Growth and Characterisation of Gold-seeded Indium Gallium Arsenide Nanowires for Optoelectronic Applications

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University

Amira Saryati Ameruddin

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Declaration

This thesis, to the best of my knowledge and belief, does not contain any results previously published by another person or submitted for a degree or diploma at any university except where due reference is made in the text.

Amira S. Ameruddin
Department of Electronic Materials Engineering,
Research School of Physics and Engineering,
College of Physical and Mathematical Sciences,
The Australian National University,
Canberra, ACT 2601,
Australia.
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Publications


Abstract

Semiconductor nanowires have been the spotlight of the last two decades owing to their novel properties and quantum confinement properties with their unique rod-like structure. In particular, III-V semiconductor nanowires have been shown as promising candidates to serve as building blocks in electronic and optoelectronic devices such as transistors, lasers, light emitting diodes, photodiodes and solar cells. Among the III-V semiconductors, ternary III-V alloy semiconductors such as In$_x$Ga$_{1-x}$As have the advantage of tunable bandgap by varying their alloy composition. In$_x$Ga$_{1-x}$As has a bandgap that is tunable in between GaAs (870 nm) to InAs (3500 nm) covering the important wavelengths used in optical telecommunication systems and sensing in near infra-red region. Therefore, it is essential to gain an understanding and control of ternary nanowires in terms of their composition, crystal structure and morphology prior to incorporating them in device applications.

This thesis presents a progressive advancement of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth by metal-organic vapour phase epitaxy (MOVPE), towards achieving highly uniform composition, morphology and pure crystal phase. Several techniques have been employed to investigate the nanowire properties. Scanning and transmission electron microscopy, atomic force microscopy, X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) have been used for structural and compositional analysis, while photoluminescence (PL) has been used to provide insight into their optical properties.

Pure zinc-blende (ZB) phase In$_x$Ga$_{1-x}$As nanowires are obtained via two-temperature growth method. The two-temperature growth method involves growing an initial stub at a higher temperature. Then, a lower growth temperature is employed as the growth continues. Low-temperature growth is found to be a non-competitive regime for the two group III species favouring higher In concentration to be incorporated into the nanowire either via the vapour-liquid-solid (VLS) mode or the vapour-solid (VS) mode on the nanowire sidewall. In$_x$Ga$_{1-x}$As nanowires with highly homogenous composition and pure ZB phase are achieved when the In incorporation rates in both modes are equivalent.
Homogenous composition along and across the In$_x$Ga$_{1-x}$As nanowires can also be achieved at relatively high temperatures with tunable phase. Detailed TEM analysis in combination with the EDX show that the crystal phase is dependent on the V/III ratio, and correlates with the Ga incorporation rate in the nanowire. The composition and crystal phase is tunable with V/III ratio and Au seed particle size. In particular, pure wurtzite (WZ) phase, uniform and taper-free nanowires are obtained with a combination of relatively high growth temperature, low V/III ratio and small diameter Au seed particle. The optimized pure WZ phase nanowires capped with InP show luminescence properties around 1.54 µm, a wavelength region of importance to the optical fibre telecommunications.

Understanding the growth evolution of In$_x$Ga$_{1-x}$As nanowires is improved by developing a model based on a nucleation kinetics approach. The modelling correlates well with the experimental results revealing the key factors governing the composition and growth rate of In$_x$Ga$_{1-x}$As nanowires. Small diameters and low V/III ratios result in As-limited regime VLS growth while for larger diameter nanowires and higher V/III ratios, the growth is group III limited. The In content in the nanowires is noticeably larger than that in the vapour phase and this is found to be highly related to the high In diffusivity at higher temperatures and low cracking efficiency of the Ga precursor at lower temperatures.

Finally, tunable emission wavelengths of In$_x$Ga$_{1-x}$As /InGaP core-shell structures within the range of 1100 – 1420 nm are achieved by tuning the shell thickness. The growth of the complex ternary/ternary system is studied using TEM and EDX analyses, revealing some challenges in the growth of the ternary shell on the pure phase WZ and the defective ZB phase In$_x$Ga$_{1-x}$As nanowires. Despite the challenges, the emission from the In$_x$Ga$_{1-x}$As core can be tuned by changing the shell thickness, indicating a strain related blue-shifting of the In$_x$Ga$_{1-x}$As bandgap.

Overall the thesis makes a significant progress in understanding the growth of Au-seeded In$_x$Ga$_{1-x}$As nanowires. From the systematic study, the growth of highly uniform In$_x$Ga$_{1-x}$As nanowires grown via Au-seeded VLS method is demonstrated. A growth model is developed to further understand the growth mechanism. The optimized nanowires in combination with an InP or InGaP shell show luminescence properties which is tunable within the near infra-red region that is promising as future optoelectronic building blocks for near infra-red applications.
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>A.U</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>As</td>
<td>arsenic</td>
</tr>
<tr>
<td>AsH₃</td>
<td>arsine</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>BSE</td>
<td>back scattered electrons</td>
</tr>
<tr>
<td>DI</td>
<td>de-ionised</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
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<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
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<tr>
<td>FESEM</td>
<td>field-emission scanning electron microscopy</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>Ga</td>
<td>gallium</td>
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<tr>
<td>HAADF</td>
<td>high angle annular dark field</td>
</tr>
<tr>
<td>In</td>
<td>indium</td>
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<tr>
<td>MOVPE</td>
<td>metal organic vapour phase epitaxy</td>
</tr>
<tr>
<td>P</td>
<td>phosphorous</td>
</tr>
<tr>
<td>PH₃</td>
<td>phosphine</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PLL</td>
<td>Poly-L-lysine</td>
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<tr>
<td>QD</td>
<td>quantum dot</td>
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<tr>
<td>QW</td>
<td>quantum well</td>
</tr>
<tr>
<td>QWR</td>
<td>quantum wire</td>
</tr>
<tr>
<td>QWT</td>
<td>quantum well tube</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SAED</td>
<td>selected area diffraction pattern</td>
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<tr>
<td>SE</td>
<td>secondary electron</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TMGa</td>
<td>trimethylgallium</td>
</tr>
<tr>
<td>TMIn</td>
<td>trimethylindium</td>
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</table>
**VLS**  vapour-liquid-solid

**VS**  vapour-solid

**WZ**  wurtzite

**ZB**  zincblende

**µ-PL**  micro-photoluminescence
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Chapter 1

Introduction

Overview

Nanowires, nanowhiskers, nanobelts or in general, 1-dimensional (1D) semiconductor nanostructures have been the subject of intense research in the past few decades since the first attempts at understanding their growth mechanism by Wagner and Ellis in the 1960’s and Givargizov in the 1970’s [1], [2]. In the late 1990s, the research expanded significantly to include not only interest towards the understanding of fundamental nanowire growth, but also exploration of their electronic and optical properties as well as for device applications [3]–[11]. As part of the still expanding effort in the field of semiconductor nanowire research, this thesis is focused on trying to understand the fundamental nanowire mechanisms, especially of the ternary compound semiconductor, indium gallium arsenide (InGaAs or In$_x$Ga$_{1-x}$As). The study covered in the thesis provides insight into the foundation of ternary compound semiconductor nanowire growth, which is highly tunable for various device applications including transistors, lasers, photodiodes, solar cells and many more high-speed electronic and optoelectronic devices. This chapter provides a brief introduction to InGaAs semiconductor, review the challenges and progress of ternary III-V semiconductor nanowires including InGaAs and briefly discusses the outline of the thesis.
1.1 Ternary In$_x$Ga$_{1-x}$As semiconductor material

In$_x$Ga$_{1-x}$As system is one of the most interesting III-V ternary alloy semiconductors because of several key properties such as very high carrier mobility ($\mu_e \approx 10000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_h \approx 300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and a large range of direct bandgaps tunable between InAs and GaAs. For example, In$_x$Ga$_{1-x}$As can be tuned to the telecommunication wavelengths range of 1.3 - 1.55 $\mu$m (0.80 - 0.95eV) and to an even longer wavelength (near infra-red, NIR) region for detection applications such those used in agriculture at 1.9 $\mu$m (0.65 eV) and in environmental monitoring [12].

![Figure 1.1: Band gap versus lattice constant diagram for the common semiconductor materials. Highlighted line represents InGaAs while the vertical line across InP shows the lattice matched condition of In$_{0.53}$Ga$_{0.47}$As to InP.](image)

Figure 1.1 shows the common semiconductor bandgap versus lattice constant at room temperature, highlighting the line representing In$_x$Ga$_{1-x}$As alloys. As can be observed, In$_x$Ga$_{1-x}$As bandgap can be tuned from $\sim$0.35 to 1.424 eV and the lattice constant varies between $\sim$5.6 to above 6.0 Å.
The lattice constant of In$_x$Ga$_{1-x}$As given by Vergard's Law is:

$$a = 6.0583 - 0.405 (1 - x)$$

At room temperature (300 K) the dependency of the energy gap on the In content $x$ can be calculated using an equation given by [13] as follows:

$$E_g(x) = 1.425 - (1.501) x + (2 \times 0.436) x^2 \text{eV}$$

In$_x$Ga$_{1-x}$As can be lattice matched to InP by tuning the composition to In$_{0.53}$Ga$_{0.47}$As which is highly desirable especially in growing 2-D structures where lattice-matching is required. However, in nanowire form, a higher level of strain can be accommodated thus In$_x$Ga$_{1-x}$As can be combined together with many other materials such as Al$_x$Ga$_{1-x}$As, In$_x$Ga$_{1-x}$P, In$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ a nanowire heterostructure which can provide an extension to their tunability of properties through bandgap engineering. Heterojunction is highly important in making semiconductor devices [14]. The concept of nanowire heterostructures will be further discussed in chapter 2. In$_x$Ga$_{1-x}$As properties together with other advantages of nanowires as shall be discussed later in chapter 2, makes In$_x$Ga$_{1-x}$As nanowires desirable for nanowire devices. In the following section, a review on ternary III-V nanowire growth including InGaAs nanowires and their applications are presented.

### 1.2 Ternary III-V semiconductor nanowires

A wide range of semiconductor materials such as group IVs, III-Vs, II-Vs, oxides and II-Vs for nanowire growth have been investigated in the last decades [3], [4], [9], [15]. In particular, III-V materials have been of great interest due to their outstanding properties [3], [5], [11], [16]. Extensive efforts have been dedicated to synthesizing and optimizing III-V nanowires because of their demonstrated superior optoelectronic properties, but efforts have focused largely to date on binaries and their heterostructures. Ternary III-V alloys such as In$_x$Ga$_{1-x}$As, In$_x$Ga$_{1-x}$P, InAs$_x$P$_{1-x}$ and GaAs$_x$Sb$_{1-x}$ on the other hand have not yet been explored as deeply as the binary nanowires despite of their ability to access a larger controllable range of bandgaps, which in turn provides more room for tunability of their optical emission/absorption.

Contrary to binaries, where composition homogeneity is achieved simply by ensuring strict stoichiometry, easily accessible under a broad range of growth parameters,
ternary nanowires suffer from intrinsic issues of composition inhomogeneity or variation over certain growth directions. Composition homogeneity is highly essential as a prerequisite to use III-V ternary nanowires in device applications. This is to avoid additional problems such as severe electron scattering [17], induced strain field or any other additional problem due to the alloy fluctuation in the crystal, such as alloy ordering affecting the bandgap of the material [18]. In addition to homogeneity, having control over the composition range is important as to be able to provide the range of properties afforded by the appropriate choice of alloy composition.

Nevertheless, other common challenges encountered with many nanowires such as controlling the morphology and crystal structure of the nanowires are equally important and not avoidable for III-V ternary nanowires as shall be discussed later in this section. In fact, they are even more challenging as more consideration has to be taken into account for the alloy composition. Hence, there is still plenty of room for further understanding and optimizing ternary III-V nanowire growth for device applications. This section gives an overview of the existing knowledge on growth and characteristic properties of ternary III-V nanowires focusing on In$_x$Ga$_{1-x}$As nanowires including recent development of In$_x$Ga$_{1-x}$As nanowire device applications.

### 1.2.1 Growth of ternary III-V nanowires

As with other semiconductor nanowires, ternary III-V semiconductor nanowires can be grown via the common nanowire growth methods such as vapour-liquid-solid (VLS) (foreign metal seed or self-seeded) and direct (particle-free) vapour-solid (VS) growth through methods such as selected-area epitaxy (SAE). These basic concepts of the growth methods will be further discussed in chapter 2. In this chapter, the focus is to give a review on the progress and challenges of ternary III-V nanowire growth including In$_x$Ga$_{1-x}$As nanowires. The review is split into the two, based on their method of growth to provide the insight on the different challenges faced by each method.

#### 1.2.1.1 VLS growth of ternary III-V nanowires

The VLS growth mechanism for binary III-V nanowires has been fairly well developed and shown to be able to control the crystal structure, size and morphology of various systems including GaAs, InAs, InP, GaP, GaSb, InSb [19]–[25], and nitride-based systems [26], [27].
Hence it is obvious that the fundamental mechanisms of VLS growth for ternary III-V nanowires should be similar to their binaries, but more intricate due to the additional species involved.

Early VLS growths of ternary III-V nanowires include GaAsP and InAsP [28], InGaN [29], AlGaN [30], AlGaAs [31], [32], and InGaAs [33]. Growth of Au-seeded GaAsP and InAsP nanowires was considered successful using laser-assisted catalytic growth method with composition close to the given target composition [28]. The nanowires show nearly pure zinc-blende phase and were uniform in diameter along the length of the nanowires, which exceeded 10 µm [28]. However no composition tunability was reported in this initial growth report. On the other hand, the growth of self-catalysed In$_{x}$Ga$_{1-x}$N via low-temperature halide chemical vapour deposition has been shown to be successful across the entire compositional range x=0-1 by Kuykendall et al. [29]. As indicated by the transmission electron microscopy (TEM) contrast for their InGaN nanowires, no phase segregation or any large variation of In distribution was observed. This was believed to be due to the low-temperature process and the ability for nanowires to relieve strain as compared to growth of InGaN thin films. However, their nanowires completely lacked control in terms of morphology, dimensions and growth directions.

