to the patterns and NPs remaining and not migrating for all temperatures studied. The Au NPs do not dewet from the surface to form liquid droplets until approximately 400 °C as discernible by the insets in Fig. 4.2. Between 400 to 600 °C the NPs have a droplet morphology, evident that the particles entered into the liquid phase or that the surface premelting is occurring and forms a droplet to reduce the surface energy. These
4.1. NANOPARTICLE ANNELLING

Figure 4.1 – SEM images detailing the overview of the annealing experiments. (a) Total lithography design showing the 25 arrays with varying pitch and diameter with (b) showing an overview of an individual array of 200 x 200 µm in size. (c) 100 nm Ag NPs after lift-off and before annealing. (d) 45° tilted SEM image of Au NPs showing the NP diameters used for annealing ranging from 25 nm up to 150 nm. The inset in (d) shows a 150 nm NP with $h$ denoting the deposition thickness of 15 nm.

Results are consistent Tchernycheva et al. (2006) who observed by in situ RHEED diffraction the solidification of Au at 340 ± 20 °C and melting at 400 ± 10 °C when annealing of Au thin films in an MBE.

At 500 °C and above, triangular pits form around the NPs along we assume to be <111> directions for the (111)B orientation and circular pits for the (100). Additionally, for the (100) orientation at 600 °C larger pits form on two sides (trenches) of the NPs along the <110> direction. In conjunction with the formation of trenches on (100), the Au NPs show a splitting behaviour. The splitting is observed to be dependent on particle diameter and pitch distance shown in Fig. 4.3. Upon cooling and resolidifying the NPs form into the equilibrium structure (Wulff construction) to minimize its surface energy ii, which gives the particles their faceted

iiThe Wulff construction is dependent on the substrate orientation and therefore the NP equilibrium shape for
CHAPTER 4. PREGROWTH CONDITIONS

Figure 4.2 – SEM images of MBE annealing of 100 nm Au NPs arrays with a 0.5 µm pitch on GaAs (111)B and (100) substrates with annealing temperatures of 250 ºC to 600 ºC. All images have the same scale. Insets show an 85 º side view image of a characteristic NP with 100 nm scale bar.

geometry rather than perfect spheres.

In Fig. 4.3, plan view SEM images detail the pitch and diameter splitting of Au NPs on GaAs (100). From left to right the particle diameters increases from 25 nm to 150 nm and from top to bottom the pitch increases from 0.5 µm to 1 µm. Focusing first on Fig. 4.3 (a-d), as the diameter of the NP increases the splitting behaviour of the NPs is suppressed. This is observed with the 100 nm diameter arrays where the splitting ceases (Fig. 4.3 (c)). If the pitch for the 100 nm particles increases from 0.5 µm to 1 µm as in Fig. 4.3 (c → g), then the NPs split. Therefore, there is a diameter and a pitch dependence for the NP splitting.

In direct comparison to the MBE annealing results, the MOCVD NPs are more stable, with no splitting behaviour observed. In Fig. 4.4, plan view SEM images show the annealing stages of 100 nm Au NPs annealed at 400, 500, 600, and 650 ºC on both GaAs (111)B and (100). Above 400 ºC the NPs formed droplets, and have a characteristic Wulff shape similar to the MBE annealing. However, at 600 ºC, instead of forming voids as in the MBE, the particles begin to form tails, and evolve into planar NWs at 650 ºC. These planar NWs are also dependant on particle diameter and pitch, whereby, the diameter of the NW is similar to the particle diameter, and an increasing pitch increases the length of the NW. The length of the NW is also noticed to be dependant on substrate orientation with (100) having much longer NWs.

(111)B and (100) differ as discussed in section 1.3.2.
4.1. NANOPARTICLE ANNEALING

Figure 4.3 – SEM images of annealing of Au NPs on GaAs (100) in a MBE featuring the diameter and pitch dependence on the splitting behaviour of the Au NPs. The arrays have diameters of (a,e) 25 nm, (b,f) 50 nm, (c,h) 100 nm, (d,h) 150 nm and pitches of (a-d) 0.5 µm and (e-h) 1 µm. (a-d) and (e-h) are the same scales with scale bars of 1 µm.

Discussion

This section examines the various phenomena observed for the Au NPs. First, for the MBE system the pit formation and directional dependence is discussed, and how it could relate to the splitting phenomena seen on GaAs (100). Then for the MOCVD samples, the formation of the planar NWs is analyzed.

The formation of pits can likely be attributed to decomposition of the substrate and, due to the proximity of the pits to the NPs, it is anticipated that the NPs catalyze the decomposition. The catalytic decomposition could be the result of reverse VLS growth evaporating the GaAs or NP-substrate alloy formation with the NP alloying with both or either Ga and As.

Compositional Analysis

Cross-sectional EDS was performed to investigate the potential formation of Au-GaAs alloys after annealing. The EDS analysis routine is in Appendix D. To detect if a particle alloy formed is a non-trivial task, because the goal is to determine if Ga or As is present in the Au NP, while the particle resides on a GaAs substrate. It should also be noted that the compositional analysis has arbitrary units, and is not to be taken as an empirical value of the composition. To summarize the procedure, point spectra were obtained at specific locations starting with the
bulk substrate (1) and moving towards the particle (2), then the NPs (3-5) shown in Fig. 4.5(a). For each spectrum, the characteristic Ga and As peak areas enclosed by their full width at half maximum (FWHM) were obtained. The spectrum taken at location 1 (red diamond) allowed for Cliff — Lorimer $k$ factors to be set for equal stoichiometry for GaAs (1:1 ratio), thus allowing for the other spectra’s Ga and As content to be compared by relating the Ga and As area ratios.

In Fig. 4.5(a), the different point spectra locations are shown on a cross-sectional SEM image. The corresponding calculated As molar fraction is presented in Fig. 4.5(b) for both annealing at 400 and 600 °C. Already at 400 °C, there is a decrease in the As molar fraction as the scan location nears the NP or in other words an increase in Ga content. These data suggest that there is a higher Ga content in or around the droplet, suggesting that an alloy between Au and Ga has formed. This depression in the As molar fraction is even more pronounced at 600 °C, where the intermediary substrate location (2) shows a much larger decrease in As. Based on these two scans, we supposed that an Ga from the substrate is alloying with the Au NP, which would show a decrease in the As molar fraction.

These results are consistent with results found by Ghosh et al. (2009), where they investigated the pit formation caused by thin film annealing of Au on GaAs (100). In their work, they preform a cross-sectional TEM EDS line-scan over the substrate, pit, UV - grown oxide and Au NPS formed by annealing at 500 °C, which is presented in Fig. 4.5(c,d)*. They observe that the pit regions have a As-rich composition, while the oxide and Au NP have a high Ga composition. They attribute the pit regions to having a high As content due to the reaction...
4.1. NANOPARTICLE ANNEALING

Figure 4.5 – (a,c) Cross-sectional SEM images and the corresponding EDS data (b,d). (a) The characteristic locations where EDS point spectra were obtained. The red shapes correlate to the spectrum locations in (b). (b) Calculated Cliff — Lorimer factors for the scan locations in (a). There is a decrease in the As molar fraction as the scan nears the NP. A similar trend is observed in (d) where the As content decreases and the Ga content increases towards the Au particle. (c,d)* are adapted from [91]

of the UV-grown oxide layer with the substrate. Due to these samples having an oxide layer grown on the substrates, the results are not entirely correlated to our results. However, they preformed similar annealing experiments with both fresh native oxides and HF etched samples and attribute the pit formation to be due to the interaction of Au with the GaAs surface. For these cases, they propose that the pit formation is the result of Au NPs reacting with the Ga until reaching thermal equilibrium (at 500 °C Au can have a maximal Ga content of 40% Ga content based on the Au-Ga binary phase diagram).

This theory is supported by Zannier et al. (2014). In their study, Au thin film annealing on deoxidized GaAs (111)B substrates was preformed in a MBE with in-situ X-ray photoelectron spectroscopy (XPS). By employing XPS the interaction between the substrate and the Au film was probed at different temperatures. Below 400 °C there is no interaction between the substrate and Au is observed. However, at 400 °C an interaction between Ga and Au alloy formation is detected and by increasing the annealing temperature, the Ga content in the Au increases. Zannier et al. (2014) suggest that Ga atoms from the substrate interdiffuse into the Au to form an alloy, and the As evaporates.

It is believed that a similar scenario is occurring for the pit formation in our experiments.
in Fig. 4.5(a,b), i.e., the Au droplet is alloying with Ga from the substrate while the As can be deabsorbed and evaporates in a process similar to:

$$2\text{GaAs(solid)} + \text{Au(solid)} \rightarrow \text{AuGa}_2(\text{solid}) + 2\text{As(gas)}$$

resulting in the residual pits around the NPs.

Pit Formation

The EDS results prompted us to inspect the pit formation in the MBE experiments. We believe that there are two possible explanations to their formation. The first theory is that the pits form by the Au alloying Ga surface atoms and the As will deabsorb and reform As$_2$. This process is supported by the results shown in Fig. 4.2 for the (111)B orientation, where the pits form directly around the NP along the <111> directions. For the (100) orientation at 600 °C, two trenches form on either side of the NP illustrated in Fig. 4.3. The trenches appear to originate at the NPs and have the same width as the NP diameter. This suggests that these pits are caused by the Au NP. However, the position of the larger NP does not seem to be altered, while trenches form one or both sides of the NP. It would be expected that if the trench creation was dominated by Au-Ga alloy formation, then the Au particle should migrate along the trench while etching the Ga. This will be discussed more in the next section on Ag NP annealing. Based on the above argument, we propose the phenomena of a running droplet as a second alternative explanation.

Recently, there has been a large effort to understand a phenomenon termed ‘self-propelled droplets’ on III/V semiconductors. In this process, the III/V surface is evaporated by annealing the substrate. Under a congruent temperature ($T_C$) the evaporation of the substrate’s species preserves the 1:1 stoichiometry of the Ga and As. However, at temperatures above $T_C$, the Group V elements will evaporate more rapidly than the Group III elements (noncongruent evaporation), thereby leaving behind an influx of group III. This influx is able to form into a droplet which is able to interact with the substrate by alloying or sublimation. This will change the surface energy around the droplet, making it energetically favourable to "run" away from its’ origin.

The process of non-congruent evaporation (Langmuir evaporation) has been well documented in the past. However, to realize the formation of Ga running droplets it requires the implementation of in-situ MBE technologies. With such tools, Tersoff et al. (2009) were able to study this process in detail on GaAs (001). Tersoff et al. (2009) observed the formation of Ga droplets that preferred to run along the [110] direction. Tersoff et al. (2009) proposed a model to explain the motion of the self-propelled Ga droplets based on local surface energies around the droplet. However, their experiment lacked the positioned metallic particles that we have in our experiments.

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iii The congruent temperature is composition and orientation dependant. For GaAs (100) the congruent temperature is reported to be $\sim 625$ °C, 640 °C and 663 °C and for (111)B to be 630 °C.
4.1. NANOPARTICLE ANNEALING

A recent study relevant to our studies, by Zakharov et al. (2015), investigated the formation of Ga running droplets on GaP and use aerosol Au NPs to alter the surrounding substrate to help control the Ga droplets. Using multiple in-situ observation methods the Au NPs were observed to accelerate oxide and substrate nanostructure desorption. Zakharov et al. (2015) suggest that the Au NPs amplify desorption of As, which would alter the energies (temperatures) for deoxidation and could supplement the formation of Ga droplets. Furthermore, they observed that the Ga droplets tend to avoid high-density Au regions, and are immobile if surrounded by Au.

![Figure 4.6](image)

**Figure 4.6** – Formation of a Ga running droplet. (a-d) Cross-section and (e) top view schematic of the formation of Ga droplet catalyzed by a Au NP. (a) A solid (s) Au NP is deposited on a GaAs (100) substrate and annealed at temperature $T$ to form a liquid (l) Au-Ga alloy NP. (c) The annealing temperature is increased above the local congruent evaporation $T_C$ temperature and As vapor (v) is emitted from the surface leaving behind a Ga droplet (l). (d) The Ga droplet is driven away from the Au NP leaving behind residual trench. (e) Plan view perspective of (d).

Based on these two studies, we propose that the NP splitting observed in Fig. 4.3 is related to the formation of Ga droplets. **Fig. 4.6** schematically illustrates the side-view projection of the process involving the formation of a Ga droplet by a Au NP. This figure details the corresponding surface energies $\gamma$ for the different interfaces, initially (a) with freshly deposited Au NPs on a GaAs (100) substrate with vapour-solid surface energy $\gamma_{vs}$. This was followed the substrate being annealed under $T_C$ ($\sim 500^\circ$C) in the MBE (b) where the Au NP start to alloy with the substrate. The alloying alters the substrate’s surface composition, which we postulate acts as a catalyst for dissociation of Ga and As, thereby lowering the local $T_C$. In Fig. 4.6(c) the annealing temperature is above $T_C$, i.e., attains the Ga liquidis point and Ga begins to collect as a droplet while As evaporates. The freshly exposed surface between the Au and Ga NP has a new surface energy $\gamma'_{vs}$ due to the change in chemical composition and structure.

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$^\text{iv}$The GaAs surface has a chemical potential $\mu_s$, which is equivalent to $\mu_{Ga} + \mu_{As}$ at equilibrium. The $\mu_s$ increase with temperature which promotes As evaporation. The $\mu_{Ga}$ will increase to equilibrate with the As evaporation, until it reaches the liquidus point. During annealing in the MBE As overpressure is used to reduce the
CHAPTER 4. PREGROWTH CONDITIONS

Following the formalism of Tersoff et al. (2009), if $\gamma_{vs} > \gamma'_{vs}$, then the Ga droplet with diameter $D$ will experience a force away from the Au NP shown in Fig. 4.6(e) given by

$$\vec{F} = (\gamma_{vs} - \gamma'_{vs}) D. \quad (4.1)$$

By investigating the nonequilibrium surface energy $\gamma_{vs}$ in relation to the new surface energy and expanding to lowest order in $T - T_C$ Tersoff et al. (2009) found that $\gamma_{vs} = \gamma'_{vs} + \alpha(T - T_C)^2$ and the force on the Ga droplet to be

$$\vec{F} = \alpha(T - T_C)^2 D \quad (4.2)$$

where $\alpha$ is the coefficient related to the properties of the surface. In Fig. 4.6(d) the Ga droplet migrates away from the Au droplet, leaving behind the newly exposed surface energy $\gamma'_{vs}$ (dark Ga-Rich substrate). This exposed surface will try to equilibrate with unaltered substrate $\gamma_{vs}$ by gaining or losing Ga by diffusion or evaporation. It is well documented that liquid Ga on a GaAs substrate will increase the melting rate. This process leaves behind a net loss of both Ga and As that we think is the cause of the trenches.

**Nanoparticle Splitting**

We then propose that the splitting of Au NPs is caused by the formation of these trenches. The trenches form directly next to the Au NP and could expose energetically lower surfaces. Thus, NPs could split by relaxing onto these new surfaces. We explain the diameter and pitch dependence behaviour of the Au NPs observed in Fig. 4.3 to be due to that the Ga droplets avoided regions with Au NPs, consistent with the results Zakharov et al. (2015). The net Au density increases per area with increasing diameter that could explain the cessation of splitting. Alternatively, when the pitch distance is enlarged the net Au density is decreased thus allowing for splitting to occur.

Another possibility is the effect of melting point suppression, as outlined in section 1.2.3. The Au NP can alter the deabsorption temperature for the substrate, and considering melting point suppression if the Au NPs diameter is decreased it could decrease $T_C$. If $T_C$ is decreased then the Ga droplets would form at even lower temperatures and was a consequence would have a longer time to run along the surface (when compared to larger NPs). This would lead to a more pronounced splitting for smaller diameters.

Alternatively, understanding the splitting behaviour can be addressed by looking at the surface energies influencing the evolution of NPs, as developed in section 1.3.4. We investigate the case where one larger NP splits into two smaller NPs shown in Fig. 4.7. The same principles can be used higher order splitting. If we assume that the volume of the particle that undergoes splitting and the contact angle remains constant then a relation between the radii is,

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1. This is a reasonable approximation since the contact angle will only change if the surface energies change as shown by Young’s equation.
4.1. NANOPARTICLE ANNEALING

Figure 4.7 – Schematic of a liquid droplet constrained by a triple-phase boundary splitting into two equally sized NPs.

\[ V_1 + V_2 = V_3 \]

and

\[ R_1^3 + R_2^3 = R_3^3 \]

Then the Gibbs free energy for a system with two split particles can be expressed by,

\[ G_s = \gamma_{LV} \frac{2\pi (R_1^2 + R_2^3)}{1 + \cos \theta} + \gamma_{SL} \pi (R_1^2 + R_2^3) + \gamma_{SV} (S_o - \pi (R_1^2 + R_2^3)). \]

(4.5)

We can assume without loss of generality, that the two particles have the same radii, therefore \( R_1 = \frac{R_3}{\sqrt{2}} \). With this relation, we can compare the Gibbs free energy of splitting with the Gibbs free energy of the original particle

\[ G_s = \sqrt{2} \gamma_{LV} \frac{2\pi R_3^2}{1 + \cos \theta} + \sqrt{2} \gamma_{SL} \pi R_3^2 + \gamma_{SV} (S_o - \sqrt{2}\pi R_3^2). \]

(4.6)

From this it is evident that when a particle splits the LV and SL interfaces increase, while there is a commensurate decrease in the SV interface. This can be realized by that the two particles are covering a larger solid area, which would reduce the net SV interface. Therefore, if particle splitting is to be energetically favourable, both \( \gamma_{LV} \) and \( \gamma_{SL} \) must be smaller than \( \gamma_{SV} \).

\[ \gamma_{SV} > \gamma_{LV} + \gamma_{SL} \]

(4.7)

Particle splitting results in the minimization of the interface between the solid-vapour phase \( (S_o) \). Strictly speaking, the NP splitting increases the surface area covered by NPs, therefore decreasing the SV interface\(^{vi}\).

\(^{vi}\)It should also be noted that Eq. 4.7 violates Young’s equation. This could lead to the NP wetting the solid surface to form a 2D liquid film instead of a 3D liquid droplet.
similar sense for increasing pitch. Therefore to minimize $S_o$, the NP can split to cover more area. Pierret et al. (2010)\textsuperscript{105} observed the effect of Au particles splitting on InP. They explained this phenomenon by surface tension, where for smaller thicknesses a NP has a large surface to volume ratio. Due to surface tension the particles will therefore split to decrease the liquid/air interface.

**Pit Directionality**

We observe an anisotropic behaviour on GaAs (100) whereby both the trenches and the planar NWs only form only along two of the four possible $<110>$ directions. We explain the interaction with As-dimers on the GaAs (100) surface.\textsuperscript{106, 107} Bonapasta et al. (2002)\textsuperscript{106} investigated how Au adatoms bind and migrate on GaAs (100) surface through first principle density function theory. Bonapasta et al. (2002)\textsuperscript{106} report that the binding energies of sites is dependent on the location of the GaAs dimers. Bonapasta et al. (2002)\textsuperscript{106} also show that migration paths parallel to the As dimers are faster (less energy) than those perpendicular to the As dimers, therefore giving rise to this anisotropic behaviour of Au.

**Planar Nanowires**

In Fig. 4.4 for both (111)B and (100) planar NWs form by annealing Au NPs at 650 °C by MOCVD. We theorize that their formation could be due to a reverse VLS growth process. In this process the substrate could be evaporating at equal rates and be reabsorbed by the Au NP. Then just as with traditional VLS growth, if the Au NP became supersaturated then growth could occur. Since the planar NWs are attached to the substrate they must obey the difference in directional surface energies.\textsuperscript{108} This gives rise to the different directions the planar NWs grow shown in Fig. 4.4.

Planar NW growth is developing field within NW growth.\textsuperscript{108–111} In these reports, planar NWs are grown by initiating growth by supplying Ga to the growth chamber. The planar NWs in our results are formed by annealing the substrates with a background overpressure of As. If it is possible to form planar NWs from annealing alone, this could dramatically reduce the cost of planar NW growth since a growth system would be unnecessary.
4.1.3 Annealing of Ag Nanoparticle Arrays on GaAs

We observe many dissimilarities in the annealing of Ag NPs on GaAs in comparison with Au. Ag has a lower melting point\textsuperscript{vii} than Au under similar environment conditions. Making the approximation that only annealing temperature influences the NP evolution, we can assume that the effects will occur earlier for As than for Au.

Results

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.8.png}
\caption{SEM images of MBE annealing of 100 nm Ag NPs arrays with a 0.5 µm pitch on GaAs (111)B and (100) substrates with annealing temperatures of 250 °C to 600 °C. All primary images share the same 0.5 µm scale bar. The insets show an 85 ° side view image of a characteristic NP with 100 nm scale bar.}
\end{figure}

The temperature evolution of Ag NPs on GaAs (111)B and (100) in the MBE is shown in Fig. 4.8. The NPs appear to have entered the liquid phase even at the lowest temperature attained in the MBE during degassing. This is evident not only by the droplet morphology seen in the inset of Fig. 4.8, but also in the clear particle splitting. The splitting on both (111)B and (100) becomes more pronounced with increasing temperature.

At 400 °C the splitting is reserved to shedding of smaller particles from a larger nucleus NP, while at 500 °C the larger nuclei split. The shed NPs tend to be on the order of 5 - 25 nm in diameter. The average number of constituent parts a 100 nm particles splits into is 6.6 particles.

\textsuperscript{vii}The melting point of metals is dependent on pressure of the system, as well as the curvature of the particle as discussed in section 1.2.3.
CHAPTER 4. PREGROWTH CONDITIONS

Strikingly, the splitting of particles is observed to follow a chain reaction trend, with NPs dividing into further constituent parts. Additionally, at 500 °C both the predefined 25 nm NPs or the small NPs that shed off of the larger NPs appear to dig holes into the substrate and also have a noticeable shift in contrast, which could imply a change in material composition. It is assumed that this NP digging leads to a decrease in the final particle size.

![Figure 4.9](image)

*Figure 4.9* – SEM images depicting the diameter and pitch dependence for the migratory behaviour exhibited by Ag NPs on GaAs (100) subjected to 600 °C annealing.

Increasing the temperature to 600 °C shifts the NP behaviour to reincorporate Ag and with less chance of splitting. However, at this stage in the annealing, the smaller NPs have disappeared (≤ 25 nm). This results in the remaining nucleus having a reduced size (diameter) that varies due to the uncontrolled splitting behaviour observed in the 400 - 500 °C annealing. The compelling distinction between the (111)B and (100) orientations arises at 600 °C. Whereas (111)B particles remain roughly at their position location and dig down into the substrate along the three <111> directions, the (100) particles display an anisotropic diffusive behaviour, migrating only along the [110] and [1$ar{1}$0] directions. Because of this lack of unidirectionality, a temperature gradient effect can be ruled out. The migration behaviour shown in *Fig. 4.9* to be dependent on pitch and particle diameter similar to the Au splitting behaviour in *Fig. 4.3*. 
The MBE and MOCVD experiments both show that the Ag NPs first display a splitting behaviour at lower temperatures and then reincorporate at elevated temperatures. The splitting behaviour is not observed to have any diameter or pitch dependencies, unlike the Au NP splitting. The splitting of Ag NPs tend follow a positive feedback trend of recursive splitting of the daughter NP. This behaviour can be observed by virtue of the large spread in the shed NPs diameter, with the majority having dissimilar sizes. By referring to Eq. 1.20 in Chapter 1.2.3
CHAPTER 4. PREGROWTH CONDITIONS

\[ E_{np,c} = E_{B,c} - \frac{6V_a \gamma_{np}}{d}, \]  

we will attempt to explain this behaviour by cohesive energy \( E_{np,c} \) of the NP assuming that we have a liquid NP.

This equation illustrates the role that the NPs diameter (d) plays on cohesive energy. As the NP diameter decreases there is a corresponding decrease in the NPs cohesive energy, essentially due to the increase surface energy term. We presume that at a certain diameter the surface energy term will be larger than the bulk energy allowing for the particle to split to minimize the surface energy. At this point, the resulting daughter NP will have an even smaller diameter and this process will be further intensified.