Despite the demonstration that the global composition in a nanowire ensemble could be tuned over the full composition range, further studies on single nanowire revealed a more complex behaviour. Detailed studies of VLS grown AlGaN [30], AlGaAs [31], [34], InGaP [35], InGaAs [36] and GaAsP [37] nanowires show similar trends in terms of composition inhomogeneity along the nanowire growth axis. This inhomogeneity is believed to be due to the competitive mode of VLS growth and the vapour-solid (VS) growth on the sidewall of the nanowires [30], [31], [36].

Among these reports, Lim S. K. et al. [34] managed to control the tapering effect and minimise the inhomogeneity of the composition of Al$_{0.10}$Ga$_{0.84}$As by growing the nanowires at low temperature (420 °C) and low V/III ratio (20.0) [34]. This control was achievable based on their understanding of how radial VS and axialVLS growth modes are affected by accessible by the growth parameters during metal-organic vapour phase epitaxy (MOVPE) growth. In their proposed mechanism, the decomposition rate of TMG and TMAI together with diffusion rate of the adatoms were claimed to be responsible for the formation of the spontaneous core-shell structure. Although the resulting samples were homogenous in composition, their study did not focus on controlling the growth direction, hence straight nanowires were not achieved, likely due to them growing on GaAs (100) substrates. Straight
nanowires are important for many device applications and are required to allow for controlled heterostructures to be formed within the nanowires (where crossing and merging would occur for nanowires grown in random directions).

Later in 2010, Wu et al. [38] reported that vertical Au-seeded InGaAs nanowires can be grown on InAs (111)B substrate with reasonable uniformity within a limited length. Non-uniformity was claimed to be due to the competition of In adatoms towards the axial and the radial growths. By controlling the In diffusion area and only promoting axial growth, nanowire tapering was minimised, which in turn, resulted in better composition uniformity. They found that the diffusion area can be controlled by density of the seed particles. This is similar to the previous work shown in ref. [33] where InGaAs nanowires grown in high density region had better morphology with less tapering. However, this method is limited by the diffusion length of In adatoms from the substrate towards the growth front. Longer nanowires will eventually be tapered due to the insufficient diffusion length of In adatom from the substrate [38]. Furthermore, the nanowires had stacking faults which are undesirable [39] and can promote more radial growth [40].

Aside from the composition inhomogeneity, the composition of ternary nanowires was often found to be significantly different in the nanowires than the ratio of the precursors used in the gas phase [36], [41], [42]. For example in GaAsP nanowires, P incorporation into the nanowire via VLS is different than the expected incorporation in thin film growth which indicates that a different kinetic approach has to be taken into account in understanding the growth of ternary alloy semiconductor nanowires grown by the VLS method [42]. Growth of InAsSb also shows that incorporation of Sb radially differs from the VLS grown core [43]. In other cases, limitation of species incorporation into solid nanowire were reported [36], [44]. This in turn limits the composition tunability of the alloy composition. For instance, in Ga-assisted growth of InGaAs nanowires, Heiss et al. [41] were only able to incorporate 3-5 % In into the core of their nanowires while the rest of the In are found to deposit on the sidewalls forming In-rich quantum dots. Similar findings were reported for growth of Ga-seeded InGaAs segments on GaAs nanowires where In only contributed to an increase of diameter but was insufficient to incorporate into the nanowire core [45]. On the other hand, Guo et al. [36] reported that InGaAs nanowires grown using Au seed had to surpass a certain In threshold in the Au alloy to be incorporated into the nanowire.

Ghalamestani et al. [46] showed that the composition of InGaSb nanowires can be affected by growth temperature and related this effect to the Au-In-Ga phase diagrams. It
was claimed that the phase of the Au-alloy might change with temperature and in their case, Ga was found to be more thermodynamically favoured in the Au-alloy at higher temperatures (>450 °C) leading to more Ga incorporated into the nanowires. Hence, the role of Au is much more critical in ternary nanowires as it can determine their final composition. Therefore it is essential to gain more knowledge of the growth mechanism of Au seeded ternary nanowires.

The presence and the amount of an additional species can affect the composition of the alloy particle which in turn changes the nucleation energy at the interface of Au particle-nanowire, thus affecting the nanowire crystal phase and morphology [43]. The interplay between the alloy composition and nucleation energy can also be observed in the growth of axial heterostructures involving ternary alloys where an additional species is introduced to a binary stem such as in growth of Au-seeded InGaAs on GaAs [47]. In such system, the heterointerfaces indicates that there is a significant difference in between different interfaces (ie; InAs/InGaAs and InGaAs/InAs interface) indicating that the VLS method is sensitive to change in composition and indicates that In can be residual in the Au alloy even after In supply is ended. In the case where tunability of alloy composition was achieved (InGaAs and GaAsP nanowires) [48], [49], the crystal phase was shown to be affected by the composition, although no clear trend was observed.

From these reports, it is clear that the composition plays a large role in controlling the crystal phase, which result from the change at the alloy particle-nanowire interface. However no clear understanding is yet presented for such a trend. These trends clearly indicate that alloying phase and composition of the seed particle is highly important and solubility of individual species may affect the final nanowire composition when growing ternary nanowires.

Other than the composition inhomogeneity caused by the competition between VLS and VS growth modes, there are also reports on segregation of species in certain facets in ternary nanowires leading to inhomogeneity of composition across the nanowire. For example, As-rich bands in the corner of the side facets has been observed in GaAsSb [50], [51]. Other ternary nanowires such as InGaAs and GaAsP also show In-rich and P-rich bands in the <112> direction respectively [37], [52]. Similar type of segregation has also been previously observed in AlIn1-xP shell [53], [54], AlGaAs shell nanowires [55]–[58] and more recently reported in GaAsP shell [59] grown on GaAs core nanowire. The mechanism behind the formation of this segregation is believed to be due to the difference in adatom diffusion length on different facets [53]. Although it leads to inhomogeneity in the nanowire, this
spontaneously formed segregation can be beneficial in designing the quantum confinement region within a nanowire [60].

Overall from these reports, VLS ternary III-V nanowires including InGaAs are yet to be optimised for simultaneously achieving composition homogeneity, crystal phase purity and desirable untapered vertical morphology suitable for device applications. Correlation between crystal phase and composition has been presented and remains as an interesting area to be explored. Such observation can provide more knowledge on the limitation and interplay between the composition and crystal phase of VLS nanowires. The growth of VLS ternary III-V nanowires is certainly complex, particularly when involving other metals such as Au. Understanding the growth mechanism behind all these observations is required to control the growth of ternary nanowires with desired properties.

1.2.1.2 Particle/droplet free growth of InGaAs nanowires

Apart from VLS growth, ternary III-V nanowires can also be grown without the apparent use of a droplet. Self-assembled growth of In$_{x}$Ga$_{1-x}$As nanowires grown on Si reported by Shin et al. [61] show composition inhomogeneity despite of being taper-free. The inhomogeneity was indicated by the strain related bending their nanowires. The composition was also found to be related to the crystal phase where In-rich InGaAs had a higher density of ZB segments than the Ga-rich InGaAs. However over the wide range of composition reported, nanowires are highly defective [61]. On the other hand, pure WZ phase micro-sized InGaAs pillars were reported with high composition uniformity as shown by EDX mapping of the pillars [62], [63]. However these large cone-shape pillars and the low density could limit their application in devices.

Growth of InGaAs nanowires on graphene were successfully demonstrated using van der Waals epitaxy [64]. However the nanowires spontaneously formed a core-shell structure with InAs core and InGaAs shell. The core-shell structure was elucidated due to the use of graphene substrate, where InAs core was formed as its lattice parameter was nearly matched to that of the graphene substrate.

SAE growths of tunable InGaAs nanowires with uniform composition along the nanowires have been reported [65]–[69]. A recent review of InGaAs nanowires grown on Si reported that the nanowires were more uniform in composition from wire to wire when grown by SAE as compared to self-assembled growth [70]. This was claimed to be due to the
uniform arrays contributing to a more uniform composition of InGaAs among the nanowires. However these nanowires grown by particle-free SAE methods still suffer from a high density of stacking faults [65]–[70].

From the limited amount of particle-free growth of ternary InGaAs nanowires, it can be concluded that these nanowires can be obtained with uniform composition far more easily due to the absence of a metal seed which creates anisotropy in adatom incorporation. However this growth method still faces severe challenges such as the lack of the crystal phase purity or the limitation in certain cases to tunability over a restricted composition range.

1.2.2 Application of ternary III-V nanowires in devices

Despite some issues in either the crystal phase or the composition, ternary III-V nanowires have already been used in some devices. Sun and Ng et al. [63], [71], have reported lasing in their InGaAs nanopillars grown on Si despite the In deficient segment within their structure. A good p-n junction was demonstrated in a photovoltaic device fabricated by Shin et al. using InGaAs nanowires despite the polytypic crystal structure [61]. Single GaAsP nanowire solar cell [72] and ternary nanowires transistors [73]–[75] were successfully fabricated and characterised. However, these reports do not give any structural or composition detail. Nonetheless the reported devices clearly highlight the potential of ternary nanowires.

Additionally, nanowire devices incorporating heterostructures containing ternary alloy materials have also been demonstrated as light emitters from InGaAs quantum dots embedded in GaAs nanowires [76]; InGaN multi quantum well laser [77], solar cells with InGaAs/GaAs axial junction [78] and InGaAs/GaAsP/GaAs LEDs [79].

All these reports briefly mentioned here, show that ternary nanowires hold great promise in becoming the building blocks that are tunable in bandgap and can provide a greater range of properties required for advanced device architectures. Through greater control and understanding of the growth fundamentals of ternary nanowires and their heterostructures, the control over their properties such as crystal phase, composition and morphology could be achieved, leading to devices with improved performance and functionality.
1.2.3 Ternary III-V nanowires review summary

In summary, the brief review of the growth of ternary group III-V has been presented. Ternary III-V nanowires are challenging due to the composition inhomogeneity of the alloy within the nanowire. Despite some of the reported composition homogeneity, there are still some issues such as defects, crystal phase control, tapering, and time dependent limitation as presented briefly in this chapter. Hence, this thesis is devoted towards understanding the growth of one ternary alloy III-V semiconductor, \textbf{InGaAs}. The objective is to gain in-depth knowledge of how Au-seeded InGaAs nanowires grow under different growth conditions and how to control the growth and properties of these Au-seeded InGaAs nanowires to simultaneously achieve desired morphological, crystal phase and composition homogeneity. Composition tunability and the effect of composition on the crystal structure are two other interesting areas to be further understood in order to be able to control growth of ternary nanowires. By having control of the composition of ternary nanowires and their structural properties, more complex heterostructures and devices can be realised with improved performance.

1.3 Thesis synopsis

This thesis is divided into 8 chapters.

The first (current) introduction chapter includes the basics of InGaAs as a semiconductor material, a brief review of ternary III-V nanowires and introduces the global aims of this thesis. This chapter also highlights the areas which require attention which could be enhanced further to improve our knowledge in understanding the growth mechanism of ternary alloy nanowires, especially InGaAs nanowires which has great potential in high-speed telecommunication and near infra-red application.

Chapter 2 discusses the basic concepts of semiconductor nanowires, growth of nanowires and their heterostructures and their crystallographic structural properties.

Chapter 3 describes the experimental technique used in this study. The first section in this chapter explains the growth method used for growing InGaAs nanowires including the wafer preparation and MOVPE. The following 4 sections in the chapter briefly discuss the techniques used to characterise the nanowires including electron microscopy and photoluminescence technique.
In chapter 4, the results obtained via two-temperature growth method are discussed. Although the two-temperature growth technique has been a great success to synthesise high quality GaAs nanowires, it is more challenging in growing ternary InGaAs nanowires which results in further complexity. This chapter discusses the effect of growth temperature, precursor ratios and vapour composition. Albeit challenging, successful InGaAs nanowires with pure ZB phase could be achieved for high In content (In$_{0.95}$Ga$_{0.05}$As). Such nanowires are useful to replace InAs nanowires as they have lower leakage current due to the larger bandgap with the introduction of Ga. Hence, it is highly important to be able to grow such structures with highly pure crystal phase in order to realise fast-switching devices which require high electron mobility.

In chapter 5, growth of InGaAs nanowires aiming at a uniform pure WZ crystal structure and high compositional homogeneity is presented. V/III ratio is shown to have control over the tunability of InGaAs composition and crystal phase. The key factors for achieving uniform composition are summarised. In$_{0.65}$Ga$_{0.35}$As nanowires are shown to grow with negligible tapering, uniform composition and were shown to have strong emission at the desirable wavelength for telecommunications applications around 1.55 µm when capped with an InP shell.

A growth model is then proposed and developed to further understand the growth trend observed as detailed in chapter 6. The main factors affecting the axial growth rate and the composition of InGaAs nanowires are extracted based on correlation of the model to the experimental results. The model provides a better understanding on the growth of InGaAs nanowires.

Chapter 7 shows and discusses the results of InGaAs/InGaP core-shell heterostructures. It explores tuning of the bandgap of the InGaAs core using various shell thickness. The chapter also discusses the growth of InGaP shell on WZ phase InGaAs and ZB InGaAs nanowires. The bandgap of InGaAs nanowires is shown to be tunable using InGaP shell with various shell thicknesses.

Finally, conclusions and future work are provided in chapter 8 discussing the outcomes achieved from the thesis and potential research extension that can be followed to develop more knowledge and potential devices based on ternary and quaternary alloy nanowires.
References


1. Introduction


1. Introduction


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1. Introduction


1. Introduction


1. Introduction


1. Introduction
Chapter 2

Basic concepts

Overview

This chapter introduces the general concepts used throughout the thesis. It specifically focuses on semiconductor nanowire growth principles and their structural properties. These concepts make up the foundation for the interpretation and discussion of results presented in chapters 4 to 7. Sections 2.1 to 2.3 briefly introduce semiconductor nanowires, their heterostructures and applications. This is followed by nanowire growth concepts in section 2.4, focusing exclusively on metal seeded nanowire growth via vapour-liquid-solid (VLS) mechanism. This section also includes the challenges faced in growing nanowire heterostructures by VLS. The chapter then continues with III-V nanowire crystal structure including a brief discussion of crystal phase control reported for III-V Au seeded nanowires.

2.1 Semiconductor nanowires

Semiconductor nanowires are 1-D nanostructures with a diameter of the order of few to tens of nanometers and length of up to several micrometers (or even millimetres). Due to these dimensions, the properties of nanowires are found to be different than their bulk
counterparts. For example, the small diameter allows for quantum confinement in the 1-D direction, thereby enabling the tuning of the optical and electrical properties with diameters [1]–[4]. The large surface area of nanowires and proximity of the surface to the core make them sensitive to changes on the surface thus making them suitable for applications such as chemical/biological sensors [5] and gas detectors [6]. Additionally, their large surface-to-volume ratio also enables effective strain release which is an advantage for various heterostructures required for semiconductor devices [7]. Furthermore, their geometry also makes them great optical cavities, perfect for making tiny lasers [8]–[11]. This is highly promising for integration with nanoscale electronics enabling smaller, yet more functional devices for the future.

Another advantage of nanowires is the ability to grow in different crystal phase unlike bulk semiconductors. For example, many III-V nanowires can grow in the wurtzite (WZ) phase whereas in the bulk form they exist as zinc-blende (ZB) phase. WZ and ZB crystal phases have different bandstructures, which can provide another avenue for tunability. This shall be further discussed in section 2.4.

Due to these interesting properties, nanowires offer many opportunities for building nanoscale electronic and optoelectronic devices. In the electronics field, nanowire transistors have been realized [12]–[19] which shows the potential in further reducing the size of electronic chips and increasing the speed of devices. Multi-colour lasers [9], light emitting diodes (LED) [20]–[22], solar cells [23]–[25] and photodetectors [26], [27] are some other optical devices that have been demonstrated with nanowires. Furthermore, nanowires show the prospect for water splitting applications [28] and self-powering sensors [29]. Nanowires are also suitable for energy conversion other than solar cells such as electrochemical energy storage and thermoelectric applications [30], [31]. Other potential nanowire applications also include bio-applications such as single cell endoscopy [32].

2.2 Semiconductor nanowire heterostructures

Heterojunctions are formed when two semiconductors are brought together. They are engineered to create discontinuity in the band structure which affects the carrier flow at the interface. Heterojunctions within a single freestanding nanowire can be fabricated as shown in figure 2.1. Figure 2.1 (a) shows an axial heterostructure nanowire fabricated by switching
materials in the growth chamber and growing in modes that favour axial growth. On the other hand, figure 2.1 (b) shows a radial heterostructure nanowire by switching materials and growing in a mode that favours radial growth.

Due to the small dimensions of nanowires, quantum dots (QD) or quantum discs can be created within the nanowire structure simply by tuning the thickness of the axial heterostructures (figure 2.2 (a)). A similar approach in radial heterostructures results in a quantum well (QW) tube as shown in figure 2.2 (b). Figure 2.2 (c) shows an example of the bandgap of a heterojunction where electrons are confined in the thin layer of a smaller bandgap material.

**Figure 2.1:** Schematic diagrams of nanowire heterostructures. (a) axial nanowire heterostructure (b) radial (core-shell) nanowire heterostructure.

**Figure 2.2:** Schematic diagrams of (a) a quantum dot embedded in a free-standing nanowire (b) quantum well tube and (c) electronic bandgap of a heterostructure with a quantum confinement region. The solid circles represent the electrons while the hollow circles represent the holes in the semiconductor.
Forming quantum wires and 0D quantum dots along the nanowire length are also feasible by selectively growing these confined regions on certain facets or edges [33], [34]. Figure 2.3 shows the schematic of these structures and their cross-sections as adapted from [33], [34].

Figure 2.3: a) Quantum wire along the nanowire length formed by selective growth on the corners of the nanowire side facets. b) Formation of quantum dot in the corners of the side facets. Adapted from [33], [34].

Owing to the nanowire's small diameter and large surface-to-volume ratio, strain from lattice mismatch can be relieved effectively in nanowire structures while it is not possible with the planar system. Hence, various axial heterojunctions are possible despite large lattice mismatch [35]. Strained core-shell nanowire heterostructures have also been reported [36]–[38]. Strain alters the band gap structure thus altering the optical and electrical properties. Pistol and Pryor [39] have used $k.p$ theory to theoretically consider the band structures of various combinations of core-shell III-V nanowires without incorporating the likely occurrence of plastic relaxation. An example of band diagram and the band structure of a core-shell nanowire (InAs/GaAs) is shown in figure 2.4. From the observation of the bandstructure, the core size or the total radius can be chosen to tune the strain-induced properties as desired. For example, for InAs/GaAs shown in figure 2.4, as the core radius/total radius ratio becomes smaller, the bandgap of the core nanowire shifts towards larger value. A strained In$_x$Ga$_{1-x}$As/In$_x$Ga$_{1-x}$P core-shell nanowire heterostructure is presented in chapter 7 showing optical emission tunability with shell thickness.
Figure 2.4: Calculated band structure of InAs/GaAs core-shell structure showing a change of band alignment with the core radius/total radius ratio. A typical band diagram on the right is taken for the core radius/total radius ratio of 0.2. Image is taken from [39].

Although nanowire heterostructures can be fabricated and designed as discussed here, there are challenges in relation to their growth that can be unfavourable. Such challenges will later be presented in section 2.3.4.

2.3 Semiconductor nanowire growth

Semiconductor nanowires are most often grown using metal seed nanoparticles through the vapour-liquid-solid (VLS) method as first described by Wagner and Ellis [40]. Via this method, metal nanoparticles are introduced to assist the nanowire growth. Gold (Au) is the most widely used metal particle for the growth of semiconductor nanowires. Other foreign metals such as Cu, Ag and Ni have also been reported in the growth of semiconductor nanowires [41]–[44]. A promising sub-category of metal-assisted nanowire growth is the so called "self-catalysed" method, which use the metallic droplet from the group III elements of the nanowire system itself; e.g. Ga-assisted GaAs nanowires [45].
An example of the growth process for Au-seeded Si nanowire is shown in the schematic in figure 2.5. In growth of III-V semiconductor, the growth proceeds in similar manner although slightly more complex with more elements involved in the process. The Au nanoparticles first react with the substrate or reactant species and create a eutectic alloy of Au-reactants. With subsequent supply of reactants, the Au alloy nanoparticles become supersaturated and crystal nucleation begins at the interface of the liquid alloy and the substrate. As reactants supply continues, the crystal grows in a way that it is elongated beneath the particle forming nanowires. The nanowire growth direction depends on the total free energy of the system and the free energy of the particle/substrate interface. The nucleation theory of catalyst-assisted nanowire growth is presented in detail in section 2.3.1.

![Figure 2.5: Schematic of VLS growth of Si nanowires. The top image shows the growth progress as Si continues to alloy with Au. The bottom image shows the phase diagram as the process progresses from left to right (0 to III) with more Si incorporation in the Au-alloy.](image)

Another method for growing nanowires is selected-area epitaxial (SAE) growth method [46] shown in figure 2.6. This method involves using a partially open mask to guide the growth of the crystal. The mask is lithographically defined (e.g., using electron-beam (EB) lithography) with small opening patterns where the nanowires are to be grown. SiOx
and SiN, are among the common mask materials employed for this method. The mechanism behind the growth relies on the fact that nanowires have a preferential growth direction. This direction is typically in either <111>A or <111>B. As the crystal grows within the holes of the mask, the preferential growth direction will guide the morphology of the crystal, forming nanowires with certain facets based on the lowest surface energy. Although SAE growth produces a highly uniform array of nanowires, the throughput is much smaller due to the time consuming and cost issues related to mask preparation. On the other hand, Au-seeded nanowire growth can be produced in higher yield as required for large-scale mass production. Furthermore, Au-seeded VLS nanowire is now very mature for binary III-V systems, which helps both in terms of control (e.g. phase purity and complex heterostructures [47]–[50] and understanding via in-situ TEM studies [51]). Hence, VLS Au-seeded growth is used throughout this thesis and shall be further elaborated in the next section.

![Diagram of selective-area growth of nanowires](image)

**Figure 2.6:** Schematic of selective-area growth of nanowires using a combination of processes involving deposition of the mask, electron beam lithography, and growth of epitaxial nanowires.

### 2.3.1 Nucleation theory

Nanowire growth can be described by a mix of thermodynamic aspects and kinetic aspects which cannot be completely decoupled. To simplify here, in a thermodynamical view, the growth of nanowires proceeds in the direction that minimizes the total free energy of the system. This total free energy includes the bulk energy of the nanowire, the particle-nanowire (liquid-solid) interface energy and the nanowire-vapour (solid-vapour) interface energy. Several works have focused on the total energy calculations in order to understand
nanowires after they have been formed [52]–[54].

A schematic of the VLS growth is shown in figure 2.7 showing the components of the three-phase system, the supply (vapour), collector (liquid) and the crystal (solid). $\Delta \mu_{sk}$, $\Delta \mu_{sc}$ and $\Delta \mu_{ck}$ are the chemical potential difference (supersaturation) between the three phases (e.g. $\Delta \mu_{sk}$ is between supply and crystal). The triple phase boundary (TPB) is the perimeter around the particle-nanowire interface known as the growth front [52]–[54].

![Diagram of VLS growth](image)

**Figure 2.7**: Schematic of VLS growth with the supersaturation relevant to the three phase system. Reproduced from [55].

The change in Gibbs free energy due to nucleation can be expressed as the difference between the energy released from chemical potential and the energy needed to create a new interface. Hence, the free energy change at the TPB can be written as follows:

$$
\Delta G_{TPB} = -n\Delta \mu_{sk} + P_{ck}h s_{ck} + P_{sk}h s_{sk}
$$

(2.1)

where $P_{ck}$ and $P_{sk}$ are the perimeter length of the collector-crystal (ck) and supply-crystal (sk) respectively. $s_{ck}$ and $s_{sk}$ are the interfacial energy, $n$ is the number of atoms nucleated and $h$ is the height (often one monolayer). The second and third term of equation 2.1 relates to the edge energy at TPB. TPB is a preferable nucleation site due to the flexibility to minimize the Gibbs energy and the relatively higher supersaturation point due to direct contact with the vapour [55]. Once nucleated, the growth then follows as ledge formation and layer by layer growth as observed by in-situ TEM [51], [56]. This growth dynamic also holds for other types of catalytic growth such as vapour-solid-solid (VSS) [57].
The growth rate is given by the classical Zeldovich nucleation rate as follows:

\[ J = n \Gamma C v \exp \left( \frac{-\Delta \mathcal{G}}{kT} \right) \]  

(2.2)

where \( v \) is the frequency of attachment of molecules at the growth interface, \( \Gamma \) is the Zeldovich factor dependent on the change in Gibbs free energy of nucleation \( \Delta \mathcal{G} \), thermal energy \( kT \), number of molecules in nucleus \( n \) and \( C \) is the concentration of the growth species in the supply phase [52].

### 2.3.2 Phase diagram

The VLS growth of binary and ternary nanowires is more complex than the Si nanowires as briefly introduced earlier. The process involves at least three or four elements during the alloying process of the metal seed. Therefore, a ternary or quaternary phase diagram is required to understand the phase of the alloy particle during nanowire growth. In the case for Au-seeded InGaAs nanowires, at least the ternary Au-In-Ga phase diagram has to be considered. To be more precise, the quaternary phase diagram Au-In-Ga-As should be considered when growing ternary InGaAs. However, due to the lack of knowledge in this complex quaternary phase system, we rely on the existence of the available ternary phase diagram.

Figure 2.8 shows the ternary phase diagrams for Au-Ga-As, Au-In-As reproduced from Tsai and Williams [58]. They show eutectic pseudo-binary tie-lines between the III-V and the Au-III compounds with the eutectics near the Au-III binary edge. Pseudo-binary systems are pairs of phases that can exist in equilibrium without reacting with one another. For Au-GaAs, the GaAs region dominates under As-rich conditions. For Au-InAs, pseudo-binaries are found between As and the Au-In compounds \( \zeta_1, \zeta, \alpha_1 \) and \( \alpha \).
Due to the small amount of As presence in the Au particle (measured post-growth [59], [60]), the ternary Au-In-Ga phase diagram could be considered in providing a view of the possible phase of the Au alloy during growth of Au-seeded InGaAs nanowires. A calculated monovariant Au-In-Ga has recently been reported by Ghasemi et al. [61] together with their experimental investigation as shown in figure 2.9. From the diagram, the possible liquid phase of Au-In-Ga can be extracted which can be used to predict the ternary composition. The Au-In-Ga ternary phase is used in understanding the growth of InGaSb nanowires reported by Ghalamestani et al. [62].

**Figure 2.8:** Ternary phase diagram for a) Au-Ga-As and b) Au-In-As. Reproduced from [58].

**Figure 2.9:** Calculated monovariant lines (in red) of the Au–In–Ga system along with isothermal liquidus projections with 20 °C temperature increments. Green triangles represent the experimental liquidus temperatures. Figure is taken from [61].
Although the phase diagram may assist in understanding the resulting phase of the alloy particle [63], the exact phase can be difficult to assess. This is due to few reasons; i) the small scale of the alloy particle which can be governed by the Gibbs-Thomson effect, ii) challenge in determining alloy particle composition information during growth and iii) possible melting-freezing hysteresis especially in growth conditions where there are significant temperature changes during growth. With the complexity of a ternary or quaternary phase, understanding the phase of the alloy particle during growth can be more challenging, and naturally more uncertainty can arise. Furthermore, group V such as As could be well involved in the Au alloy particle and cannot be simply neglected despite the small As fraction in the Au alloy found post-growth.