This process can be described by inverse Ostwald ripening. Ostwald ripening theory was advanced by Lifshitz and Slyozov (1961),\textsuperscript{112} and Wagner (1961),\textsuperscript{113} which explains the mechanism for growth of larger particles at the expense of smaller particles. An alternative mechanism formally known as ‘digestive ripening’\textsuperscript{114–118} has recently been observed where instead the number of small particles grows at the expense of large particles. To the best of our knowledge this mechanism has only been reported for colloidal solutions. Lee et al. (2007)\textsuperscript{114} propose a characteristic Gibbs-Thomson equation to incorporate the charge of the NP along with the classical surface energy term. This alters the chemical potential to classical case, gaining a local maximum that allows for a regime where NPs prefer to decay instead of growing. We expect a similar result by using a modified Gibbs-Thomson relation in Eq. 1.15 similar to the solution for a sphere in Eq. 1.16. Instead, we could use the Gibbs free energy for a liquid droplet presented in Eq. 1.34 to derive the chemical potentials.

It follows that when the annealing temperature is increased to 500 and 600 °C for the MOCVD and MBE, respectively, that the digestive ripening ceases and Ostwald ripening dominates. The resulting NPs after annealing at 600 °C have a decreased size compared to their original state.

**Nanoparticle-Substrate Alloy**

The compositional analyses of Ag NPs, when subjected to annealing in the MBE (Fig. 4.11), is presented in a similar manner to Au (Fig. 4.5). Analogous to the Au results, the Ag analysis shows that there is a decrease in As content from the substrate and towards the NP. The As composition drops further for elevated temperatures. As discussed for Au, we assume that this data suggests that a Ag-Ga alloy is forming.

The annealing of 25 to 150 nm of both Au and Ag NPs (increasing diameter from bottom to top) at 500 C in the MBE is illustrated in Fig. 4.12 that is used to establish the phase-diagram size dependencies. The melting point suppression for a spherical NP, presented in chapter 1.2.3, can be represented by

\[ \frac{T_{np,m}}{T_{B,m}} = 1 - \frac{6V_a \gamma_{np}}{d}. \]
4.1. NANOPARTICLE ANNEALING

Figure 4.11 – Calculated As molar fraction from EDS scan data of Ag particle annealed at 400°C and 600°C.

\[
\text{As Molar Fraction [a.u.]} \\
\text{Spectrum}
\]

Figure 4.12 – SEM images of Ag and Au NPs annealed at 500 °C with diameters ranging from 25 nm to 150 nm from bottom to top. The stage of annealing is size dependant, where the smaller Ag particles are digging into the substrate and the smaller Au particles are migrating and splitting.

The correlation of a NP size to a shift in the corresponding solidus and liquidus lines, are given as

\[
k_B T \ln \left( \frac{x_{\text{solidus}}}{x_{\text{liquidus}}} \right) = C_A \left(1 - \frac{T}{T_{m,A}} \right) \quad (4.10)
\]

\[
k_B T \ln \left( \frac{1 - x_{\text{solidus}}}{1 - x_{\text{liquidus}}} \right) = C_B \left(1 - \frac{T}{T_{m,B}} \right). \quad (4.11)
\]

This Fig. 4.12 makes apparent how the size of a NP effects its’ stage in the annealing process. The 25 nm Ag NPs, along with the small NPs resulting from the splitting behaviour, dig holes into the substrate whereas the larger NPs do not. This behaviour is also observed for the 25 nm Au NPs, i.e., they form trenches and split while the larger NPs remain stable. In both
cases, when the annealing temperature is increased to 600 °C the behaviour of these 25 nm NPs at 500 °C is exhibited by almost all NPs. This is a clear display of the size dependence on the the phase diagram.

This behaviour raises an interesting question about the role of the surface oxide. Since the deoxidation of GaAs’s native oxide occurs at \(\approx 580 \, ^\circ C\), the annealing presented in Fig. 4.12 is below this temperature. In this case either the native oxide does not influence the formation of substrate-metal alloys or the metal NPs catalyze the deoxidation. The catalytic deoxidation has been reported elsewhere to occur for Au NPs on GaP.\(^93\)

**Migration**

![Figure 4.13](image)

**Figure 4.13** – Schematic representation of the pitch dependant migratory behaviour of Ag NPs arrays on GaAs (100). (a) Ag NP are deposited on a GaAs (100) substrate with two different pitches. (b) At 400 °C surface adatoms begin to form and (c) the Ga adatoms become loosely bound and form an alloy with the Ag NPs. (d) At 600 °C the migration behaviour occurs for the smaller pitch as the NPs need to shift to incorporate an equal Ga concentration as the larger pitch.

The migratory behaviour of Ag NPs annealed at 600 C in the MBE is detailed in Fig. 4.9, where the diameter and pitch dependencies are displayed. The migratory behaviour of the Ag NPs is dominant for larger particle and smaller pitches. This is the complete opposite to the splitting behaviour of Au NPs. Furthermore, the Ag NPs appear to be etching the surface as they migrate, which leaves trenches, while the larger Au NPs remain in their positioned locations with trenches forming to their sides.

We propose, using Fig. 4.13, a theory for this behaviour. In Fig. 4.13(a) lithographically defined Ag NP arrays are defined on GaAs (100) with two different pitches. Then in Fig. 4.13(b) the Ag NPs begin to split and GaAs adatoms begin to form, and in Fig. 4.13(c) the Ga atoms become loosely bound to the GaAs substrate.\(^119\) The latter leads to further surface diffusion and alloy formation with the Ag NPs.

\(^{viii}\) We have observed this deoxidation process in the MBE by RHEED.
4.1. NANOPARTICLE ANNEALING

The array with a smaller pitch will therefore be able to absorb a larger amount of the Ga adatoms. We then propose that in Fig. 4.13(d) when the temperature is increased to 600 °C the Ag NPs will tend to have a higher solubility of Ga. Additionally, since the array with a smaller pitch will have absorbed all the Ga adatoms, the NPs will need to migrate and dig into the substrate to gain the same amount of Ga as the larger pitch. By a similar argument the diameter of the NP would have the same effect. This theory is supported by our results on Ag seeded GaAs NW growth,\textsuperscript{120} where a high Ga flux was required to achieve NW growth.
4.1.4 Annealing of AgAu Nanoparticles Arrays on GaAs

Results

The annealing of AgAu 100 nm NPs at 600 °C in both a MBE and MOCVD on GaAs (111)B and (100) is presented in Fig. 4.14. The MOCVD annealings on both orientations are stable with all NP arrays remaining and retaining their patterns. In the case of the MBE annealing experiments, the NPs are resilient to the annealing as they are resistant to the vanishing behaviour noted for Ag NPs. Furthermore, the MBE annealing experiences a more dynamic substrate evolution. For the (111)B orientation the NPs dig triangular pits (see inset of Fig. 4.14) and for the (100) the NPs migrate along long the <110> direction.

![Figure 4.14 – SEM images of MBE and MOCVD annealing at 600 °C of AgAu 100 nm NP arrays with a 0.5 μm pitch on GaAs (111)B and (100) substrates. Insets are 85 ° tilted SEM images of characteristic NPs. All primary images share the same 0.5 μm scale bar and the insets have a 100 nm scale bar.](image)

The diameter dependence for the MBE experiments is highlighted for the (100) and (111)B respectively in Fig. 4.15(a) and (b). In Fig. 4.15(a) the smaller NPs (25 to 50 nm) show a splitting behaviour. When the NP diameter is increased to 100 to 150 nm, the splitting behaviour decreases and the NPs appear to migrate along trenches etched into the substrate. In Fig. 4.15(b) the stability of the 25 nmNPs is shown.

In Fig. 4.15(c) the EDS scan of a AgAu NP is shown similar to the method presented in Fig. 4.5. A noticeable decrease in the As molar fraction is measured as the scan location nears the NP and further decreases inside the NP.
4.1. NANOPARTICLE ANNEALING

Figure 4.15 – SEM images of Annealing of AgAu alloy NPs on (a) GaAs (100) and (b) GaAs (111)B substrates at 600 °C. Each row of NPs has a different diameter which corresponds to the number next to the NP measured in nm. In (a) the NPs display both splitting for smaller NPs and migration behaviour for larger diameters. (c) Calculated As molar fraction from EDS scan data of AgAu particle annealed at 600°C.
Discussion

The annealing of the AgAu NPs in the MOCVD for both orientations is more stable than for either the pure Ag or Au NPs at 600 °C. The Ag NPs showed a tendency to split and for smaller NPS to disappear and the Au NPs shift slightly from their defined patterns or begin to form planar NWs. None of these effects are noticed for the AgAu NPs in the MOCVD. The NPs form uniform arrays (see inset of Fig. 4.14 of the MOCVD) that are resilient to annealing.

The MBE annealing of AgAu NPs on (111)B is similar to that of Au NPs. The NPs reside in triangular holes evident by the inset for the (111)B annealing in Fig. 4.14. Contrary to the (111)B, the MBE annealing on (100) demonstrates irregular behaviours. For NP diameters equal to or less than 50 nm the NPs display a splitting behaviour comparable to the annealing of Au on (100). Increasing the diameter suspends the splitting behaviour which is also observed for Au or could be the Ostwald ripening shown for Ag. These larger NPs migrate along <110> direction leaving residual etched trenches in their path. This migratory behaviour is similar to what was reported for the Ag annealing on (100). It appears that the AgAu NP diameter influences the behaviour of the NPs, with smaller diameters being dominated by Au characteristics and larger diameters functioning as Ag NPs. This could also be another manifestation of melting point suppression.

The interest AgAu NPs is increasing within the plasmonic community. Ag is often referred to as the most important metal for plasmonic applications due to its ability to function over a large parameter space while maintaining the largest quality factor. However, Ag is inherently unstable in many chemical environments, which reduces its functionality. Gao et al. (2014) circumvent this problem by alloying Au NPs with Ag, which successfully combined the chemical stability of Au with the high quality properties of Ag.

This exemplifies the use of AgAu NPs for EBL defined NW growth in both MBE and MOCVD. As we report above, the NP arrays could both retained their patterns and withstand the annealing without vanishing at 600 °C. Based on this stability, these AgAu NPs could be substitute for place of Au NPs as catalysts for NW growth. This would also widen the growth parameter space. Furthermore, by incorporating Ag into the seed particle, the plasmonic properties of the NWs could be enhanced. Lee et al. (2006) report that through ex-situ deposition of Ag NPs on NWs to form a shell, the luminescence intensity is increased by two-fold.
4.2. FURTHER RESEARCH

4.1.5 Annealing Experiment Conclusion

The annealing of Au NPs reveals many interesting characteristics in relation to annealing temperature, substrate orientation, and growth system. In a MOCVD the NPs are stable up until 600 °C and at 650 °C planar NWs begin to form which we believe is caused by a reverse VLS mechanism. In a MBE the Au NP annealing are surrounded by pits and trenches which we attribute NP catalyzed substrate desorption at temperatures between 500 and 600 °C. For the (100) substrates, a diameter and pitch dependent splitting behaviour of the NPs is observed we theorize to be caused by the running droplet phenomenon.

The Ag NPs exhibit many features not found in Au. In both MBE and MOCVD at temperatures between 250 to 500 °C, the Ag NPs show a tendency to split into smaller NPs similar to reported accounts of the digestive ripening. At 600 °C the splitting ceases and the Ag NPs seem to shift to a Ostwald ripening regime. At 600 °C in the MBE substrate desorption is present. A diameter and pitch dependent migratory behaviour is observed for the (100) substrates. The dependence is speculated to be caused by the difference in accessible Ga adatoms for individual NPs based on diameter and pitch. Ag NPs arrays showed a sensitivity to annealing with arrays with diameters ~25 nm disappearing at 600 °C. Furthermore, the Ag NP arrays at 600 °C lose diameter uniformity resulting from the uncontrollable Ostwald ripening. For both Ag and Au NPs a diameter dependence on the melting point and the corresponding solidus-liquidus lines is observed.

AgAu alloy NPs showed to be interesting candidates as alternative seed particles. In both MBE and MOCVD the AgAu NPs are more stable than Ag and Au in the MOCVD. A diameter dependence is observed for the annealing on (100) substrates in the MBE where smaller NPs split and larger NPs migrate.

In general the NPs on (111)B substrates are more stable than on (100). Further, the annealing in a MOCVD results in more stable arrays compared to MBE. We assume that the stability is based on that the MOCVD are in an environment, while the MBE is UHV. EDS scans of annealed Ag, Au, and AgAu NPs showed a decrease in the As molar fraction near the NPs and in the NPs.