2.3.3 Mass transport

The growth conditions and the final nanowire morphology can also be influenced by growth kinetics such as mass transport. While VLS mechanism drives the nanowire axial growth, radial growth is governed by the vapour-solid (VS) growth on the nanowires sidewall. The VS growth typically depends on the diffusion length of the adatoms and the preferable nucleation sites on the sidewall such as defects [64], type of facet and crystal phase [65]. VS growth on the sidewall is often needed to be suppressed to avoid nanowire tapering or enhanced to promote shell growth as is required for core-shell heterostructures. This shall be discussed in section 2.4.4.

Apart from the competing VS growth contributing to the radial morphology of the nanowire, the growth kinetics can also be axial growth rate limiting [66]–[69]. The amount of species that arrives at the particle-nanowire interface can be limited by the growth kinetics. There are three main routes for reactants to reach the particle-nanowire interface; i) incorporation of species from vapour into the liquid, ii) diffusion through liquid phase to the nanowire-particle interface and iii) incorporation from the liquid into the solid. The kinetics of each species depends on their properties such as diffusivity in liquid, diffusion length on the surface and desorption. These properties are highly dependent on the growth condition such as growth temperature.

Hence, in order to understand the growth of nanowires, both thermodynamic and kinetic approaches are essential and in some cases, one would be more applicable than the
other. In chapter 6, a growth model for InGaAs nanowires based on the kinetic approach is proposed.

2.3.4 Growth of nanowire heterostructures

As previously discussed in section 2.2, heterojunctions are the key to semiconductor devices. In the growth of axial heterostructures, nanowires release strain due to the lattice mismatch via expansion of the lattice at the interface [7]. Hence, defects can be avoided in high lattice mismatch heterojunctions unlike in the case of 2-D system where strain is released by introducing defects.

However, other challenges apart from the lattice constant constraint arise especially in the growth of VLS metal-seeded nanowires. For example, sharp interfaces are challenging in axial heterojunctions of Au-seeded nanowires due to the effect of reservoir in the Au-alloy particle [70], [71]. Lack of sharp interfaces degrades the quality and functionality of the heterojunction. Hence, many studies have been devoted towards understanding and improving the sharpness of the interfaces of axial [71], [72] and radial [73] heterostructure nanowires. In addition, introducing a different material into the growth chamber for the formation of axial heterojunctions changes the supersaturation condition leading to the formation of stacking faults, polytypism and nanowire kinking [74]–[76].

On the other hand, radial heterojunctions would adopt the crystal phase of the core, commonly known as the crystal phase transfer [77]. However, in different kind of crystal phase, the radial growth rates are different due to the surface energy of the facets. It has been found that the growth of shell on the WZ phase is much slower due to the nature of their facets [65], [78]. Owing to this nature of growth, selective shell growth can be performed [79].

Apart from defects transferred from the core, other defects may arise during the growth of the shell. For example, misfit dislocations can be introduced in a strained core-shell structure [80]–[83]. In recent work by Conesa-Boj et al. [84], a new type of cracking defects created during shell growth can also lead to the formation of secondary defects such as stacking faults.

An unfavourable concomitant radial or axial growth during the growth of heterostructures is another issue among the other challenges presented here [65], [66].
Hence, the growth of nanowire heterostructures remains as an interesting area to further explore and understand towards optimizing more complex heterostructures in the future. Chapter 7 of this thesis explores the growth of WZ and ZB phase In_{x}Ga_{1-x}As/In_{x}Ga_{1-x}P core-shell nanowire heterostructures.

2.4 III-V nanowire crystal structure

As previously mentioned, nanowires may grow in a different crystallographic sequence to their bulk counterparts. The most common crystal structures for III-V nanowires are ZB and WZ crystal phase. Although very similar, these two phases can be easily distinguished under transmission electron microscopy (TEM). Figure 2.10 depicts the structural difference between the ZB and WZ crystal phase. Along (111), the stacking sequence of a ZB phase follows the pattern ABCABCA while in WZ phase in ABABAB.

![Diagram](image)

**Figure 2.10:** Stacking sequence of the crystal phase for a) zinc-blende and b) wurtzite structure.

The structures are very similar apart from their stacking sequence and lattice constants. Due to the nature of nanowire growth in the <111> direction, the likelihood for the change in stacking sequence is very high and the structure can easily transform from ZB to WZ phase or vice-versa. There are several known stacking modes often found in ZB or WZ phase nanowires. For example, a twin occurs when there is a misplaced stacking in ZB resulting in the sequence ABCACBA. The stacking sequence changes direction mirroring the previous stacking sequence with A as the twin plane. Double twin may also occur, forming a
unit of WZ phase as underlined in the sequence ABCACBC. In WZ phase, a stacking fault can occur when the sequence is misplaced forming the sequence ABA\text{BCBCB} where ABC is a ZB unit within the surrounding WZ. To observe these sequences, nanowires are examined in TEM in the zone axis, [110] for ZB phase or [1120] for WZ phase. Sourribes et al. 2014 [85] have presented various types of planar defects and its stacking sequence with three main categories as shown in figure 2.11 with the respective TEM images.

![TEM images with the stacking sequences in InAs and InAsAsb nanowire showing pure phase WZ and ZB together with several kinds of defects including rotational twins and stacking faults. Figure is taken from [85].](image)

Despite the similarities in the structure of ZB and WZ, their electronic properties were reported to be altered depending on the structural phase [86], [87]. WZ/ZB segments in nanowires may form type I or type II band alignment which can very much depend on the size of the segments and nanowire diameter [88]–[91]. While controlled polypytism provide room for bandgap engineering, random polypytism and crystal defects may deteriorate the nanowire properties and device performance [85], [92]. Driven by these two aspects of polypytism, understanding and control of the nanowire crystal phase and formation of defects from theoretical and experimental parts has been studied immensely [49], [93]–[101].

The crystal phase of VLS grown nanowires depends on the supersaturation condition and the surface energies at the Au-particle and the nanowire interface [53], [99]. The V/III ratio, in particular, has been found as one of the main factors governing the crystal
phase [48], [96], [102]-[104]. Lehmann et al. [102] observed that WZ to ZB transition can occur on both sides of the V/III ratio regime with WZ being in the mid-range and are highly sensitive. WZ/ZB crystal phase switching has also been reported with sources supply pulsing [47], [105]. From these reports, it can be clearly observed that crystal phase is highly affected by either group III or V species via the change in the surface energy at the nanowire-particle interface affecting the supersaturation. Chapters 4 and 5 of this thesis discuss some of the findings required to optimize the crystal phase purity and phase control of In$_x$Ga$_{1-x}$As nanowires.

2.5 Summary

The chapter presented several key concepts widely used throughout the thesis. The basics of nanowire growth have been introduced, with emphasis on the VLS mechanism. The chapter also presented some of the growth challenges of nanowire heterostructures via VLS technique. Lastly, III-V nanowire crystal phases were introduced including some of the reports on crystal phase control and the advantage of controlled polytypism.
References


2. Basic concepts


2. Basic concepts


2. Basic concepts


2. Basic concepts


2. Basic concepts


2. Basic concepts


Chapter 3

Experimental techniques

Overview

This chapter discusses the experimental techniques and procedures used throughout the thesis for sample growth, and structural and optical characterisation. Basic principles of each technique are briefly discussed and the main methods of analysis are presented.

3.1 Introduction

This chapter represents the overview of the experimental techniques used to grow and characterise nanowires in this thesis. This includes the growth using metal-organic vapour vapour epitaxy (MOVPE), morphological and structural characterisation using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), compositional mapping using scanning transmission electron microscopy energy dispersive X-ray (STEM-EDX) spectroscopy and optical properties measurements using photoluminescence (PL) setup. In this chapter, I include the basic principles of each technique that are highly relevant to the work presented in this thesis. I used all of the techniques mentioned above to grow and characterise my samples except for PL measurements at the longer wavelength range, which were carried out in collaboration with University of Oxford.
The chapter begins with the basics involved in growth of nanowire by MOVPE followed by the characterisation of the nanowires using electron microscopes, SEM and TEM. Then, the basic STEM-EDX operation and how EDX quantitative analysis is being used in my experimental work in determining the composition of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires is explained. PL experimental setup is discussed in the last section of this chapter.

3.2 Metal-Organic Vapour Phase Epitaxy (MOVPE)

3.2.1 Basic principles of MOVPE

MOVPE is one of the methods used to grow crystalline materials. Epitaxy refers to the deposition of thin crystalline layers on a similar crystalline substrate. MOVPE involves a highly complex process in which the crystals are formed by chemical reactions at an elevated temperature ambient. There are many processes that can occur in parallel or series prior to deposition/epitaxy. Some examples of these processes involved include gas phase reactions, adsorption, surface diffusion, redesorption, desorption, nucleation and step growth as shown in figure 3.1.

![Figure 3.1: Schematic representation of examples of processes and mass transport that can occur in epitaxial growth. Adapted from [1].](image)

In MOVPE, metalorganics (MO) and hydrides are used as precursors. For example, to grow GaAs, MOs such as trimethylgallium (TMGa) and hydride such as arsine (AsH\textsubscript{3}) are used as the precursors. These precursors react over a heated substrate with the following reaction:
3. Experimental techniques

Ga(CH₃)₃ + AsH₃ → GaAs + 3CH₄

Different precursors and various combinations may be used to produce various types of crystals. For the growth of InₓGa₁₋ₓAs nanowire, MO precursors commonly used are TMGa, TMIn and AsH₃. The decomposition of each precursor varies depending on the temperature and the ambient of the reactor. For example, TMIn has lower decomposition temperature than TMGa [2].

3.2.2 Components of MOVPE

The main components of MOVPE can be grouped into three major sub-systems: the gas delivery system, reactor growth chamber and exhaust system. In general, the MOVPE components can be simplified as shown in the schematics in figure 3.2.

![Schematic diagram of major components in a typical MOVPE system.](image)

**Figure 3.2:** Schematic diagram of major components in a typical MOVPE system.
3. Experimental techniques

3.2.2.1 Gas delivery system

The gas delivery system consists of stainless steel tubing, manifolds, purifiers, filters, valves, pressure controllers (PC) and mass flow controllers (MFC). The function of the gas delivery system is to provide the right amount of precursors and carrier gases into the reactor growth chamber. All the metal-organic precursors required for the growth are transported by a carrier gas (usually hydrogen) into the reactor via their own run lines and will only meet at the reactor growth front. These actions are made possible with pressure-balanced switching manifolds that can prevent transient flow and pressure condition that can affect the growth chamber. In the switching manifold, individual precursor gas flow can be switched, combined or routed to run or vent lines while maintaining a stable differential pressure between run and vent lines.

MO precursors are contained in stainless steel bubblers in which the temperature and pressure are kept constant for a certain desirable flow throughout the growth. To ensure the temperatures are kept constant, these bubblers are placed in a temperature controlled baths. Carrier gases are transported through the bubblers to carry the precursor vapour into the reactor (run line) or through the vent line. The pressure in the bubbler is stabilised via a pressure controller. Figure 3.3 shows a schematic diagram of the MO precursor transport system.

![Figure 3.3: Schematic diagram of bubbler configuration of a standard bubbler. Adapted from [3].](image)

The molar flow rate of a MO precursor \( Q_{MO} \) (mol/min) is calculated with the following equation:

\[
Q_{MO} = \frac{F_{bubbling\text{-}gas}}{C_{STP}} \times \frac{P(\text{Eq.T})}{P} \quad (3.1)
\]
where $F_{bubbling\ gas}$ is the flow rate of the gas flowing through the bubbler (in standard cubic centimeters per minute, sccm), $P$ is the bubbler pressure (Torr), $P(Eq,T)$ is the vapour pressure of the MO (Torr) at bath temperature and $C_{STP}$ is a constant for molar volume of an ideal gas at standard temperature (298.15K) and pressure (760 Torr).

As for the hydrides, most of the precursor compounds are in a liquefied gas phase in high-pressure cylinders and generally are transported directly. The molar flow of a hydride precursor $Q_{hydride}(\text{mol/min})$ is calculated from the following equation:

$$Q_{hydride} = \frac{F_{hydride}}{C_{STP}}$$  \hspace{1cm} (3.2)

where $F_{hydride}$ is the flow rate of the gas from the cylinder (sccm), which is regulated by a mass flow controller.

3.2.2.2 Reactor system

The direction of the primary flow injection into the chamber generally defines the chamber geometries. Horizontal reactors have gas phase precursors flowing horizontally in parallel to the susceptor and the substrate, while vertical flow reactors have gas phase precursor flowing vertically normal to the susceptor and the substrate surface. In this thesis, the MOVPE used is a horizontal planetary reactor system. The system is designed to improve uniformity by employing two modes of rotation. The main susceptor rotates to average any thermal imbalance while the satellite discs holding the substrates on the susceptor rotate in the opposite direction to average radial reactant depletion.

3.2.2.3 Exhaust system

Vent lines and byproducts from the run line passes through a scrubber where the chemicals are treated to safe environmental level. In the scrubber, the unreacted precursors and byproducts are captured, isolated and/or transformed. The scrubber used in this work utilises activated carbon to capture toxic compounds produced by the MOVPE process. Controlled oxidation in the system turns harmful gases into solid oxides that can be disposed more safely.

In addition to all of the above, the MOVPE facility is also equipped with a safety system. The safety system includes hydride and precursors handling, proper sealing for the
3. Experimental techniques

gas flow system, alarm and interlock system. Together with proper training, the safety system is to ensure MOVPE can be used routinely in a safe manner.

3.2.3 Au-assisted InGaAs nanowire growth by MOVPE

For this thesis, all nanowires were grown with the horizontal flow Aixtron 200/4 MOVPE located at The Australian National University. Growth was carried out in a hydrogen atmosphere at 100 mbar reactor pressure, with a total flow of 15 standard litres per minute.

Gold colloids in the form of a commercially bought suspended solution (Ted Pella®) were used as seeds for the In_xGa_{1-x}As nanowire growth. First the substrate was immersed in poly-L-lysine solution (PLL) for one minute and rinsed in deionized (DI) water. Then the gold colloid solution was dispersed onto the substrate for 60s and finally rinsed again in DI water prior to loading in the growth chamber. The PLL solution creates a positively-charged surface which immobilizes the gold colloid when the solution is dispersed onto the substrate.

In the growth chamber, the sample is heated to a temperature of 600 °C for 10 minutes and then ramped up or down to growth temperature for the growth of nanowires. Figure 3.4 shows the standard operational growth temperature versus time graph of a typical InGaAs nanowire. The highlighted areas are the times when the precursors flow into the reactor. The AsH_3 is switched into the reactor when the temperature reaches 390 °C to protect the GaAs substrate from decomposing at higher temperature. TMIn and TMGa flows are introduced into chamber only during the growth of the nanowires. At the end of growth, both TMIn and TMGa are closed and the AsH_3 is left to flow into the reactor until the temperature has cooled down to 200 °C to protect the nanowires from decomposing.
3. Experimental techniques

Figure 3.4: Growth temperature versus time for a typical nanowire growth.

3.3 Scanning Electron Microscopy (SEM)

3.3.1 Basic principle of SEM

SEM is a powerful technique widely used for characterisation of materials. Electron microscopes use a beam of electrons generated either by tungsten or a field emission gun. This allows the SEM to reach magnifications up to 500,000 times and deeper depth of field as compared to the optical microscopes. The electrons are accelerated through a high voltage and a series of electromagnetic lenses and aperture to produce a fine beam of electrons. SEM images are obtained by scanning the fine beam onto a sample in a raster pattern and collecting the signal as it scans. The intensity of the signal is translated as the brightness and contrast in the images. The brightness and the contrast represent certain characteristics of the sample depending on which signals are collected for that particular scan. When an electron beam hits a sample, several interactions can occur, which generate a number of signals for detection. Various signals provide different types of information of the sample like topography, surface morphology, composition, crystal and electronic structure. Figure 3.5 shows the various interactions that can occur when an electron beam hits the sample.
In SEM, two main signals that are commonly collected are the secondary electrons and back-scattered electrons. The secondary electrons are electrons that are ejected by the material near the surface and have low energies. Hence, the image retrieved from the secondary electrons signal can provide more topographic details. Backscattered electrons, on the other hand, have higher energy and are more sensitive to the atomic mass (Z) of the sample. Hence, the contrast obtained by the signals corresponds to the elements in the sample. Heavier elements would appear brighter due to the higher amount of backscattered electrons than the lighter elements.

### 3.3.2 Components of SEM

Figure 3.6 shows the schematic of an SEM comprising of the main components such as the electron gun, electromagnetic lenses, apertures, detectors and the vacuum chamber. Each of these components has their own detailed principle of operation. However, in this thesis, they are briefly explained in the following sub-sections.
3. Experimental techniques

Figure 3.6: Schematic of a typical SEM showing the main components

3.3.2.1 Electron guns

Electron guns can either be thermionic guns or field emission guns. Thermionic guns (e.g., tungsten filament) produce electrons by applying thermal energy onto the filament to emit electrons. The electrons are then accelerated towards an anode. Field emission guns, on the other hand, use a very strong electric field to extract electrons from the filament. This in turn gives a brighter source as compared to thermionic guns. However, it requires a higher vacuum condition to operate.

3.3.2.2 Electromagnetic coil lenses

Since the principle of SEM uses electrons instead of light, the lenses are magnetic instead of the conventional glass used for the light microscopy. Similar to glass lenses, the role of the electromagnetic lenses is to form a smaller and finely focused probe incident on the sample. Two main lenses are used in SEM, the condenser lenses and the objective lenses as shown in figure 3.7. The condenser lenses control the number of electrons in the beam for a given aperture size while the objective lenses focus the electrons on the sample at the working distance. The lenses are controlled by adjusting the amount of current flowing through the coils around the iron core of the magnet.
3.3.2.3 Detectors

SEM uses the Everhart-Thornley detector to collect signals from secondary and back-scattered electrons. The detector mainly consists of a scintillator surrounded by a Faraday cage. The schematic of the Everhart-Thornley detector is shown in figure 3.7. The Faraday cage is maintained at low positive potential (~+200 V) to attract low energy electron and the rest of the electrons are then attracted by the higher positive potential (~+10 kV) scintillator. The electrons are then converted into light photons and guided to a photomultiplier tube for amplification ready to be processed as the output signal.

![Figure 3.7: Schematic of Everhart-Thornley detector for collecting secondary electron signals.](image)

By applying a negative voltage to the Faraday cage, the detector can act as a back-scattered electron detector. However, a dedicated back-scattered electron detector is often used for this purpose.

3.3.2.4 Vacuum system

A standard SEM operates in high vacuum (10⁻⁶ Torr) to allow electrons to travel freely between the sample and the detector. In addition the high vacuum also protects the electron guns of the system. Commonly the SEM comprises of a combination of pump system to reach the high vacuum. This usually includes a rotary mechanical pump pumping on the excess gas pumped by a diffusion pump or a turbo-molecular pump.
3.3.2 Determining the parameters of nanowires using SEM images

In this thesis, SEM images using secondary electron mode are either obtained with a Zeiss Ultra FESEM, FEI Helios 600 Nanolab or FEI Verios system. The SEMs are normally operated with low voltage (1-3 kV) and small apertures to obtain high resolution details of the surface. The SEM images are used to determine the basic morphological detail of the nanowires such as the facets, roughness and shape of the nanowires. Such information generally gives more insight on what to expect when performing other characterization such as TEM. Nanowire parameters such as their height, tapering factor and facets are extracted from the SEM images. This is basically done using software like Image J. In figure 3.8, a standard evaluation of a nanowire is shown. Measurements are done on more than 20 nanowires for each sample and the average values with its standard deviations are used for plots in this thesis.

![Image of SEM images with dimensions and angles for nanowire evaluation]

**Figure 3.8:** Evaluation of nanowire dimensions from tilted SEM image and facet determination from top view SEM image using calculated angles from the known cleaved edge.

### 3.4 Transmission Electron Microscopy (TEM)

#### 3.4.1 Basic principle of TEM

Similar to SEM, TEM uses an electron beam to interact with the sample. In TEM, the transmitted electron signal is used to form the final image. Hence, higher energy (200-300 kV) is used in TEM to accelerate the electron beam to produce more transmitted electrons. Similar to the principle of the light microscopes, electron beams are focused onto the sample using electromagnetic lenses and the transmitted beam is then focused onto the phosphor
3. Experimental techniques

screen or the charge couple device (CCD) camera by the objective lenses. TEM can be operated in two modes, diffraction and imaging mode. Diffraction pattern (DP) is formed on the back focal plane of the objective lens. Images are formed on the image plane after translated by the objective lens and the intermediate lenses.

Electrons that pass through a crystalline lattice will undergo a Bragg scattering (figure 3.10) and the scattering is collected as a diffraction pattern (DP). Bragg’s law is defined as

\[ n\lambda = 2d \sin\theta \]  \hspace{1cm} (3.3)

where \( n \) is a positive integer, \( \lambda \) is the wavelength of incident wave, \( d \) is the interplanar distance between the lattice planes and \( \theta \) is the scattering angle as shown in figure 3.9. The relation of d-spacing and Miller indices is defined with the following equation:

\[ d = \frac{a}{\sqrt{h^2+k^2+l^2}} \]  \hspace{1cm} (3.4)

where \( a \) is the lattice constant of the cubic crystal, and \( h, k \) and \( l \) are the Miller indices of the Bragg plane. With the two equations above, the lattice constant of a particular cubic crystal can be expressed with the following equation:

\[ \left( \frac{\lambda}{2a} \right)^2 = \frac{\sin^2\theta}{h^2+k^2+l^2} \]  \hspace{1cm} (3.5)

In order to obtain a useful DP, an aperture is used to select a region of interest for diffraction. The diffraction pattern resulted from this technique is known as the selected area electron diffraction pattern (SADP) or selected area electron diffraction (SAED) pattern. The SAED pattern can be used to determine the crystal structure of the sample and examine crystal defects. Often the samples have to be tilted to a certain zone axis so as to
identify the SAED pattern. Using the SAED pattern, two basic types of imaging of the samples can be performed: bright field (BF) and dark-field (DF) imaging. This can be done by simply inserting the objective apertures to select either the bright spot in the centre of the SAED pattern for BF imaging or by blocking the central spot (selecting other nearest spot) for DF imaging. Bright field image would give the mass-thickness and diffraction contrast. For example, thick areas, areas in which heavy atoms are enriched, and crystalline areas appear with dark contrast. Dark field image on the other hand gives more specific contrast about planar defects, stacking faults or particle size which appears as bright contrast as it only uses the nondiffracted beam on the sample.

### 3.4.2 Components of TEM

Figure 3.10 shows the photo of a TEM and the schematic showing the main components. Similar to SEM, the main components consist of the electron gun, electromagnetic lenses, apertures and vacuum column. In terms of their components, TEM have a taller electron beam column to allow higher acceleration for higher energy beam. In this thesis, TEM-FEG JEM 2100F located at the Centre for Advanced Microscopy, Australian Microscopy and Microanalysis Research Facility, The Australian National University was used for all of the TEM characterisation.
3.4.2 Nanowire specimen preparation for TEM

Since TEM uses the transmitted electrons for imaging, the sample has to be thin enough, i.e. electron transparent. Due to the nanometer scale dimensions of nanowire thickness / diameter, this can be easily achieved. Nanowire samples are prepared for TEM by careful mechanical transfer of the nanowires from the substrate onto a holey carbon-coated copper grid. In some cases, nanowires are suspended in the iso-propanol by means of putting a piece of substrate (about ~5 mm²) with nanowires into a beaker with about 10 ml of iso-propanol which is then ultrasonicated for about 1 minute. Then, few drops of the solution are transferred onto the holey carbon-coated copper grid and left to dry.

The cross-sections of the nanowires are prepared by first embedding the nanowires into Spurr resin. Slicing nanowires in an embedded epoxy resin is one of the more practical
ways of having thin enough cross-sections for characterisation under the TEM. This technique has been introduced in previous reports [5], [6]. The Spurr resin is based on four components ERL 4221, D.E.R. 736, (diglycidyl ether of polypropylene glycol), NSA, Nonenyl succinic and dimethylaminoethanol (DMAE). The Spurr mixture is often prepared fresh prior to embedding the nanowires. However, a recently defrosted one can also be used. The mixture is made with the ratio given by the manufacturer for a suitable hardness and viscosity.

To embed nanowires into the Spurr resin, a small piece of the as-grown nanowires on the substrate is placed in a mould facing up. The Spurr mixture is then transferred into the mould using a syringe. The mould is left to dry in an oven at 70 °C for 8 hours. Once the mould is dry, the resin block is taken out of the mould and reshaped to suit the process of microtoming. Prior to shaping the slices, the substrate is first removed from the resin. This can be done by trimming the resin on each side of the substrate and immersing the substrate in liquid nitrogen. The thermal effect of quenching the substrate into the nitrogen makes the substrate fall off from the resin easily. Once the substrate is off, only nanowires are left in the resin. The exposed surface is also smooth and shiny making it perfect for aligning with the microtome knife for shaping and slicing. The resin is then sliced into thin sections using the ultramicrotome with a diamond knife. Generally, the cutting surface is aligned with the knife-edge to ensure that the slices are uniform in thickness and to protect the knife from damage due to thick cuts. In rotary microtome such as the ultramicrotome, the knife is fixed in a horizontal position and the cutting surface is brought towards the knife-edge in a rotary motion (figure 3.11). The slicing begins as the surface touches the blade and the slices are delivered into the trough. The trough is filled with water levelled with the knife-edge to allow slices to slide smoothly. The slicing continues in rotation and the slices are delivered with each rotation aligned on top of each other as shown in the inset of figure 3.11. The slices are then lifted up onto a TEM grid and left to dry.
3.5 Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray (EDX) Spectroscopy

3.5.1 STEM

STEM is a combination of both SEM and TEM. It uses the scanning principle of SEM however through a thin sample and collects the transmitted electrons like a TEM. The advantage of this is that STEM can spatially correlate the signal unlike TEM and can be in higher resolution than that of SEM. STEM scans in raster pattern with a finely focused electron beam across the sample and collect serial signals which are then correlated with the beam position. This is very useful in determining the characteristic of a certain area. For example, EDX signal can be collected in the STEM mode, which can provide information on the composition distribution of the sample. Furthermore, STEM can also be used for highly dependent z-contrast imaging using the high-angle annular dark field (HAADF) mode. A combination of both the EDX and HAADF can provide detailed information on the concentration of elements present in the sample up to atomic level in an optimised condition.
3.5.2 EDX spectroscopy

As represented earlier in figure 3.5, X-rays can be produced by electron-sample interaction. X-rays are the inelastic scattering of electrons that can be triggered in two ways, the Bremsstrahlung (continuum) or the characteristic x-ray emission. Bremsstrahlung X-rays result from electrons that lose energy due to the deceleration when it interacts with an atom (figure 3.12 (a)). The emission is a continuous energy spectrum of X-ray photons as shown in figure 3.12(c). Characteristic X-rays are the X-ray emission caused by the transition of an electron from an inner shell towards the outer shell. This transition occurs due to the hole created in the first place by high-energy incident electron (figure 3.12(b)). The energy of the X-ray emission is equivalent to the energy level difference between the outer and inner shell electron involved in the transition. Hence, the characteristic X-ray emissions are seen as sharper peaks in the spectra with the wavelength or energy representing the energy of the atom from the shell or subshell concerned (figure 3.12 (c)). This can be then translated into determining the nature of the atom and inner shell that is involved in the process.

![Figure 3.12](image)

**Figure 3.12:** (a-b) The process of Bremsstrahlung and characteristic x-rays emission and c) an example of EDX spectrum characterizing the Bremsstrahlung and the characteristic x-ray emission energy/wavelength.