4.2 Further Research

Although these annealing experiments have shown many interesting results and the amount of parameters investigated was considerable, there are still many interesting studies that can be done. In general it would be interesting to investigate the effect that As overpressure has on the annealing. More specifically, if changing the As overpressure could eliminate the substrate desorption in the MBE then this could be useful for NW growth.

In the case of the Au NP annealing, it would be interesting to conduct a similar study as Zakharov et al. (2015) but use EBL defined arrays to investigate if the Ga droplets are dependent on Au NP diameter and pitches.

Another interesting study would be to attempt to preload the NPs with Ga or other growth
species to improve stability of the arrays and perhaps remove the need for NPs to dig down or migrate in the MBE. This has been shown to improve the yield of Au seeded GaAs NWs arrays.\textsuperscript{34}

Finally, for the AgAu alloy NPs it would be of interest to change the order in which the metals are placed (with Ag on the bottom instead) and the Ag:Au ratio.
Chapter 5

GaAs Nanowires Grown by Molecular Beam Epitaxy

5.1 Thin Film Growth

Part of this work is in the process of becoming a manuscript for submission and others are adapted from our recent report on Ag seeded GaAs NW growth.120

5.1.1 Introduction

Electron beam lithography systems are costly, and the seed particles fabricated may not be the correct size needed to nucleate NWs. An alternative approach to EBL patterned substrates is to preform thin film (TF) annealing to create seed particles. While with this approach you loose the precise control over NW growth offered by EBL arrays, TF annealing can be a precursor for EBL arrays. TF can investigate the size of seed particles needed for NW growth since the annealing process creates a wide range of sizes.

The process of thin film annealing begins with first depositing metal either in-situ in the MBE or ex-situ from a metal evaporator of a desired thickness. The substrates are then loaded into the MBE and subsequently annealed at a desired temperature to form particles. The native de-oxidation temperature for GaAs is around 580°C, and therefore the annealing temperature is usually chosen to be 600°C for a varying amount of time.

In this study, we detail how to control the growth of Ag seeded GaAs NW growth in a MBE by varying growth temperature, film thickness, and V/III ratios for both (111)B and (100) substrate orientations. The growth temperature is used to tune the growth direction, morphology of the NWs. By systematically varying one source flux at a time, their effect on NW growth is revealed, uncovering that the NWs favour a high Group III flux and are Ga limited, while varying

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1We measure the deoxidation temperature in-situ by RHEED in the MBE.
the As has little effect. Using the ideal growth conditions achieved for vertically aligned GaAs on (111)B, a study of film thickness remarkably revealed that the NW density and diameters do not behave as Ostwald ripening would predict.

### 5.1.2 Methods

Ag was deposited on epi-ready GaAs (111)B and (100) wafers by electron beam evaporation, monitored by a quartz crystal thickness meter. The wafers were transferred into a Varian Gen II solid source molecular beam epitaxy (MBE). Standard degassing procedure of annealing at 250 °C for 1 h. To form Ag nanoparticles, annealing at 580-600 °C for 10 min under As$_2$ over-pressure was found to be sufficient. The deoxidation of the GaAs wafer was confirmed by reflection high-energy electron diffraction (RHEED). NW growth was initialized by opening the Ga effusion cell shutter, and terminated by closing the shutter. To verify that NW growth was caused by Ag a region of each substrate was left covered during Ag evaporation. This area was able to act as a control since it did not have any Ag.

### 5.1.3 Results and Discussion

#### Preparation of Ag Catalyst Particles

In this study a metallic Ag particle is used to catalyze GaAs NW growth. Before attempting growth, it is necessary to confirm that the formation of Ag particles is possible on GaAs, and if they are stable. Therefore, a series of nanoparticle (NP) annealing experiments was performed inside a MBE at 600 °C with As$_2$ over-pressure on both GaAs (111)B and (100) substrates, by annealing electron beam lithography defined particle arrays. Standard lithography techniques were employed to define particles with diameters ranging from 25 to 150 nm on both GaAs (111)B and (100). The entire study can be found in chapter 4. In summary, when annealed at 600 °C, the NPs on (111)B substrates form triangular pits in their vicinity but reside on the surface, while Ag NPs on the (100) exhibit an anisotropic migration behaviour, where the NPs etch trenches into the substrate along the <110> direction and reside in these trenches after annealing. The anisotropic behaviour can be explained by the interaction with As-dimer on the GaAs surface.$^{106, 107}$

Furthermore, the predefined Ag NPs showed a tendency to split into smaller particles for both orientations and being more pronounced for particles larger than 75 nm. From this, we can infer that larger Ag seed particles formed by thin film annealing are unstable, and prefer to split into smaller constituent particles.

#### Influence of Growth Temperature

To study the effects of growth temperature on GaAs NWs, a series of four samples for each of (111)B and (100) substrate orientations were grown with temperatures ranging between 400 to 600 °C with a fixed source fluxes. Here we investigate the total density, vertical yield, and NW
morphology in relation to temperature for the (111)B orientations. A similar investigation is conducted on the (100) which will follow.

![SEM images depicting the temperature series on GaAs (111)B.](image)

**Figure 5.1** – SEM images depicting the temperature series on GaAs (111)B. (a) Overview of the samples with top images being plan view and bottom being 45° tilted. Scale bars are 1 µm. (b) 45° titled SEM images showing the characteristic morphologies of the vertical NWs in the temperature series. (a) and some NWs in (b) are from our publication[120].
GaAs(111)B Substrates

First focusing on the (111)B substrate orientation, vertically aligned NWs are grown over the entire temperature window with distinct morphological differences. In Fig. 5.1(a) GaAs NWs are grown with fixed Ga and As fluxes but with incremental growth temperatures of 400, 450, 500, 550, 600 °C in plan and tilted by 45 °. The growth temperature has a large influence on vertical NW yield and the total density of NWs as shown in Fig. 5.2. At 600 °C, a 100% yield of vertical NWs is achieved that we assume grow in the <111>B direction. Decreasing the growth temperature to 550 °C sustains nonvertical NW growth. With a decreasing growth temperature there is a higher density of total NWs sustained, however, this is at the expense of vertical NW yield. An interpretation of this data could be that by increasing the growth temperature, the nonvertical growth is filtered out and only vertical NWs are attained.

In Fig. 5.1(b), SEM images show the morphology evolution of Ag seeded GaAs NWs for the temperature series. The NWs have been grouped according to particle size and morphology. To compare NW morphology with growth temperature only the vertical NWs are discussed here. At a growth temperature of 400 °C, the NWs take on a tapered shape, which can be attributed to surface adatom diffusion length lower than the wire length. When the temperature is raised to 500 °C, the NW’s diameters becomes more uniform, and at 550 to 600 °C the tapering vanishes expect for the towards the end of some NWs. We are still unsure why this tapering occurs for some NWs but we assume it is not due to diffusion length. By comparing NWs grown for two different times, shown in supplementary Fig. C.1, both NWs have the same tapering morphology. If this narrowing was due to diffusion length, then the NWs grown for 60 min should start tapering once it reaches the length of the NW grown for 30 min. We assume this morphology is due to some cooling phenomenon.
Another factor that has not been discussed is the fact that over this large temperature window, the Ag particle could undergo a phase transition. This could manifest with solid particles at 400 °C which mostly grow nonvertical NWs, then at 500 °C, a minority of smaller particles could enter the liquid phase due to melting point suppression. In Fig. 5.1(b) the NWs grown at 500 °C with smaller particles (bottom two NWs) have a more uniform morphology while the NW with the larger droplet has a varying morphology. Further, at 600 °C either most of the particles could be liquid, or the growth temperature is outside of the VSS window, resulting in only uniform vertical NW growth.

NW were able to grow with wide range of particle sizes ranging from 20 nm to 150 nm as shown in Fig. 5.3. The particle regulates the NW diameter and therefore its volume and morphology. With a smaller particle the NW is able to use the same amount of source material to grow longer than a NW with a larger particle because the reduced axial volume. This is apparent in Fig. 5.3 where a smaller particles correlates with a longer NW. Furthermore, by comparing the growth rate of the 30 min growth to that of the 60 min we assume that the growth rate is constant. This is useful because if longer NWs are desired, then increasing the growth time should result in longer NWs.

The NWs grown at 600 °C have nearly pure WZ crystal structure as shown appendix Fig. 5.4(a) and in the inset of (b). The NWs tend to have defects near the Ag NP as shown in Fig. 5.4(b,c) which is assumed to be the result of the cooling neck phenomenon. Photoluminescence measurements were preformed in support of the pure crystal structure results from the TEM shown in Fig. 5.4(d). This reveals that the NWs have a strong and narrow peak emission at 1.52 eV. If contaminates (i.e., from Ag diffusing into the GaAs NW) or unseen crystal de-
Effects are present in the NWs then the photoluminescence measurements should have additional peaks.

The bottleneck morphology for the NWs shown in Fig. 5.4(b) can be attributed to the cooling neck phenomenon.\textsuperscript{36,126} With the cessation of growth, the Ga source is turned off, and the substrate is cooled down under As\textsubscript{2} over pressure. The Ag particle acts as a reservoir to Ga which can recombine with the As\textsubscript{2} over-pressure to form GaAs and subsequently be expelled from the droplet. By comparing NWs grown for two different times shown in supplementary Fig. C.1 the longer growths only have tapering at the end and are not being limited by diffusion.

As reported in our previous work,\textsuperscript{120} the NWs were confirmed to be catalyzed by a Ag particle with a composition after growth of 99\% Ag when cooled down in As\textsubscript{2} over-pressure. NWs that were cooled down without As\textsubscript{2} over pressure will accurate representation of the source concentrations in the particle during growth. However, further EDS analysis of NW particles cooled down without over pressure did not reveal any significant differences, however this could be the result of the slight cooling neck.

\textbf{Figure 5.4} – (a-c) TEM images of a GaAs NW grown on (111)B substrates at 600 °C. The NW has a pristine WZ crystal structure as confirmed by the inset diffraction pattern of b). The viewing direction is the <110> direction. (d) Photoluminescence emission spectrum measurement of similar NW shown in (a-c). This figure is adapted from our publication.\textsuperscript{120}
5.1. THIN FILM GROWTH

GaAs(100) Substrates

The same parameters are used to grow the GaAs NWs on the (100) substrates as for the (111)B between 550 to 600 °C. This resulted in vertical NW growth (growing in the [100] direction) shown in Fig. 5.5(e-g). The vertical NWs have a rectangular cross-section and their yield is 45 to 50% which we believe to be the highest reported yield for NWs grown in the [100] direction. TEM analysis reveals that the NWs have a pure ZB crystal shown in Fig. 5.5(a-d). We note that the NW particle is not perpendicular to the growth direction, but at an angle of 14°.

The growth of vertical NWs is more unstable than on (111)B with the vertical growth window being diminished to ~ 550 to 575 °C using the same growth parameters as for (111)B. Similar to the (111)B orientation, a high density of non-vertical NWs grow at 400 °C (see Fig. 5.6(c,d)), and follows a similar trend of decreasing nonvertical density as the temperature increases. When the growth temperature is reaches 550 °C, the majority of all NW growth ceases with a low density of vertical and nonvertical NWs, and the surface is covered with ridges formed along the <110> direction with catalyst particles on top shown in Fig. 5.5(e) and (i).

These ridges form as a direct consequence of Ag particles, which is confirmed in chapter 4 and in Fig. 5.5 (h) and (i) where ridges only form inside EBL defined Ag particle arrays. A reason for these formations could be that when the Ag particles migrate along the <110> and dig trenches, thus exposing new surfaces as nucleation sites that allow ridge growth.

Once the growth temperature is increased to 575 °C, the catalyst particles present on the ridges at 550 °C are able to nucleate more NW growth and the NW density increases as shown in Fig. 5.5(e,f,g). It is believed that there is a strong competition between NW and ridge growth which causes the overall low density of NWs on the (100) when compared to (111)B. When the growth temperature is increased further to ~ 600 °C, all growth ceases completely, and the surface is dominated by ridges and is void of all particles and NWs shown in Fig. 5.5(h,i).

Effects of Group III and V Fluxes

To investigate the impact that source fluxes has on NW growth, a series of samples were grown by changing either the Ga or As flux separately. First we will investigate the (111)B orientation and then the (100). Fig. 5.6(a) shows the surface of the (111)B substrate as the Ga flux is increased from 75% to 100% of the total available Ga flux for a growth temperature of 600 °C with a film thickness of 10 nm. The entire Ga series from 25 to 100% can be seen in Fig. C.2.