3.5.3 Qualitative and quantitative EDX analysis

A qualitative method offers a quick and an effective way to present the elements of the samples. In general, the qualitative method is straightforward, indicating elements of the samples by their characteristic X-ray peaks. This process can be automatically done with the
help of analysis software such as Analysis Station Software, which is used in this thesis. The intensity of the peak can be compared qualitatively from one sample to another as the value is close to the expected signal emitted from the sample. Qualitative analysis has been carried out in this thesis for determining the elements in the Au-particle. This is due to the fact that, it is difficult to have a standard reference for such alloy composition. As a general rule, the peak that will be considered has to be significant (above background level) and this usually has to be manually checked to be assured that the automatic qualitative system done by the software is correct. Figure 3.13 shows an example of the spectrum taken from a spot EDX analysis on the Au-particle alloy. From the spectrum it is clearly seen that there is no significant Ga peak, hence the Ga element shall not be considered to be present in this analysis. This step is important for element pre-selection for the quantitative analysis.

![EDX spectrum of Au particle](image)

**Figure 3.13:** Representative of an EDX spectrum of a Au particle showing the selection of In, Ga, As and Au (element selection are highlighted in green). The Ga and As peaks are by common sense should not be included in the analysis due to low counts almost levelled with the background level.

Quantitative analysis involves measuring the intensity of the spectral peaks corresponding to pre-selected elements for both samples and standards under known operating conditions, calculating intensity ratios ($k$ values), and converting these $k$ values into chemical concentration. The $k$ values are the constant retrieved from the known standard of two elements, A and B with the following equation [7]:

$$\frac{c_A}{c_B} = k_{AB} \frac{i_A}{i_B}$$

(3.6)
The ratio of X-ray intensities, $I_A$ and $I_B$ for two elements A and B, is independent of thickness and can be simply related to the corresponding weight or atomic fractions of the elements, $C_A$ and $C_B$ where $k_{AB}$ is a factor (the $k$ value) that relates to the efficiency of X-ray production and the detection of the X-ray. $K$ values vary with microscope condition hence will be most accurate when measured in the same system as the sample to be analysed. This ratio method is only valid for thin samples, such as those used in TEM. In SEM, absorption and fluorescence effect has to be taken into account since the samples are thick and these effects are not negligible.

There are two methods of quantitative analysis; standardless quantitative and standard quantitative. Standardless quantitative uses the $k$ values provided by the standard sample measured elsewhere in a different system provided by the analysis software. On the other hand, standard quantitative requires one to determine the $k$ values using a standard sample measured by the same system with the same conditions. In this thesis, all the EDX data are collected using the same STEM setup. The $k$ values are determined using GaAs and InAs nanowires as the standards. First, GaAs and InAs nanowires are statistically measured by considering Ga (L), In(L) and As (L) peaks. Then the $k$ values are determined (in Analysis Station software) for various size (30 -250 nm) nanowires. The average $k$ values are used since they are found to be independent of the nanowire diameter as shown in figure 3.14. This result strengthens the fact that thin samples can be quantified without any absorption or fluorescence effect taken into account for samples up to 300 nm thick using 200 kV electron beams. The average $k$ value is used for InAs and GaAs with As as a reference point for the entire InGaAs samples to ensure uniformity across all measurements. For InGaP, similar method was carried out using InP and GaP nanowires considering Ga (L), In(L) and P (K) peaks. The final composition of InGaP is determined using P as a reference. It is found that there is a random error of about ±4% for reference sample contributing to similar error for the calculated data. Random errors could come from non-uniformity of the sample shape, crystal structure and facets of the nanowires.
3. Experimental techniques

Figure 3.14: Graph of k values for a) GaAs and b) InAs nanowires versus diameter. Arsenic is taken as a reference point for the calculation of the k values and the average k values for both InAs and GaAs are used for InGaAs alloy composition using Analysis Station software.

3.6 Photoluminescence (PL)

3.6.1 Basic principle of PL spectroscopy

PL spectroscopy is a non-contact, non-destructive method of probing the electronic structure of materials. PL is the spontaneous photon emission from a material under optical excitation. Typical luminescences process in semiconductor can be simplified as shown in figure 3.15. When photons with energy higher than the bandgap of the material, $E_g$ are incident on the sample, the sample is excited from the ground state. This creates electron-hole pairs due to the transfer of electrons from the valence band into the conduction band. The non-equilibrium electron and hole distribution relaxes via interband relaxation back to ground state and then recombine resulting in emission of light with an energy $E_g$. 
Figure 3.15: Schematic of the basic processes involved in a typical luminescence experiment in optically excited semiconductors representing the process of a) excitation, b) interband relaxation and c) recombination.

With different variants of PL spectroscopy techniques such as temperature-dependent PL and excitation power dependent PL, one can determine the bandgap of the material, the crystal quality, detect impurity level and defects and study the recombination mechanisms [8]. The bandgap of a semiconductor material depends on temperature due to the expansion of the crystal lattice. Temperature dependence of the bandgap can be fitted using the empirical Varshni equation given by the following:

\[ E_g (T) = E_g (0) - \frac{\alpha T^2}{T+\beta}, \]

where \( E_g (0) \) is the bandgap value at 0 K, \( \alpha \) and \( \beta \) are constants corresponding to different materials.

Other than the shift of bandgap due to lattice expansion, an increase in temperature can also cause a change of carrier population of the conduction and valence bands. Free carriers at higher temperature perturb the band-edge and induce a tail of band states into the energy gap. At low temperature when the thermal energy is lower than the exciton binding energy, exciton related emission could be observed [8]. Hence the transition or the changes observed with temperature-dependence PL can help determine the bandgap, recombination mechanisms, elemental composition, and whether there are defects related states.

Excitation power dependent PL can identify some underlying recombination mechanisms. The intensity of the excitation light can control the density of photoexcited electrons and holes. Low carrier density means that the measurement is dominated by
3. Experimental techniques

defects and impurities at the interfaces. The increase in intensity with the excitation power should provide information whether this is the case. The rate of recombination at these sites is proportional to the dominant carrier density, \( n \). Discrete states can be filled as the excitation power increases and bulk radiative recombination plays a greater role. The radiative rate is proportional to \( n^2 \) with the intensity.

3.6.2 Components of PL setup

The main components of a typical PL system consist of a laser, lenses to align the laser beam, detectors and spectrometer. Additional components include a microscope with magnification lenses for micro-PL and cryostat for temperature-dependent measurements. Figure 3.16 shows the typical setup for photoluminescence spectroscopy.

![Figure 3.16: Schematic of a typical PL setup.](image)

Two different experimental PL are carried out in this thesis, micro-PL for single nanowire measurements and macro-PL for measurements of nanowire ensembles. For single nanowire measurements of bandgap below 1600 nm, HORIBA Jobin Yvon T64000 Raman/PL system located at The Australian National University is used. The setup consists of a 632 nm He-Ne laser, Si CCD detector (detection wavelength: 350 – 1100 nm) and InGaAs array detector (800 – 1700 nm) and 50X magnifications near-infrared (NIR) objective lenses.
For narrow bandgap (above 1600 nm) samples such as high In concentration InGaAs nanowires discussed in chapter 3, macro-PL measurements on ensembles of nanowires are carried out with a continuous-wave, frequency doubled Nd:YAg laser (532 nm), liquid nitrogen cooled mercury cadmium telluride (MCT) detector connected to a lock-in-amplifier by collaborators at University of Oxford.

3.7 Summary

In summary, the experimental techniques for the growth of nanowires and their characterization used for this thesis have been presented in this chapter. Principles of MOVPE, SEM, TEM, EDX and PL were briefly discussed. Each of these techniques on its own is highly complex, but relevant details to the work in the thesis are covered. Further details can be found in the cited references provided.
References


Chapter 4

Pure zinc-blende phase high Indium $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires grown by two-temperature growth method

Overview

In this chapter, two-temperature growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires is discussed with regards to the crystal phase and composition distributions in a 3-dimensional perspective. In a wide range of growth parameters within this two-temperature growth method, the composition distribution along and across the nanowires are found to be non-uniform. However, within a certain growth window, a uniform composition can be achieved but limited to high In concentrations. The crystal phase remains a pure zinc-blende (ZB) phase similar to those achieved for GaAs nanowires in the two-temperature growth regime. The high quality phase is favourably required for device applications while the high-In concentration $\text{In}_x\text{Ga}_{1-x}\text{As}$ can replace InAs nanowires to reduce leakage current issues. The study has overall shed more insight into understanding the limitation of In and Ga incorporation and composition distribution in the low growth temperature regime.
4. Pure zinc-blende phase high Indium In\(_x\)Ga\(_{1-x}\)As nanowires grown by two-temperature growth method

4.1 Introduction

Crystal quality is highly important to ensure the performance of nanoscale semiconductor devices. In recent years, much work has been devoted to improving and controlling the crystal phase of nanowires [1]–[6]. High crystal phase purity nanowires with no defects, twinning or stacking faults are highly essential to exploit the full potential of nanowire related devices. Nanowire crystal phase are affected by the growth conditions such as growth temperature, V/III ratio and flow rate [1]–[6]. One of the methods shown to be successful in producing perfect ZB phase nanowires for Au-assisted GaAs nanowires is the two-temperature growth method [6]. This method involves growing GaAs nanowires sequentially in two different growth temperature regimes. A higher initial growth temperature known as the nucleation temperature, \(T_n\), enables nanowires to nucleate properly for vertical growth. Then, the temperature is lowered to another growth temperature, \(T_g\), while the nanowires continue to grow. The subsequent low growth temperature eliminates the twinning and minimizes tapering which exist for nanowires grown with single-growth temperature [6].

In the quest of achieving similar results from the GaAs nanowires, this chapter studies In\(_x\)Ga\(_{1-x}\)As nanowire growth using the two-temperature growth method. However, since the ternary In\(_x\)Ga\(_{1-x}\)As is more complicated than the binary GaAs, the results reveal a few challenges such as limitation of Ga incorporation and composition inhomogeneity along the nanowire. It is believed that this is due to higher competition between the Ga and In adatoms at the low temperatures due to the large difference of decomposition parameter and the difference in diffusion lengths of Ga and In adatoms [7]. Hence, a deeper understanding of the growth of ternary material is achieved, which could be implied not only for In\(_x\)Ga\(_{1-x}\)As nanowire growth, but for other ternary materials too. Nonetheless, the two-temperature growth is found to be successful for growing uniform, pure zinc-blende phase In\(_x\)Ga\(_{1-x}\)As nanowires with high In concentration within a limited growth window.

4.2 Experimental method

In\(_x\)Ga\(_{1-x}\)As nanowires were grown using 50 nm Au seeds on GaAs (111)B substrates. The substrates were first prepared with Au-seed solution as previously described in chapter 2. The precursors involved were trimethylgallium (TMGa), trimethylindium (TMIn) and arsine
4. Pure zinc-blende phase high Indium InGa1-xAs nanowires grown by two-temperature growth method

(AsH₃). The growths begin with an annealing step in AsH₃ ambient at 600 °C for 10 minutes. Two temperatures were used in this set of experiments referred as the nucleation temperature $T_n$ and growth temperature $T_g$. The temperature was ramped down to nucleation temperature straight after the annealing process. The nucleation time was 1 minute in AsH₃ and the group III precursors, TMGa and TMIn. The temperature was further ramped down to growth temperature while all three precursors continue to flow into the reactor. The growth time at $T_g$ together with the time for the temperature to drop from $T_n$ to $T_g$ (~3-7 minutes) is kept constant at 20 minutes for all experiments in this chapter. The growth ended by removing the group III precursors and cooling down to room temperature. AsH₃ was only removed when the temperature had cooled to 200 °C to protect the sample from decomposing. The nucleation temperature was kept constant at 450 °C in all experiments while the growth temperature varied from 400 to 350 °C. Further investigations on the effect of TMIn molar ratio in vapour phase, $X_{v(\text{In})} = \frac{\text{TMIn}}{\text{TMIn} + \text{TMGa}}$ were carried out in the range of 0.10 to 0.30 while maintaining the total group III flow rate at $1.3 \times 10^{-5}$ mol/min. The V/III ratio was maintained at 40 in all sets of experiments presented in this chapter.

Nanowires were characterized by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Nanowire cross-sections were prepared by ultra-microtome as previously discussed in chapter 2. The cross-sections were characterized by scanning transmission electron microscopy (STEM) with an energy dispersive x-ray (EDX) spectroscopy to investigate the composition distribution across the nanowires.

4.3 Two-temperature growth method for crystal phase purity

Growth temperature is known to be one of the dominant parameters affecting the growth of nanowires [1], [8]–[11]. Changing the growth temperature affects many processes involved in the growth of nanowires including the phase and composition of the metal seed alloy, decomposition of precursors and adatoms diffusion lengths. These processes will then further affect the final nanowire structure in terms of their morphology, crystal phase and composition. Hence, in this section, two-temperature growth of InGa1-xAs nanowires is explored to improve the crystal phase quality and investigate the effect of growth temperature on the composition.
Prior to proceeding with the two-temperature growth, In$_x$Ga$_{1-x}$As nanowires are grown at 450 °C with a V/III ratio of 40 and $X_{v(\text{In})}$ ratio of 0.30. This initial growth is performed to examine the basic properties of ternary In$_x$Ga$_{1-x}$As nanowires as compared to binary GaAs nanowires. The parameters are kept similar to the growth of GaAs nanowires by Joyce et al. [6]. The only difference is the additional TMIn and reduction of TMGa flow to keep the group III total flow rate at $1.3 \times 10^{-5}$ mol/min. The SEM image of the nanowires is shown in figure 4.1 a) where it can be clearly observed that the nanowires are highly tapered and the sidewalls are rough signifying the presence of structural defects [12]. Further TEM characterization proves that the rough sidewalls are the result of stacking faults in the crystal structure as shown by figure 4.1 (b-d). The crystal phase is mainly ZB as indicated by the selected-area electron diffraction (SAED) pattern in figure 4.1 e) and has random twinning along the nanowires as indicated by the arrows in high-resolution TEM images in figure 4.1 (c-d). Common faceting found related to the twinning in ZB phase can be observed in figure 4.1 (c-d) especially at the base of the nanowires (figure 4.1(d)) where concomitant radial growth enhances the presence of these facets [1]. A high-angle annular dark field (HAADF) image of the nanowire in figure 4.1 f) shows dark fringes in line with the facets confirming the twin defects are related to faceting. The nanowire is tapered and accompanied with a composition gradient as shown by the EDX spot analysis below the HAADF image. Compared to GaAs nanowires grown with similar parameters as shown by Joyce et al. [6], these initial results indicate that the presence of In increases the chances of tapering, and also creates composition inhomogeneity. Furthermore, the defective crystal phase can be detrimental to the optical and electrical properties of the nanowires. Hence, using two-temperature growth method may eliminate the stacking faults in In$_x$Ga$_{1-x}$As nanowires and reduce tapering which is observed to relate to the composition inhomogeneity along the nanowire.
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Figure 4.1: a) 45°-tilted FESEM image of In$_x$Ga$_{1-x}$As nanowires grown at a (single) temperature of 450 °C. b) TEM image taken in the <110> zone axis of a single nanowire from the sample shown in a). c-d) HRTEM of the tip and base areas of the nanowire shown in b). e) SAED pattern of the nanowire shown in (b-d). f) EDX line scan representing the composition distribution of each element along the nanowire. The image above the line scan is the dark field image of the corresponding nanowire lying on the TEM grid.

To investigate the effect of the two-temperature growth method on In$_x$Ga$_{1-x}$As nanowires, three samples of In$_x$Ga$_{1-x}$As nanowires with $X_{\text{In}}$ of 0.30 are grown at lower growth temperatures, $T_g = 400, 375$ and 350 °C after 1 minute of nucleation growth step at 450 °C. Other parameters such as V/III ratio and the flow rate are kept the same as those used for the single growth temperature discussed above. The 45° tilted SEM images are shown in figure 4.2. The two-temperature growth method allows the nanowires to grow vertically even when the temperature is as low as 375 °C. Further lowering $T_g$ to 350 °C resulted in all kinked nanowires, indicating the limit of the low growth temperature. From the morphological aspect, nanowires grown at $T_g = 400$ °C shows a higher degree of tapering.
than the growth at $T_g = 375 \, ^\circ\text{C}$. Growth rate is higher for nanowires grown at 375 °C than those at 400 °C is possibly due to the reduced competition between radial and axial growths. Radial growth is commonly observed to be competing with the axial growth as the temperature increases [8, 21]. This is due to the increase in the amount of available adatoms (due to more decomposition) with increasing temperature. This is also supported by the parasitic growth on the substrate, which is found to be more prominent in the higher growth temperature sample as seen in figure 4.2 a). The difference in growth rate can also indicate a difference in composition between the two samples. As previously shown by Kohashi et al. in their selective-area growth of In$_x$Ga$_{1-x}$As nanowires, growth rate can be highly related to composition [9].

![Figure 4.2: 45°-tilted FESEM views of nanowires grown at various $T_g$ of a) 400 °C, b) 375 °C and c) 350 °C. Scale bars represent 1 µm.](image)

In order to assess the composition of the In$_x$Ga$_{1-x}$As nanowires grown at $T_g = 400$ and 375 °C, STEM EDX measurements are performed. The EDX line scan along the nanowires shows two different trends as shown in figure 4.3. Nanowires grown at $T_g = 400$ °C have a composition gradient after the first 0.5 µm from the base with lower In concentration near the nanowire tip. The first 0.5 µm from the base is the segment formed during the nucleation period where the growth temperature is $T_n = 450$ °C. Interestingly, growth at $T_g = 375$ °C on the other hand shows very little Ga after the first 0.5 µm length from the base. The
cause for such an occurrence could be due to the change of Au alloy condition. Recent work by Ghalamestani et al. [13] predicts the phase diagram for Au-In-Ga and claim that it contributes to the change in composition found in their Au-seeded GaAsSb nanowires. Hence, it could also be possible that there occurs a change in the alloy phase condition for nanowires grown at $T_g = 375 \, ^\circ C$ as compared to $T_g = 400 \, ^\circ C$. Higher In captured by the Au-alloy at lower temperature can be due to a few possible reasons including high-In Au alloy as the preferred alloy phase, a higher amount of available In adatoms attributed to the fully decomposed TMIn as compared to TMGa and higher In diffusion length as compared to Ga adatoms allowing more In to reach the Au alloy particle.

**Figure 4.3:** EDX line scan representing the composition distribution of each element along the nanowire for samples grown at $T_g$ of a) 400 and b) 375 °C. The image above the line scan is the dark field image of the corresponding nanowire lying on the TEM grid.
4. Pure zinc-blende phase high Indium $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires grown by two-temperature growth method

Despite the limitation of Ga incorporation, the crystal phase is found to improve as compared to the single-growth temperature method. Stacking faults are eliminated and pure ZB phase is attained. Figure 4.4 shows the TEM image of the two-temperature growth at $T_g = 375 \, ^\circ\text{C}$ showing an improved crystal phase as opposed to the single growth temperature shown previously in figure 4.1. The two-temperature sample shows a pure ZB phase as shown by the representative high-resolution TEM (HRTEM) image in figure 4.4 b). The only exceptions are at the base which is grown at the nucleation temperature and twins near the tip area of the nanowire as shown by the arrows in TEM image in figure 4.4 c).

![Figure 4.4 TEM image of a nanowire grown with the two-temperature growth method at $T_g = 375 \, ^\circ\text{C}$. b) HRTEM image representative of the crystal phase of the nanowire c) HRTEM image of the same nanowire near the Au droplet.]

Therefore, in conclusion, the two-temperature growths are successful in producing high quality crystal phase $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires, however are limited in terms of Ga incorporation. In the following section, the possibility of tuning these $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires is investigated by varying the ratio of the precursors.
4. Pure zinc-blende phase high Indium In\textsubscript{x}Ga\textsubscript{1-x}As nanowires grown by two-temperature growth method

4.4 Effect of flow ratio of precursors

In the previous section, it was shown that high quality ZB phase In\textsubscript{x}Ga\textsubscript{1-x}As has been successfully grown. However the composition is found to be far from the nominal ratio and of high-In concentration. Tuning the flow ratio of the precursors is anticipated to be the simplest way to tune the composition of alloy compound semiconductor. However, this has been found to be challenging and critical in growth of ternary nanowires as it strongly affects their nucleation, crystal phase and morphology [14]–[16]. Reports have shown transformations in the crystal phase with variation of precursor ratio. Kohashi et al. [9] has reported that the growth rate of GaAs nanowires and InAs nanowires differs which in turn correlates to the growth rate of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires at various growth temperatures. Although these reports are focused on the growth of selected-area In\textsubscript{x}Ga\textsubscript{1-x}As nanowires with no foreign metal catalyst, there is a clear indication that group III precursor ratio may not only affect ternary nanowire composition but also their crystal phase and morphology. In this section, investigation on how the nominal ratio of precursors flow, $X_v$, affects the final concentration of Au-seeded In\textsubscript{x}Ga\textsubscript{1-x}As nanowires is carried out. This study provides further knowledge of the ability to tune the composition of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires within the two-temperature growth mode.

Two more In\textsubscript{x}Ga\textsubscript{1-x}As nanowire samples with $X_v$ (In) = 0.15 and 0.10 were grown in addition to the sample with $X_v$ (In) = 0.30 discussed earlier in the chapter. The SEM and TEM images are shown in figure 4.5. From the SEM images, the axial growth rate of the nanowires is observed to decrease with decreasing $X_v$ (In). This could be mainly due to the lower growth rate of GaAs as opposed to InAs [17]. Figure 4.5 (d-f) shows the TEM image representing the crystal phase of nanowires grown with $X_v$ (In) = 0.30, 0.15 and 0.10 respectively. The crystal phase is found to maintain a ZB phase without defects for the three $X_v$ (In) values investigated here. However, strain contrast is clearly observed as the $X_v$ (In) decreases from 0.30 to 0.10. This indicates that a spontaneous shell with a different composition than the core nanowire is formed on the sample grown with $X_v$ (In) lower than 0.30. Further EDX measurements shown in figure 4.6 of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires grown with $X_v$ (In) = 0.10 show a composition gradient from In-rich base to Ga-rich tip suggesting that an In-rich spontaneous shell is formed surrounding a Ga-rich core. As shown earlier in figure 4.3 b), this is not the case for nanowires grown with $X_v$ (In) = 0.30 where it is uniform and no gradient is observed.
4. Pure zinc-blende phase high Indium In$_{x}$Ga$_{1-x}$As nanowires grown by two-temperature growth method

**Figure 4.5:** (a-c) 45°-tilted FESEM image of nanowires grown with two-temperature growth method at $T_g = 375$ °C and $X_{v(In)} = 0.30$, 0.15 and 0.10 respectively. (d-f) TEM image of a representative nanowire from each sample shown in (a-c).

**Figure 4.6.** EDX line scan showing the composition distribution of each element along the nanowire for the sample grown at $T_g = 375$ °C with $X_{v(In)} = 0.10$. 
Further confirmation of the radial composition distribution is obtained by analyzing the nanowire cross-section. Figure 4.7 (a-f) shows the EDX mapping of Ga and In distributions across the nanowire cross section taken 1 μm above the base for the samples grown with $X_{v(In)} = 0.30$ and 0.10. In both samples, the final shape of the nanowire cross-section is an equilateral triangle with {112} side facets as determined from the SEM image with reference to the cleaved edge as outlined in chapter 2. Nanowires grown with $X_{v(In)} = 0.30$ shows that they have a uniform cross-section with very little Ga and no significant segregation as shown by figure 4.7 (a-c). A contrast of core and shell is observed for In$_x$Ga$_{1-x}$As nanowires grown with $X_{v(In)} = 0.10$ as shown by figure 4.7 (d-f). Ga is observed to be higher in the core than in the shell region, i.e. higher In content in the shell. Similar situation is expected for nanowires grown with TMIn/TMGa flow ratio of 0.15. The spontaneous formation of a core-shell structure has been previously reported for many ternary nanowires due to the competition between the alloy species towards axial and radial growth [18]–[20].

**Figure 4.7**: EDX-STEM cross-section maps of Ga, In and the overlay of In and Ga of a nanowire grown with $X_{v(In)} = 0.30$ (a-c) showing a uniform distribution with very low Ga intensity. (d-f) nanowire grown with $X_{v(In)} = 0.10$ showing spontaneous formation of a core-shell structure with higher Ga concentration in the core.

The average nanowire composition of several nanowires for each sample taken from the tip area where there is negligible radial growth are plotted for the nanowires grown with $X_{v(In)} = 0.30$, 0.15 and 0.10 in figure 4.8. This composition is found to match the
composition taken from the core area in the cross-section maps and thus can be attributed as the core composition. As can be observed in the plot of figure 4.8, there is an increase in Ga incorporation into the core as $X_{\text{v(In)}}$ decreases. This is due to the increase in the amount of Ga species availability with the increase of TMGa flow rate. The higher amount of Ga species allows more Ga adatoms to be captured by the Au alloy particle hence incorporating more Ga into the nanowire core. This indicates that the group III precursor flow ratio can be used for tuning the composition of pure ZB In$_x$Ga$_{1-x}$As nanowires via the two-temperature growth method. However, at $X_{\text{v(In)}} = 0.30$, In dominates the core growth. Furthermore, in all cases, the radial growth is dominated by In-rich In$_x$Ga$_{1-x}$As creating a core-shell type structure with Ga-rich core. This is mainly due to the higher radial growth rate of InAs than GaAs attributed to the higher In diffusion length from the substrate [21]. While with larger diffusion length, the axial growth also increases, the higher amount of available In coming from the substrate also contributes to the radial growth [21]. Increasing the GaAs component in radial growth or eliminating radial growth by other means such as using HCl etching method during growth may offer composition homogeneity for the high-Ga core In$_x$Ga$_{1-x}$As nanowires [22].

**Figure 4.8:** Average In molar fraction in the nanowire core versus TMIn molar fraction supplied in vapour
4.6 Summary

In summary, the growth of ternary In\textsubscript{x}Ga\textsubscript{1-x}As nanowires via the two-temperature growth method has been successfully demonstrated to form a pure ZB structure although limited in composition tunability. Growth at low temperature is highly sensitive as there is a significant difference in the decomposition rates of TMGa and TMIn and the competition between In and Ga adatoms at these temperatures. The presence of In often dominates growth due to higher In diffusion length as compared to Ga. It is challenging to incorporate more Ga into the core of the nanowires while maintaining a highly uniform composition along the nanowires due to the competing In-rich radial growth.