There appears to be a transition between growth modes by increasing the Ga-flux. At 25%, the adatoms seem to act in accordance with Volmer-Weber growth with island formation dominating. The growths with 50 to 75% have the appearance of Frank-van der Merwe growth mode due to the dominance of thin film formation.

\[\text{In Volmer-Weber growth adatoms-adatom interaction is strong. This leads to island formation. In Frank-van der Merwe growth adatom-surface interaction is strong. This causes adatoms to bind with the surface sites over each other.}\]
CHAPTER 5. GAAS NANOWIRES GROWN BY MOLECULAR BEAM EPITAXY

Figure 5.5 – (a-d) TEM images of GaAs NW grown on (100) in the [100] direction. The NW has pure ZB crystal structure as seen in the diffraction pattern in the inset of (a). The viewing direction is <110>. (e-g) SEM images of (100) substrates showing the morphology and density of NWs. (h-k) SEM images detailing the formation of ridges on (100). (h,i) EBL defined NP arrays after growth with a zoom in on the array in (i). Ridge formation is only where arrays were and therefore a direct consequence of Ag particles and not just surface growth. (j) shows the typical ridge formation after thin film growth. (k) shows the trench etching behaviour of the EBL defined Ag NPs on GaAs (100). (a-g) are adapted from our publication.\textsuperscript{120}

With 100% Ga flux, a mixture between thin film growth and island growth is observed. The substrate is dominated by thin film growth, but with islands forming clusters on top of the thin film growth. This is evocative of Strankski-Krastanow mode where a thin film wetting layer forms first, followed by 3D island growth.\textsuperscript{43}

Vertical NWs grow for 100% Ga flux, at the boundary between Ag and non-Ag regions, shown in the inset of Fig. 5.6(b) where the dashed line denotes the boundary. This is not observed for lower Ga-fluxes. NWs growth occur only at the boundary could be the result of two factors. First, the average NP size formed by thin film annealing could be too large to nucleate NWs since the growths were preformed with 10 nm film thickness. However, at

70
the boundary smaller Ag NPs could form due to Ag diffusing into the uncovered region and becoming supersaturated and nucleate NWs. Another factor could be that at the boundary there is more total flux per NP which would increase the Ga content in the NP. NW growth only occurring at 100% and only at the boundary further expands the assumption that Ag seeded GaAs NWs require a high Ga flux.

For the (100) growths, we choose to investigate the effect of Ga flux at 400 °C because of the higher density of NW growth. These growths had a 2 nm Ag thickness. As shown in Fig. C.2(c,d) both vertical and nonvertical NWs are obtained at 400 °C. By increasing the Ga flux from 75 to 100% an increase in total NW nucleation is observed as in Fig. 5.6(c,d).

Another study was preformed at around 600 °C for two different Ga fluxes. The sample with the lower Ga flux has a total NW density of 0.3 /100µm². Increasing the Ga flux increases the total density of NWs to 2.0 /100µm².

Alternatively, when the As flux is varied and Ga flux is held constant, only slight changes are observed. For the (111)B orientation grown at 600 °C, when the As flux is increased the total density of NWs decreases while the yield of vertical NWs remains constant, detailed in supplementary Fig. C.3. A similar result is noted for the (100) substrates grown at 400 °C. It is assumed that As has a low solubility in Ag similar to Au, and therefore becomes supersaturated already at low values. This causes a changing As flux to have little effect for Au seeded NWs.

Phase Diagram Correlation

We will now try to relate the Ga flux results for both the (111)B and the (100) with the Ag-Ga phase diagram. Here we assume that increasing the Ga flux correlates to a higher Ga content in the Ag droplet. By consulting the liquidus curve on the Ag-Ga phase diagram, the liquidus line decreases in temperature with increasing Ga content. Since the Ag droplets require a certain Ga-content to become supersaturated and nucleate NWs, by increasing the growth temperature more Ga compositions in the Ag droplet are able to be reached. Inversely, by increasing the Ga content in the droplet lower growth temperatures are now accessible for growth.

Comparing this theory to our results we see a similar trend. The Ga-series on (111)B showed that the NWs only nucleated for high Ga-fluxes. For the (100), the density of NWs increases by increasing the growth temperature from 550 to 575 °C. Further, as discussed above for the (100) growths at 400 and 600 °C, when the Ga flux is increased (with constant temperature) there is an increase in total NW density.

It is believed that by increasing the Ga content in the Ag particles here, more of the particles transition into the liquidus phase. Additionally, when only particles reside on the ridges, such as Fig. 5.5(j) it is presumed that if the Ga flux is increased the total NW density would also increase. In other words, with increasing Ga content comes a higher probability of nucleating NWs. Based on these observations the growth mechanism here is strongly in favour of VLS. This is because the above argument assumes that the Ag particle is a liquid.
Figure 5.6 – Ga series for (a,b) (111)B and (c,d) (100) where Ga flux is at 75% for (a,c) and 100% for (b,d). Insets of (b) show vertical NWs growing at Ag / non-Ag boundary. Insets of (c,d) show vertical NWs. (a-d) Top image is plan view and bottom image is 45° tilted. Plan view, tilted and insets are of the same region. (a,b) and (c,d) have the same scale and their insets share the same scale.
Effect of Film Thickness

Figure 5.7 – SEM images showing the effects of increasing the thin films on GaAs NW growth. (a-d) are plan view and (e-f) are 45° tilted images of the same region. All images have the same scale.

Figure 5.8 – Data taken for the thin film experiments. Diameter, growth rate and density as a function of film thickness.

The results of the annealing experiments encouraged further research into how changing the film thickness would effect NW density and diameter. Using the growth parameters for attaining 100% vertical yield for the (111)B substrate, a series of (111)B samples shown in Fig. 5.7 were prepared with varying film thicknesses (0.2, 0.5, 1, 2, and 5 nm). The thin films were transformed into NPs by using standard thin film annealing procedure and is the same for all the
growths in this series. NW growth was only possible in the 0.5 to 2 nm film thickness regime, with 0.2 nm resulting in only substrate growth. It is noted that a 5 nm film thickness produces crystalline structural formations which disappeared over the course of 2 months or NWs grew but were eaten by the large particle due to sulphurdization\textsuperscript{127}

Increasing the film thickness increases the NW density shown in Fig. 5.8. This result can be explained by the preparation of Ag particles during annealing where the thin film dewetting from the surface, forming large particles that become unstable and split into smaller particles that do not recombined. This explanation is consistent with the results from the EBL annealing experiments where Ag particles were observed to split into smaller particles.

Surprisingly, our results of film thickness do not behave as predicted by Ostwald ripening theory\textsuperscript{112, 113, 128}. Due to Ostwald ripening, by increasing the film thickness the density catalyst particles should decrease as their diameter increases. Referring to previous work on the preparation Au NPs by thin film annealing on GaAs (111)B and (100), Lee et al. (2015)\textsuperscript{129} found that Au thin film annealing could be explained by Ostwald ripening theory, where with increasing Au film thickness the average article diameter increased, while the average particle density decreased. This behaviour was also observed by Xu et al. (2012)\textsuperscript{130} where they grew GaAs NWs by MOCVD with Au thin film annealing. Xu et al. (2012)\textsuperscript{130} observed that by increasing the film thickness both the catalyst particle diameter pregrowth, and the NW’s particle both increase while the total NW density and length decreased. An inverse behaviour is observed by our Ag seeded growth. An alternative mechanism known as digestive ripening has recently been observed where instead small particles at the expense of large particles\textsuperscript{114–118}

\subsection*{5.1.4 Conclusion}

To summaries the results, we have successfully grown vertical GaAs NWs from Ag seed particles on both (11)B and (100) substrates from by thin film annealing. Using the same growth parameters but switching the substrate orientation produced high quality crystal structures. For (111)B and (100) the vertical NWs have a WZ and ZB respectively. Systematically varying the source fluxes revealed that the NWs are Ga limited. Investigating the effects of Ag film thickness showed that NW density and diameters do not behave as predicted by Ostwald ripening.
5.2 GaAs Nanowire Arrays Grown by Molecular Beam Epitaxy

Here we will show our attempt at growing GaAs NWs by EBL positioned Ag and AgAu NPs. Fig. 5.9(a) and (b) are growths on NP arrays of Ag and AgAu respectively. The same growth parameters were chosen that resulted in vertically align NWs for the thin film experiments above. In Fig. 5.9(a) for the (111)B substrates only pyramid structures are left after growth and elongated ridges for the (100) shown in Fig. 5.5(h,i) where the EBL arrays were fabricated.

We speculate that the growth of NWs is problematic for EBL arrays due to how the NPs alloy with the substrates compared to thin film annealing. In Fig. 5.10 we propose a possible theory for the difference with Ga and As incorporation between the two techniques\textsuperscript{iii}. For the thin film annealing, the seed material atoms are dispersed over the entire substrate while for EBL arrays the NPs are at predefined locations. When forming alloys with the substrate the incorporation area is much larger for the thin film since it is able to incorporate Ga and As from the entire substrate as shown in (c). However, in the case for EBL defined NPs the incorporation area is limited to the area around the NPs and therefore dig holes into the substrate as shown in (h). This phenomenon is discussed in great detail in chapter 4.

To combat this problem, we believe it could be interesting to dope the Ag droplets with Ga or Sb before growth to reduce the amount of substrate desorption. This technique has been shown to work for Au seeded GaAs NW arrays grown in by MBE.\textsuperscript{34}

A further factor that is problematic for arrayed growth is the parasitic surface film growth that occurs between the NWs.\textsuperscript{34} It is believed that since the NPs begin the growth process in a recessed pit, that the effective surface growth buries the NPs before they are able to nucleate NWs.

NW growth is possible by using AgAu alloy NPs. In Fig. 5.9(b) faceted pyramids grow where the NPs were defined. At the top of some pyramids, GaAs NWs grow with the majority of these NWs growing vertically out of the pyramids. This growth is unexpected since the growth parameters are chosen for the Ag seeded GaAs growth. This result is encouraging for further research into AgAu seeded GaAs growth by MBE.

\textsuperscript{iii}For a detailed investigation of the role of Au NPs before and during NW growth and Ga and As dissociation processes by density functional theory analysis see [102].
Figure 5.9 – (a) Attempt at Ag seeded GaAs arrays. Surface is dominated by surface growth. (b) AgAu arrays nucleating pyramids and NW growth.

Figure 5.10 – Schematic of the different collection areas for Ag NPs formed by thin film annealing and electron beam lithography (EBL). (a,b) Thin film annealing form droplets, which (c) alloy with substrate over a large area to form (d) seed particle without digging down. (e,f) Annealing of EBL defined NPs forms droplets that (g) alloy with the substrate in their vicinity. (h) This causes them to dig into the substrate as they form a seed alloy.
Chapter 6

GaAs Nanowires Grown by Metal-Organic Chemical Vapor Deposition

6.1 Thin Film Growth

In this section I will discuss the preliminary results of MOCVD grown GaAs NWs. This is part of an extensive study with alternative seeding materials. I will comment on the main results and general trends observed for the GaAs NW growth in relation to the many growth parameter and substrate/seed material combinations we have investigated. However, a detailed discussion into the nature of these results is beyond the scope of my thesis.

6.1.1 Methods

The GaAs NW growth was performed in a AIXTRON Close Coupled Showerhead® (CSS) 3x2 inch MOCVD reactor (see chapter 2.1.2). Catalyst particles were formed by thin film annealing at 630 °C for 7 mins and by EBL arrayed substrates annealed at 600 °C for 3 min with an AsH$_3$ over-pressure. Growth temperatures ranging between 400 to 550 °C were used and growth was initiated on GaAs (111)B, (111)A, and (100) substrates with Ag, Au, AgAu alloy seed particles by introducing TMG from 3 to 6 sccm (Standard Cubic Centimeters per Minute) and with AsH$_3$ from 18 to 50 sccm. These growth parameters were chosen with the results of the Ag seeded GaAs NW MBE growth in mind and therefore a high Ga flux was used. The initial growth parameters were chosen based on a successful recipe which previously achieved Au seeded GaAs NWs. Seed-metals were deposited by e-beam evaporation with thickness of 1 and 2 nm for the thin film annealing and 5 nm for the EBL arrays.

6.1.2 Introduction

The recent success of Ag as a seed-metal for GaAs NWs grown in the MBE (see chapter 5), supports an attempt at a similar study in a MOCVD. The loading procedure in a MOCVD is
CHAPTER 6. GAAS NANOWIRES GROWN BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

less technical and time consuming compared to a MBE. This is based on that the sample holder is a horizontal plate and the growth chamber being in a hydrogen or nitrogen environment. This allows for many samples with various metals and substrate orientations to be loaded simultaneously. A detailed list of the experiments conducted can be found in appendix F.

The group headed by Kimberly A. Dick at Lund University have had a large success growing GaAs NWs by MOCVD using Au\textsuperscript{131} and Pd\textsuperscript{132} nanoparticles formed by the aerosol technique,\textsuperscript{133} in-situ Sn seeding\textsuperscript{134} and using the self seeding approach.\textsuperscript{135} Evident by these recent publications, this group is focusing on the use and understanding of alternative seeding materials. However, the technique of thin film annealing to generate seed particles has never been attempted.

Here we, in collaboration with this group, will investigate the growth of GaAs NWs on GaAs (111)B and (100) by Ag, Au, and Ag-Au alloy seed particles formed by thin film annealing in a MOCVD. On account of the vast parameter space chosen for this study, we anticipate that the results will further our understanding of alternative seeding for GaAs NW growth.

6.1.3 GaAs (111)B Substrates

Effects of Thin Film Annealing and Growth Temperature

The results of Ag and AgAu NP annealing experiments in the MOCVD (see chapter 4) exemplified their use as possible seeds for GaAs NW growth. It was therefore presumed that some favourable growth results should be achievable by thin film annealing. However, the large success we observe with the use of alternative seeding is rather unexpected.

A temperature series is performed to probe the possibility of growing GaAs NWs with alternative seeds. The growth temperature is varied from 400 to 550 °C in increments of 50 °C. The V/III ratio is held constant and chosen with a high Ga flux. Vertical NWs are achieved on all substrates in the temperature series for all Ag, Au, and Ag-Au growths except for the growth of AgAu seeded NWs at 400 °C. In the following, I will discuss the effects of thin film annealing and growth temperature.

In Fig. 6.1 the growth of GaAs NWs seeded by Ag, Au, and AgAu particles at the growth temperature of 500 °C is shown. The Au and AgAu seeded NWs appear to be similar with stable vertical NWs growing between 450 to 550 °C. The density, diameter, and morphology of the NWs are uniform over the entire sample at each growth temperature. The NWs grow in high density as seen in Table. 6.1 with the majority growing vertically. For the Au seeded growths the density is rather stable over the growth window. This observation suggests that the annealing of Au thin films has the largest effect on the density and diameters of the NWs. To tune the density and diameter, it would be worth to alter the film thickness size and the annealing time and temperature to achieve different results. In contrast, the AgAu seeded density increases with increasing growth temperature suggesting that the growth temperature has an effect on the nucleation of NWs. This could be due to the growth temperature altering the Ag: Au

\textsuperscript{1}The substrate is covered in small NPs but no NW growth is evident.
Figure 6.1 – SEM images of GaAs NWs grown on (111B) 500 °C in a MOCVD by Ag, Au, and AgAu thin film annealing. Top row are plan view and bottom row are 45° tilted images. All scale bars are the same. This growth temperature is chosen to represent the temperature series based on it being the most successful for all seeds.
Table 6.1 – Average density of Au and AgAu seeded GaAs NWs at different growth temperatures

<table>
<thead>
<tr>
<th>Seed Particle</th>
<th>Growth Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Au</td>
<td>185</td>
</tr>
<tr>
<td>AgAu</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 6.2 – Average diameter of Au and AgAu seeded GaAs NWs at different growth temperatures

<table>
<thead>
<tr>
<th>Seed Particle</th>
<th>Growth Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Au</td>
<td>24±7 nm</td>
</tr>
<tr>
<td>AgAu</td>
<td>N/A</td>
</tr>
</tbody>
</table>

A more dynamic system is observed for Ag seeded GaAs NWs. Over the entire temperature window, vertical NW growth is achieved along with nonvertical NWs and parasitic worm growth. The samples show a large difference between the different growth temperatures. At 400 °C worm nucleation dominates the growth, and between 450 to 500 °C the vertical growth seems to stabilize. At 550 °C, a large amount of radial overgrowth is noted which is not observed for the Au and AgAu seeded NWs. A large decrease in the total density of Ag seeded NWs is observed when comparing between Au and Ag-Au seeding. This is consistent with the results in the MBE, where the Ag seeding density is dramatically less than Au seeding.

This poses an interesting question as to where the Ag disappears to. To explain the low density we will turn to the results of the Ag annealing in the MOCVD (discussed in detail in chapter 4). In Fig. 6.2(c) it is shown that larger Ag NPs have a tendency to split into smaller constituent parts. Additionally, the annealing of Ag in both the MOCVD and MBE at 600 °C shows that NP arrays with diameters smaller than 50 nm have the trend to disappear which is believed to be caused by diffusion into the substrate by forming an alloy. We assume that based on these two results that when the Ag thin film is annealed, it dewets into droplets and the smaller droplets either diffuse or alloy with the substrate. This assumption is reinforced by the observation that the minimal particle size for the Ag seeded NWs is much larger than for both Au and Ag-Au seeded NWs. At 500 °C the average NW diameter is 56 ± 20 nm, 32 ± 9 nm and 27 ± 9 nm, respectively, for Ag, Au, and AgAu seeding.

The resulting NWs are confirmed to be caused by the corresponding thin films that are annealed as detailed in the particle composition found in Table 6.3. Additional experiments where different thicknesses of Ag and Au are deposited would be of interest to see how the Ag/Au ratio effects the Ga and As concentration and the resulting crystal structure. This is the
6.1. THIN FILM GROWTH

Figure 6.2 – SEM images of Au, AgAu, and Ag NP array annealing experiments at 600 °C in a MOCVD. The arrays are of varying NP diameters increasing from bottom to top with 25, 50, 75, 100, and 150 nm diameters. (c) is a back-scattered electron SEM image to showing that the 25 nm NP have vanished and that the larger NPs are splitting. All scale bars are 0.5 µm.

Table 6.3 – EDS composition analysis of Ag, Au, and Ag-Au seeded GaAs NWs grown at 500 °C. One of each of Ag and Au seeded NWs and nine Ag-Au NWs were measured. EDS measurements were performed by M. de la Mata in a HRTEM.

<table>
<thead>
<tr>
<th>Seed Particle</th>
<th>Ag</th>
<th>Au</th>
<th>Ga</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>66</td>
<td>N/A</td>
<td>33</td>
<td>N/A</td>
</tr>
<tr>
<td>Au</td>
<td>N/A</td>
<td>60</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>AgAu</td>
<td>35</td>
<td>40</td>
<td>25</td>
<td>N/A</td>
</tr>
</tbody>
</table>

approach that Chou et al. (2012)\textsuperscript{136} took to achieve different Ag-Au droplet ratios.

Crystal Structure

The most striking difference between seed-metals arises when investigating the crystal structure of the NWs. In Fig. 6.3, TEM analysis is presented of the different seeds for the growths at 500 °C. In both Fig. 6.3(a) and (b) Ag and Au seed GaAs NWs are shown to have a high density of defects resulting from switching between ZB to WZ or twinned WZ segments and vice versa. In contrast, the AgAu seeded NWs display a pure WZ crystal structure with only one stacking fault found in a single of the investigated NWs (out of 9 NWs investigated). It should be mentioned that during the investigation of the AgAu alloy growths one polytypic NW was found. No abnormalities in the Ga, As, Au, or Ag composition in the droplet or the droplet diameter is observed when compared to the pure structured NWs.

Further growths showed that by decreasing the total film thickness from 2 nm to 1 nm (0.5 nm of each Au and Ag) had no effect on the resulting NWs. However, preliminary results show
that the order in which the Ag and Au is deposited matters. Recent results show that when Au is placed under the Ag, a pure WZ NW grows, but if Ag is on the bottom then the NW has a polytypic structure.
6.2 GaAs Nanowire Arrays from Alternative Seeds

The thin film MOCVD growths demonstrate that indeed GaAs NWs growth is possible by Au, AgAu, and Ag seeds. Here GaAs NWs growth from Ag, Au, and Ag: Au NP arrays fabricated by electron beam lithography (EBL) on GaAs (111)B are investigated. By using EBL techniques the NP’s Au:Ag ratio is able to be controlled. This allows for a study into the effect that different Ag: Au compositions have on the GaAs NW growth, in addition to diameter and pitch effects. The growth temperature is chosen to be held constant at 500 °C based on the SEM and TEM analysis of the thin film annealing growths.

6.2.1 Results

The GaAs NW arrays have a similar success as the results from the thin film annealing. The Au, Ag: Au, and Ag seeded NW growths demonstrate that indeed alternative seeds can be used for array growth. For many of the samples a high yield of vertical NWs is achieved and with many remaining highly ordered. Due to the vast amount of information and data that is able to be extracted from these growths, we will first comment on some general trends that are observed on many of the samples. This will allow for a constant diameter and pitch to be chosen in order to be able to compare samples grown with different parameters.

The Au, AgAu, Ag: Au seeded GaAs NW growth behave similarly when changing NP diameter or pitch. The general trend is that vertical NWs prefer to grow from arrays fabricated with smaller NP diameters (25 nm) and with larger pitches (larger than 1 µm). When the pitch is decreased from 1 to 0.5 µm, the amount of nonvertical NWs increases. Additionally, if the NP diameter is increased from 25 to 50 nm the majority of NWs will either grow directly non-vertically or will begin vertical and then kink and grow nonvertically. Increasing NP diameter further causes the arrays to become more disordered. A detailed investigation into the pitch and diameter effects will be presented below. Therefore, the standard array that will be discussed is with a diameter of 25 nm and a pitch of 1 µm to show the most favourable vertical NW yield.

It should be noted that Ag seeds were not taken into account in this decision. This is because Ag proved to be unfavourable as a seed for EBL growth as a result of the instability in growth. For most cases the EBL pattern is lost for 25 to 50 nm NP diameter arrays and the arrays where NWs grow results in a variety of growth directions.

Ag: Au Ratio and V/III Ratio

A general overview of GaAs NWs grown from Au, AgAu, Ag: Au and Ag NP arrays with varying V/III ratio is presented in Fig. 6.4. The NWs are grown at 500 °C with a V/III ratio of 4.86, 3.37, 2.43, 1.21 for Fig. 6.4(a), (b), (c), (d) respectively. This figure is designed to highlight the effect of Ag: Au ratio with a transition from pure Au to pure Ag and effect

\[ ^{ii} \text{The Ag: Au ratio is related to the thickness of metal evaporated. In the following GaAs NWs are grown from different Ag: Au ratios. These values are pregrowth ratios and have not been confirmed post growth.} \]
individual Group III and V flow rates. The NW arrays shown are grown from 25 nm NPs with a 1 μm pitch unless otherwise specified.

**Transition from Au to Ag**

In Fig. 6.4(a-d) the transition from Au to Ag is shown from left to right. With increasing Ag content in the NP the resulting NWs become more unstable with respect to growth direction and pattern control. For instance, if we focus on the transition from pure Au to AgAu in Fig. 6.4(a), the growth yields a more disordered array. The array loses its patterning but the NWs remain vertical. Transitioning further to Ag$_2$Au allows for some NWs to grow nonvertically. The pure Ag NWs arrays have almost entirely lost their patterning and the majority of growth is nonvertical or in some form of parasitic growth. This observation of instability associated with Ag content in the NP can be observed further in Fig. 6.5. The Ag content is increased from top to bottom in Fig. 6.5 the arrays become more disordered.

Increasing the Ag content also seems to make the NWs more heavily influenced by changing the V/III ratio. For example, we will use the Ag$_2$Au array in Fig. 6.4((a) as a control because both vertical and nonvertical NWs are present. In Fig. 6.4((b) the Ag$_2$Au array result only in nonvertical growth and in Fig. 6.4((c) the same array results in primarily vertical NWs.

If the Ag content is decreased, the stability of the arrays to V/III ratio increases. Consider the AgAu arrays in Fig. 6.4((a) to act as a standard where only vertical NWs grow. Contrasting the effect of V/III ratio again by comparing the AgAu seeded NWs in Fig. 6.4((b) and (c) does not reveal significant changes in vertical yield as for the Ag$_2$Au array show. In this case the arrays maintain vertical NWs and only morphological differences are noted.

**V/III ratio**

There is a distinct difference between the doubling of As compared to doubling the Ga. Increasing the As flux leads longer NWs for all seeds, but it also increases the unstable nature of the growth. Arrays that yield a high density of vertical NWs at an As flow of 18 sccm begin to be more susceptible to kinking and growing in other directions when As is increased. This can be observed by comparing Fig 6.4(c) and (d) to Fig 6.4(a) and (b) respectively. This instability is exacerbated in Fig 6.4 (b) which has an As flux of 50 sccm. Here many of the arrays begin with vertical NW growth (stem) and then kink to other growth directions. In a particular case the Ag$_2$Au seeded NWs in Fig 6.4(b) only grow inclined to the substrate without first growing a vertical stem. This is of interest because of the stable nature of the growth. The growth direction is not yet confirmed, but the directions appear to have three fold symmetry.

The increased supply of Ga does not appear to effect the yield of vertical NWs or the morphology, however, the overall length of the NWs decreases significantly.

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The volatility of the NP arrays is material and size dependant as shown by the annealing experiments and therefore larger NP diameters sometimes is necessary for the arrays to survive.
### 6.2. GAAS NANOWIRE ARRAYS FROM ALTERNATIVE SEEDS

![Graphical Representation of Growth Parameters and Seed Material](image)

**Figure 6.4** – SEM images in a graphical representation of the growth parameters and seed material showing an overview of the parameter space. The V/III ratio for (a), (b), (c), (d) are 4.86, 3.37, 2.43, 1.21 respectively with a growth temperature of 500 °C. NWs arrays shown were grown from 25 nm NPs with a 1 µm pitch except for †, φ, Σ, Γ with a 100, 25, 50, 75 nm diameters respectively and with 1, 0.75, 0.5, 1 µm pitches respectively. In all of (a), (b), (c), and (d) the top images are plan view and the bottom row are tilted by 45°. All plan view and all tilted images are scaled the same with a 1 µm scale bar.
Surprisingly, these results on changing the V/III ratio are the opposite of the results for the MBE grown GaAs NWs. The MBE study of Ag seeded GaAs NWs in chapter 5 found that the NWs were Ga limited. By changing the Ga flux a large increase in nucleation is observed while varying the As flux had little effect.

Nanoparticle Diameter and Pitch Dependence

In Fig. 6.5, both the pitch and diameter are represented graphically for Au, AgAu and Ag$_2$Au arrays. All of these samples are grown at 500 °C and with a V/III ratio of 4.86 similar to Fig. 6.4(a). In Fig. 6.5(a-d) Au seeded GaAs NW arrays are shown. Starting with the 25 nm arrays, if the pitch is decreased from 1 to 0.5 µm the majority of NWs remain vertical. When the diameter is doubled from 25 to 50 nm in Fig. 6.5(c-d) nonvertical kinked NWs begin to form, with an increasing probability with increasing diameter.

A similar trend is noticed for AgAu seeded NWs shown in Fig. 6.5(e-h), however, the NWs are much more sensitive to the array parameters compared to the Au arrays. For the 50 nm arrays, decreasing the pitch from 1 µm (Fig. 6.5(f)) to 0.5 µm (Fig. 6.5(h)) a large majority of the NWs begin to kink. A similar but not as significant effect is noted for the increase of diameter.

In Fig. 6.5(i-l) the growth of Ag$_2$Au seeded GaAs NWs is shown. This sample is chosen to feature the ultra thin NWs obtained in (i). In Fig. 6.5(j-l) the growth is unstable. However, when the pitch is increased to 1.5 µm and above for the 25 nm arrays the growth stabilizes. In Fig. 6.5(i) rather uniform ultra thin NWs are achieved.

6.2.2 Discussion

There appears to be close relationship between the NP composition, array pitch and diameter and V/III ratio based on the results presented above. Although this study is in the preliminary stages of investigation, certain connections will be attempted to be discussed here.

Diameter and Pitch Dependence

The diameter and pitch dependencies are examined in Fig. 6.5. A general trend is observed where vertical NWs prefer to grow from arrays with 25 nm NPs and pitches greater than 1 µm. These phenomena can be explained based on the concept of collection area discussed in Chapter 2.2.3 and detailed by Fig. 2.4. By decreasing the pitch distance there is a greater overlap of the collection area of each NW and therefore they are competing for source material from the substrate. A similar scenario occurs when increasing the diameter the NP. A larger droplet on the end of a NW will require a more source material to have same composition as a smaller droplet.

Each array receives the same total amount of source material during growth. Therefore, by either increasing the density of the NWs by deceasing the pitch or by increasing the NP diameter
6.2. GAAS NANOWIRE ARRAYS FROM ALTERNATIVE SEEDS

Figure 6.5 – SEM images show the diameter and pitch dependencies of Au, AgAu and Ag$_2$Au seeded GaAs NWs. All samples were grown at 500 °C and with a V/III ratio of 4.86. The left image of each of (a-f) is plan view and the right image of each is 45° tilted. All images are the same scale.
CHAPTER 6. GAAS NANOWIRES GROWN BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

Each NW will receive less source material than ones with larger pitches or smaller diameters. It is assumed that based on these arguments that the arrays with large diameters or smaller pitches are disordered.

It is observed that the majority of nonvertical NWs begin by growing a vertical stem and then kink to a nonvertical direction that appears to obey a three-fold symmetry when viewed in plan view. The kinking of NWs is usually controlled by either significantly changing a specific growth parameter (pressure or temperature) causing the droplet wetting configuration and can lead to the droplet migrating to one of the NW’s side facets. \textsuperscript{18, 137–139} Neither scenario are present in these growths. This kinking could be the result of a decrease substrate flux contribution causing the growth to become unstable and to support kinking. Further research into the nature of the nonvertical growth and kinking of NWs would be interesting.

**Effect of Ag:Au Ratio**

There appears to be some correlation between the Ag:Au ratio and both growth direction and array stability. The growth direction could be related to the intake of Group III. As observed in Table 6.3 the AgAu droplet has a much lower Ga content than both Ag and Au individually. If this is the reason then this opens up the use of Ag:Au alloys for many applications. By using different Ag:Au ratioed EBL defined arrays, two controllable growth directions can occur simultaneously. This would allow for sophisticated NW junction to be engineered. For example, this can be realized in Fig 6.4 (b) where NP can be defined with both AgAu and Ag\textsubscript{2}Au compositions. AgAu seeding would grow only vertical NWs and the Ag\textsubscript{2}Au arrays only grow nonvertically with an apparent three-fold symmetry. Combining these two growths allows for complex NW junctions to be engineered. Additionally, the growth direction of the nonvertical Ag\textsubscript{2}Au seeded NWs could either be the <100> or <110> directions, which have been shown to have few stacking faults.\textsuperscript{140}

To explain the instability of the arrays pattern with regards to the Ag concentration in the NP we will return to the annealing results in the MOCVD at 600 °C. In Fig. 6.2 arrays with varying diameters are presented for Au, AgAu, and Ag NPs. For both the Au Fig. 6.2(a) and AgAu (b) NP arrays the pattern remains and the NPs refrain from splitting except for a small majority of the 25 nm AgAu NPs. The Ag arrays in Fig. 6.2(c) show a large tendency to split but the majority of the pattern remains. Also, the 25 nm NPs have entirely disappeared. The unstable nature of the Ag concentrated growths could be the results of these observations. The splitting behaviour shows that there is a lack of control over the pattern because these split particles could also nucleate additional NWs outside of the pattern positions.

**Comparison between Arrays and Thin Film**

In Chapter 5.2, GaAs NW growth was attempted from EBL NP arrays by MBE. These growths were rather unsuccessful compared to the MOCVD results. To further our understanding between the nature of the two seed particle preparation techniques, thin film and arrays are grown.
Figure 6.6 – SEM images comparing the growth from thin film annealing to EBL defined arrays. (a-d) Seed particles are formed by thin film annealing and (e-l) from NP arrays. Arrays in (e-h) are grown from 25 nm NPs and (i-l) from 100 nm NPs. All images scaled the same. Inset in (b) is a zoom in and has a scale bar of 100 nm.
These simultaneous growths are presented in Fig. 6.6. The growths were at 500 °C and with a V/III ratio of 3.37. In Fig. 6.6(a-d) Au and AgAu thin film NW growths are shown in plan view and 45° tilted SEM images. The corresponding EBL growths are shown in Fig. 6.6(e,f,i,j) and (g,h,k,l) for Au and AgAu respectively. The difference between top and bottom is an increase in diameter from 25 to 100 nm.

From this figure it is clearly visible that both techniques for growing GaAs NWs can be used. However, there are some dissimilarities between the two techniques. The thin film growths have vertical NWs over a wide range of particle diameters (~10 to 60 nm) and with high density. Both of these parameters have been shown to adversely effect the GaAs NW arrays.

In the above we have shown a large NP diameters causes instability in the NW growth as can be seen in Fig. 6.6(i-l). It should be noted that the deposition thickness of the EBL arrays was chosen to match the NW particle volumes attained by the thin film annealing. Further, it has been shown that by decreasing the pitch from 1 to 0.5 µm the vertical NW yield decreases.

Furthermore, the morphology of the NWs seems different between the two techniques. The morphology of the thin film NWs appears to be rather uniform and straight, while the patterned NWs are tapered. Recollecting to the results for the GaAs NWs grown from Ag thin film annealing in the MOCVD in Chapter 6.1.3. Only radial overgrowth is observed for the Ag seeded NWs, which grow with a substantially lower density than Au or AgAu. We therefore assume that the radial overgrowth is pitch related.

### 6.3 Vertical Growth on GaAs (100)

A similar study to the growth on GaAs (111)B presented above is possible since the samples are available, however, this is outside the scope of my Masters thesis. The samples have been grown and characterized but in effort to shorten this thesis I have decided to leave the majority of the (100) growth out and focus on the main results.

In Fig. 6.7 the growth of GaAs NWs on GaAs (100) oriented substrates by both thin film annealing and EBL arrays are presented. In (a) and (b) it is observed that a high yield of vertical NWs is attained by using both Au and AgAu as seed particles. If the planar surface NW growth are neglected then almost all NWs grow vertically. At present I believe this is the highest vertical yield reported and with a high density.

Growth by patterned arrays is also attempted in both Fig. 6.7(c) and (d) by using Au as seed material. In Fig. 6.7(a) a high yield of vertical NWs is also attained. Planar NWs are still present and appear to be caused by difficulties in the nucleation step. To try to remove these planar NWs it was decided that by skipping the annealing step that the surface native oxide would still be present. It was thought that this surface native oxide would act as a mask for the NWs and either stop the planar growth or force the NWs vertical. The result is presented in Fig. 6.7(d) where this only leads to a decrease in total yield and does not eliminate planar growth.
6.3. VERTICAL GROWTH ON GAAS (100)

Figure 6.7 – SEM images of GaAs NWs grown on GaAs (100) substrates with a high vertical yield. (a,b) Seed particles are formed by annealing (a) Au and (b) AgAu thin films. (c,d) Au NP arrays successfully growing vertical NWs. (d) The annealing step at 600 °C is skipped to preserve native oxide and unsuccessfully try to limit planar NWs growth. Top images are plan view and bottom images are 45 °tilted. All scale bars are 1 μm.
6.4 Conclusion

In summary we have demonstrated the use of alternative seeding of GaAs NWs with Ag and AgAu NPs in a MOCVD. Thin film annealing was used to form seed particles and this successfully grew NWs over a large temperature window. By SEM analysis the growth at 500 °C was chosen as the optimum growth temperature. TEM analysis was performed on these NWs for the three different seed materials. Crystal structure analysis reveals that AgAu seeding grows NWs with a near pure WZ crystal structure, while Ag and Au as seeds grow polytypic NWs.

GaAs NW arrays were also successfully grown from EBL defined NPS. The vertical GaAs NWs preferred to grow from arrays with 25 nm NPs and greater than 1 µm pitches. It was observed that a correlation between the amount of Ag in the NP and the stability of the EBL growth. It was observed that with increasing Ag content the NW growth became more unstable with respect to growth direction, pattern retention, and susceptibility to changing V/III.

Further, we have shown that vertically aligned GaAs NWs can be grown on GaAs (100) substrates by both thin film annealing and EBL NP arrays with a high vertical yield.
Thesis Summary

In my thesis, we investigated the use of alternative seeds for NW growth. To understand the nature of these alternative seeds, we conducted NP annealing and NW growth experiments. The annealing of NP arrays led to improved understanding of the conditions experienced by seed particles before growth.

It proved to be advantageous to compare the results from the MBE annealing experiments and the MBE NW growth. For arrays positioned on GaAs (100) annealed, a diameter and pitch dependent splitting behaviour for Au and migratory behaviour for Ag behaviour is observed. This information was useful for understand the lower density of vertical NWs on (100) compared to (111)B and contributed to our understanding of the surface growth morphology.

Ag NPs displayed a temperature dependent transition from digestive ripening to Ostwald ripening. Coupling these results with the MBE thin film series growths a justifiable reason to why the Ag seeded NWs growth do not behave as Ostwald ripening would predict. Additionally, the disappearance of small Ag NPs could be the reason for the low NW density observed compared to Au seeding.

Furthermore, the NP annealing showed signs of NP catalyzed substrate desorption which effected the stability of the arrays. This is believed to cause the difficulties when attempting growth from NP arrays in the MBE. The majority of the difficulties related to stability of the arrays are characteristic of the MBE annealing and not the MOCVD. Due to this, we assume this is why the MOCVD GaAs NW growth is more successful in terms of yield, and stability when compared to MBE.

Based on these comparisons, it is apparent that NP annealing can be used as an investigation tool to a better understand and control NW growth. Another successful tool was the growth from different Ag:Au ratio NP arrays. Many growth and array parameter dependencies were uncovered by selectively tuning the composition of the NP.

The GaAs NWs we obtained from alternative seeding show great promise. For the MBE growths, WZ and ZB crystal structure selectivity was achieved by growing on GaAs (111)B and (100) substrates respectively. The NWs were shown to have a high-quality crystal structure and the WZ NWs showed a promising emission spectrum.

Alternative seeding of GaAs NWs was also preformed by MOCVD. A particularly interesting result was that NWs grown from AgAu thin film annealing showed a pristine wurtzite structure while Au and Ag seeding produced polytypic crystal structures. Growth from alternative NP arrays was also successfully demonstrated. Furthermore, it was shown that a high yield
of vertical NWs can be grown on GaAs (100).

Based on these results, we believe that alternative seeds hold a bright future for the NW community. In this thesis, the results support a notion that by choosing seed particle composition, NW growth direction and crystal structure can selected.
Bibliography


Appendix A

EBL Recipe

A.0.1 Resist Spinning

Double Layer Resist: Co-polymer EL6(co-MMA 6% in etil-lactate), PMMA A2 (polymer 2% in anisole)

1. Center your chip on spinner head and turn on vacuum.
2. Blow with N₂ gun, and close lid.
4. Choose spinning program: 45 s at 4000 rpm and start. This should give 100 nm of EL6 and 50 nm of A2.
5. When finished, open lid, and turn off the vacuum and place chip on hot plate.
6. Bake for 90 s at 180 ºC
7. Repeat for PMMA A2

A.0.2 Exposure

Elionix 100 keV EBL system. The best particle resolution (per write time) was found at a current of 500pA and an aperture of 40 µm.

1. Arrays were designed in Raith ELine software and converted in the Elionix software.
2. Arrays are made with particle diameters of 25 - 150 nm and pitches 0.25 - 5 µm.
3. To achieve a 50 nm circular exposure a dose time of 160µs was needed for GaAs and 60 µs for InAs.

A.0.3 Development

1. Develop sample in MIBK:IPA 1:3 ratio for 90s.
2. Rinse with IPA and then millipore (MP) water and blow dry with N₂ gun
3. Oxygen plasma ash for 10 nm
4. 10 % bHF dip for 10 s
A.0.4  Metal Deposition

Metal deposition in an AJA international UHV (10^{-8} torr) e-beam evaporator. Quartz thickness monitor

1. Deposit 5-15 nm of desired metal

A.0.5  Lift-Off

1. Lift off is done in cold Acetone over night.
2. Once lift off is complete, rise with new acetone, MP, and IPA, and then blow dry with N₂ gun.

A.0.6  Before Loading into the MBE

1. Oxygen plasma ash for 40 nm
2. 5 % HF dip
Appendix B

Organic Residue Removal and Oxide Removal

For the production of EBL patterned samples, oxygen plasma ashing is used to remove resist with nanometer control. After sample development or after the samples have had their resist lifted off, a small amount of resist will remain on the surface. This resist must be removed to create a clean interface with the substrate surface prior to metal deposition or after lift off to remove residues surrounding the NPs. Organic residues have been shown to have adverse effects on nanowire growth, such as multidirectional growth and unwanted NW nucleation. Therefore, subsequent ashing for approximately 10 nm or 40 nm with remove this residue after development and lift off respectively. This process has an undesired effect of creating unknown oxides. During NW growth, stable native oxides are known to be removed at specific temperatures, however, the oxides that ashing produces differ from the fresh native oxide. Hydrofluoric acid is commonly used in the semiconductor industry to etch oxides because of its stability with SCs. HF is therefore employed to remove the nonnative oxide developed by ashing. For EBL fabricated arrays, this is done with buffered HF before metal deposition, and with HF 5 before MBE loading.

142 A recent study by Elias et al. investigated the effects of various organic residue removal techniques. They show through SEM analysis that regular cleaning processes involving acetone, IPA, and Milipour water were not enough to completely remove residues from nanoparticles. They therefore looked into the effects that plasma ashing had on oxide formation and showed that along with the original epi-ready oxides, and fresh native oxides, additional more complex oxides were formed due to $O_2$ diffusion.

Boulanger et al. showed the importance of HF dipping prior to loading into a MBE. Even though they are investigating GaP nanowire growth on Si, the result they observe in regards to oxide formation due to Au acting as a catalyst to form silicon oxide (a well-documented process) is still relevant. What is observed is that samples that were grown without HF dipping only grew from small segments of the Au seed particles, while samples with preloading HF treatment grew from the entire seeding particle. By use of FIB and Cross-sectional TEM analysis, they were able to show that Au particle alloyed with the Si substrate and thereby burying itself under the surface. Then, by initial heating of the substrate and the Au catalyzed oxide formation mention above, the Au particles become trapped underneath an oxide layer that is not removed by usual annealing conditions. Therefore, proper VLS nanowire growth was only possible if the oxide capping layer was removed prior to MBE loading to ensure all of the seeding material is available for NW growth.

Though HF should be a relatively slow etcher on semiconductor, research shows that when HF comes into contact with metal on a semiconductor surface, the metal will act as a catalyst, speeding up the etching in the vicinity. This principle has been deemed metal assisted chemical etching (MACETCH) and has been used in a variety of applications in the realm of nanowires [56, 55, 143]. MACETCH has demonstrated to allow for controlled top-down fabrication of semiconductor NWs. Because of this, one must take care of the pre-MBE HF dipping to
ensure that the particle does not etch the substrate and expose unwanted surfaces and only etches away oxides.

Figures B.1a and B.2a show the results of 5% HF dip for 10s mimicking the process before MBE loading. As one can see from the SEM images, no noticeable etching has occurred around the nanoparticles. One will notice the distinct halo formation around the nanoparticles. This is caused by the previous bHF process, which is before metal deposition. This occurs since the EBL processing utilizes a double layer resist, with the bottom layer being a co-polymer, which will act as an undercut to help with liftoff. Once this resist layer is exposed and developed, the co-polymer etch a larger circle compared to the PMMA, thus aiding in the final resist liftoff. This larger area allows for the bHF to come into contact with a larger area than where the metal is defined by PMMA and etching the surface, thus tracing out this distinct halo around the NP.

To test the stability of the HF dip, a new set of samples were subjected to a 2min HF dip Figures B.1b and B.2b. What can be seen is that no noticeable etching has yet occurred around the NP. When referring to HF etching rates, this is characteristic behaviour of HF at room temperature, and in the literature to do with MACETCH, the solutions are normally at elevated temperatures to further enable this catalytic etching. It can therefore be confirmed that the HF dip prior to MBE loading has no undesired effect.

\begin{figure}[h]
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\caption{GaAs (111)B HF Ag}
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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig_b2}
\caption{GaAs (111)B HF Au}
\end{figure}
Figure C.1 – GaAs(111)B: Cooling neck for both 30 min growth and 60 minute growth. Same growth conditions. False black background
Figure C.2 – GaAs (111)B: As Density Series Data

Figure C.3 – GaAs (111)B: As Density Series Data
Appendix D

EDS Analysis

D.1 Data Acquisition

To acquire the EDS data seen in Fig. D.1(b) and throughout chapter 4 the arrays annealed in the MBE and the MOCVD are loaded into a Jeol 7800F SEM equipped with a Oxford Instruments EDS detector. The samples are cleaved through the arrays and loaded onto a cross section sample holder. The NPs are imaged similar to the SEM images shown in Fig. D.1(a). Using Oxford Instruments AZtec software point scans are made at locations denoted in Fig. D.1(a). The acquisition time was set to around 2 minutes. Data is found similar to Fig. D.2.

D.1.1 Data Analysis

The EDS data is analyzed by loading it into Matlab. A script was written to analyze the data and give a plot similar to Fig. D.1. This script work as follows:

- First, the background is subtracted by using Kramers Law. Each peak corresponds to a certain element and has a characteristic energy. Knowing the elements in the sample allows us to determine which element corresponds with each peak.
- The peaks for Ga and As are fitted with a Gaussian curve and the full width of half maximum of each peak is calculated and used to find the two energy boundaries of the peak.
- The area enclosed by this peak is found by integrating over the full width at half max.
- This analysis is iterated over all the scan locations. As the scan location changes, the area of the Ga and As peaks shifts as the composition changes as shown in Fig. D.2
- A ratio between the Ga and As areas is calculated. We make the assumption that the substrate at the lowest point scan point (red diamond in Fig. D.1) should have an equal stoichiometry (1:1 for GaAs). This is used to calibrate all the other ratios.

This is how the data in Fig. D.1 is calculated. What is observed is that there is a shift in the Ga:As stoichiometry with a decrease in the As molar fraction compared to the Ga molar fraction as the scan goes from bottom to top.
D.1. DATA ACQUISITION

Figure D.1 – (a) Cross-section SEM of a Ag and Au NP showing the point scan locations corresponding to the data in (b).

Figure D.2 – EDS Spectra of a Au NP annealed at 600 °C. The peaks are Ga, As, and Au.
Appendix E

Additional Annealing Experiments

Figure E.1 – Annealing of Ag NP arrays on InAs(111)B

(a) 250 °C. Diameter: 150 nm, Pitch 0.5 µm
(b) 550 °C. Diameter: 150 nm, Pitch 0.5 µm
Figure E.2 – Annealing of Au NP arrays on InAs(111)B

(a) 250 °C. Diameter: 150 nm, Pitch 0.5 µm  
(b) 550 °C. Diameter: 150 nm, Pitch 0.5 µm

Figure E.3 – Annealing of Cu NP arrays on InAs(111)B

(a) 250 °C. Diameter: 150 nm, Pitch 0.5 µm  
(b) 550 °C. Diameter: 150 nm, Pitch 0.5 µm
APPENDIX E. ADDITIONAL ANNEALING EXPERIMENTS

Figure E.4 – Annealing of Cu NPs on GaAs (100).

(a) 250 °C. Diameter: 100 nm, Pitch 0.5 µm
(b) 600 °C. Diameter: 150 nm, Pitch 0.5 µm.
Appendix F

Experiment List
Table F.1 – MOCVD Annealing Experiment List. Annealing time was up to annealing temperature and annealed for 7 minutes and then down. Annealing was preformed with a As overpressure of 20 sccm. Total metal thickness set to 15 nm.

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Table F.2 – MBE Annealing Experiment List. Annealing time was up to annealing temperature and down again. GaAs and InAs annealing was preformed with a 6E-6 torr and 1.5E-5 torr As overpressure respectively. 250°C degassing preformed without As overpressure. Total metal thickness set to 15 nm.

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Table F.3 – MOCVD Thin Film GaAs NWs grown Temperature Series

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Table F.4 – MOCVD Thin Film GaAs NWs grown Parameter Series.

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Table F.5 – MOCVD GaAs NWs grown from EBL arrays

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<tr>
<td>GaAs(100) Ag2/Au</td>
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<tr>
<td>GaAs(111)B Au(T)/Ag(B)</td>
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