The results and understanding gained from this experimental study produces high-In content In\textsubscript{x}Ga\textsubscript{1-x}As nanowires with high purity crystal structure and uniform composition. This is useful for devices requiring high-In content In\textsubscript{x}Ga\textsubscript{1-x}As or in applications which can replace InAs which suffers from leakage current in transistor applications [23]. This is due to the larger InGaAs bandgap as compared to InAs. Furthermore, the pure crystal phase is also an advantage in ensuring the best performance for devices. In the next chapter, single-growth temperature method is further explored to overcome the challenges faced in the low-temperature growth method in pursuing for a larger range of composition tunability, uniform composition and morphology.
4. Pure zinc-blende phase high Indium In$_{x}$Ga$_{1-x}$As nanowires grown by two-temperature growth method

References


4. Pure zinc-blende phase high Indium In$_{x}$Ga$_{1-x}$As nanowires grown by two-temperature growth method


4. Pure zinc-blende phase high Indium $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires grown by two-temperature growth method
Chapter 5

Controlling the phase and composition tunability of $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires

Overview

In chapter 4, the composition homogeneity and pure zinc-blende (ZB) phase has been successfully achieved for $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires. However, there exists limitation of Ga incorporation into the nanowire, thus limiting the tunability of $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires. In this chapter, single growth temperature method is explored in combination with various V/III ratios. The aim is to investigate the composition and phase tunability of $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires via simple growth parameter control. Various diameter Au-seed particles were also used to investigate their effect on the growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires. Within the study, an optimum growth condition for acquiring pure wurtzite (WZ) phase, uniform and taper-free nanowires was found. The pure WZ phase nanowires capped with InP show luminescence properties around 1.54 $\mu$m wavelength close to the technologically important optical fibre telecommunication wavelength, which is promising for application in photodetectors and lasers. A large part of the results from this chapter have been published in ref. [1].
5. Controlling the phase and composition tunability of In$_{x}$Ga$_{1-x}$As nanowires

5.1 Introduction

Composition homogeneity is crucial in ternary alloy semiconductors for device applications. The composition segregation that occurs within ternary alloy semiconductors causes changes in the bandgap, thus affecting their electrical and optical properties. It has been a great challenge to control composition homogeneity in growth of ternary alloy nanowires as discussed in chapter 1. For ternary alloy nanowires, tapering generally indicates composition inhomogeneity due to the difference of incorporation rate of each species axially and radially into the nanowire crystal. In particular, the compositional inhomogeneity in Au-seeded ternary nanowires is commonly found to be strongly correlated to the competition between vapour-liquid-solid (VLS) axial growth via the catalyst and vapour-solid (VS) radial growth on the nanowire sidewall [2]–[5]. A similar case has also been presented earlier in chapter 4 for the two-temperature growth mode. Minimal tapering and good composition homogeneity have been demonstrated by controlling the growth parameters such that the radial growth is limited and axial growth is enhanced [2], [3], [6].

Wu et al. [6] have reported significant progress in growing high-quality In$_{x}$Ga$_{1-x}$As nanowires using low V/III ratio and high growth temperature. However, the authors found that in their case, tapering and composition uniformity were dependent on the growth time and nanowire density. They showed that nanowires longer than 1.4 μm at optimal seed particle areal density around 10 μm$^{-2}$ still suffer from tapering and composition inhomogeneity and also contain stacking faults [6]. High density of stacking faults or polytypic phase is often reported for In$_{x}$Ga$_{1-x}$As nanowires [2], [7]–[9]. Though this may be common in nanowires grown by self-seeded or selected area epitaxy [7], [9], similar trends are also observed for metal-seeded nanowires [6], [8]. Recently, growth of Au-seeded nanowires on SiO$_2$ deposited on Si substrate with non-tapered morphology and high quality crystal structure has been reported [10]. In$_{x}$Ga$_{1-x}$As nanopillars with pure WZ phase and composition homogeneity along the nanowire have also been reported [11], [12]. However, both of these growths were not epitaxial to the substrate which is inconvenient for vertical processing on as-grown ensembles and needed for real device applications.

Nonetheless, In$_{x}$Ga$_{1-x}$As nanowires have already been shown to have great promise in applications such as solar cells and transistors despite their defective crystal structure [7], [13], [14]. Improving the crystal quality of the nanowires will ensure better device
Controlling the phase and composition tunability of In$_x$Ga$_{1-x}$As nanowires

performance [15], [16]. Defects act as carrier scattering or trap centers, thus degrading device performance and reducing yield. Hence, it is essential to simultaneously control the crystal structure and composition homogeneity in ternary alloy nanowires to optimise their utilization.

In this chapter, an in-depth analysis of In$_x$Ga$_{1-x}$As nanowires grown with various growth temperatures and V/III ratio is presented. Sections 5.3 and 5.4 of this chapter discuss the effect of growth temperature and V/III ratio on nanowire morphology, composition and crystal structure while section 5.5 briefly investigates the effect of Au-seed particle size. From the systematic study presented, tunability of the composition can be achieved by varying the growth temperature and the V/III ratio despite keeping the nominal In/Ga ratio constant. It is also found that the crystal phase is tunable by varying the V/III ratio alone. Ga incorporation is found to increase with the amount of ZB phase suggesting a correlation between the composition and the crystal phase. There is a direct correlation between defect density and tapering of the nanowire suggesting that the nanowires are more uniform when they have a high-quality crystal phase. Pure phase WZ nanowires with uniform composition and morphology are successfully achieved and are shown to be reproducible even for longer growth period thus allowing long nanowires to grow. Photoluminescence (PL) measurement on In$_{0.65}$Ga$_{0.35}$As WZ nanowires capped with InP shell shows luminescence at room temperature at about 1.54 µm, which is below the expected wavelength for ZB phase In$_{0.65}$Ga$_{0.35}$As. The shift suggest a compressive strain in the nanowire core due to the InP shell in combination with the expected shift due to the WZ phase.

5.2 Experimental method

All nanowires in this chapter were grown on GaAs (111)B substrates prepared with gold colloid particles as detailed in chapter 2.2.3. The substrates with the gold particles were then annealed for 10 min under AsH$_3$ protective flow at 600 °C prior to cooling down to the growth temperature, varied between 450 and 525 °C. Upon reaching a stable growth temperature, group III precursors Trimethylindium (TMIn) and Trimethylgallium (TMGa) were introduced into the growth chamber to initiate growth of the In$_x$Ga$_{1-x}$As nanowires. The molar flows of TMIn and TMGa in all experiments in this chapter were fixed at 3.9 × 10$^{-6}$ and 9.2 × 10$^{-6}$ mol.min$^{-1}$, respectively. This corresponds to the TMIn molar ratio, (TMIn/TMIn + TMGa) of 0.30 in the vapour phase. The nominal V/III ratio was varied by
varying the molar flow of AsH₃ in the range of 1.8 × 10⁻⁵ – 6.0 × 10⁻⁴ mol.min⁻¹ corresponding to nominal V/III ratios of 1.4–40.0. Growth time was set constant at 20 min, unless otherwise noted.

Nanowires were investigated using field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Cross-sections of the nanowires were prepared by slicing 40 nm segments from embedded nanowires using an ultramicrotome as detailed in chapter 3.4.2. Composition mapping was investigated by energy-dispersive X-ray (EDX) spectroscopy in a scanning transmission electron microscopy (STEM) system with an electron beam spot size of 0.5 nm. The measurement error in the composition is in the range of ±4 atomic percent based on reference GaAs and InAs nanowires samples as previously discussed in chapter 3.5.3.

PL measurements were carried out by collaborators in Oxford University, using a custom-built module attached to a Fourier transform infrared spectrometer (FTIR) (Bruker Vertex 80v). The module included a continuous-wave, frequency doubled Nd:YAG laser (λ = 532 nm) source, excitation and collection optics, and an integrated cold finger helium flow cryostat. After passing through the FTIR, PL was detected using a liquid nitrogen cooled mercury cadmium telluride detector connected to a lock-in amplifier (Stanford SR830). Nanowire ensembles were transferred from the growth wafer to quartz substrate by gentle rubbing to avoid misreading the signals coming from the overgrowth on the substrate. The full-width half maximum of the spot size and power of the laser at the sample were 0.9 mm and 5.3 mW respectively, giving an average excitation intensity of 0.2 Wcm⁻² over a typical ensemble of >1000 nanowires.

5.3 Effect of growth temperature and V/III on morphology and growth rate

Growth temperature can play a large role in the growth of nanowires affecting their morphology, growth rate and crystal structure [17]–[24]. Nanowire tapering in GaAs nanowire for an example has been shown to reduce particularly in the low growth temperature regime [17]. In combination with the growth temperature, low V/III ratios were also found to reduce tapering in InAs nanowire [18]. Tapering was found to be more critical in ternary nanowires since this can be responsible for a composition gradient along the nanowire axis [25]. Hence, this section focuses on the morphology of InₓGa₁₋ₓAs nanowires.
nanowires grown with various combinations of growth temperature and V/III ratios. Figure 5.1 shows the 45°-tilted SEM views of nanowires grown with two different V/III ratios (2.4 and 40.0) as a function of growth temperature. This series illustrates the influence of temperature and V/III ratio on the morphology and growth rate of the nanowires. First, consider the temperature series for nanowires grown at the high V/III ratio of 40, illustrated by the SEM images in figure 5.1(a-d). All nanowires grown with this V/III ratio have a tapered morphology independent of growth temperature. There is neither a significant change in morphology in the sample grown over the temperature range of 450 to 475 °C, nor a difference in axial growth rate (Figure 5.1(a-b)). However, a significant increase in the radial growth rate and a concomitant drop in axial growth rate are observed when the growth temperature is increased to 500 °C, leading to a much shorter and more tapered nanowires. At 525 °C, this effect is further enhanced.

Now, consider the same temperature series for a fixed lower V/III ratio of 2.4 (Figure 5.1(e-h)), more dramatic morphological changes are observed. Excluding a relatively large hexagonal pyramidal base, the nanowires are mostly non-tapered from 450 °C [Fig. 5.1(e)] to 500 °C [Fig. 5.1(g)]. However, as growth temperature is increased to 525 °C, the nanowires show similar features as those grown with a V/III ratio of 40.0 [Fig. 5.1(d)] where tapering and large parasitic growth on the surface are observed in the SEM image [Fig. 5.1(h)]. In addition, the axial growth rate increases with temperature until 500 °C, in clear contrast to the evolution discussed above for a higher V/III ratio. However, the axial growth rate decreases slightly at 525 °C. From this set of study, uniform untapered nanowires are obtained with a combination of growth temperature of 500 °C and V/III ratio of 2.4.
5. Controlling the phase and composition tunability of In$_x$Ga$_{1-x}$As nanowires

**Figure 5.1:** 45°-tilted FESEM images of nanowires grown at various growth temperatures and V/III ratio of (a-d) 40.0 and (e-h) 2.4. The rough edges on the sidewall generally indicate crystal phase disorder. A combination of growth temperature of 500 °C and V/III ratio of 2.4 is found to produce uniform untapered nanowires with smooth wall side facets. Scale bars represent 500 nm.

The morphological evolution is understood in terms of the effect of growth temperature on the decomposition of TMGa and TMIn precursors. Indeed, at higher temperature, the pyrolysis of metal-organic (MO) precursors becomes more efficient, hence dramatically increasing the available adatom density. This, in turn, increases supersaturation and lowers the adatom mobility which enhances radial growth, yielding the observed tapering of the nanowire sidewalls, together with some parasitic planar crystallization on the substrate.

Finally, looking at the V/III ratio dependence of morphology and axial growth rate for the four different temperatures considered in this series, it is clear that a high V/III ratio favours tapering at all temperatures while a low V/III ratio reduces lateral growth and thus tapering in the moderate temperature range (450-500 °C). Very high growth temperature [525 °C, (d);(h)] also enhances tapering independent of V/III ratio. However, comparing the length of nanowires between (a);(e), (b);(f) and (c);(g), the axial growth rate is clearly in a group V-limited regime for the low V/III ratio series (e)-(g) until 500°C. From a practical point of view, a temperature in the narrow range of 475-500 °C combined with the very low V/III ratio of 2.4 seems to allow for nearly taper-free morphology and reasonable axial growth rate above the nucleation region close to the substrate, where a pyramidal base
extends from the nanowire sidewalls to the substrate region. Such a low V/III ratio and low supersaturation regime is therefore experimentally observed to virtually suppress the driving force for radial growth. The fundamental reason for this behaviour will be discussed in the next section as the growth of the nanowires are related to their crystal structure.

5.4 Effect of growth temperature and V/III ratio on crystal structure and composition

To gain more insight into the evolution of the nanowires with growth temperature, investigations were carried out to determine the crystal structure and composition of tapered nanowires grown with a V/III ratio of 40.0 at growth temperatures of 450 and 500 °C. Shown in figure 5.2 is a typical In$_x$Ga$_{1-x}$As nanowire characteristic from an ensemble that was grown at 450 °C with V/III ratio of 40. Nanowires grown in this regime have a tapered morphology and rough sidewalls suggesting crystal phase disorder [26] which is clearly observed in the SEM image of figure 5.2 (a). High-resolution transmission electron microscopy (HRTEM) image in figure 5.2 (b) confirms that the nanowire has a high density of stacking faults. The inset shows the selected-area electron diffraction (SAED) pattern of the region. The nanowire is mainly ZB with twins and some WZ phase as can been observed in the HRTEM image accompanied by the streaking and spots seen in the SAED pattern. EDX measurements of this nanowire are presented in figure 5.2 (c). The EDX measurements were carried out in STEM mode and show that the composition along the nanowire is not uniform. In particular, higher In content is observed at the base. High-angle annular dark field (HAADF) images of the nanowire cross-section with a corresponding EDX cross-section map is shown in figure 5.2 (d-g) and reveals that a spontaneous core-shell structure is formed with a higher In concentration in the shell than the core. These results are similar to those previously reported in [5], [27]. Kim et al. [27] attributed the higher In content in the shell to the difference of In and Ga diffusion lengths.
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![Image of nanowires and atomic percentages](image)

**Figure 5.2**: (a) 45°-tilted FESEM view of nanowires grown at growth temperature of 450 °C and a V/III ratio of 40. (b) HRTEM image of the nanowire showing a mixed phase of zincblende with twins and wurtzite segments. The inset on the bottom left is the SAED pattern from the same nanowire. (c) HAADF image of a single nanowire with corresponding EDX line scan along the nanowire (d-g) The cross-section of a similar nanowire presented in HAADF image and EDX cross-section mapping of Ga, In and the overlay of In and Ga showing a spontaneous formation of a core-shell structure with higher Ga concentration in the core.

Interestingly a different situation is observed for nanowires grown at 500 °C. Figure 5.3 (a) shows a typical TEM image of the nanowire grown at 500 °C with the same V/III ratio of 40.0. It shows that the crystal structure is ZB with random twinning and the composition gradient for the tapered nanowire in figure 5.3 (b) is not as prominent as those grown at the lower growth temperature of 450°C in figure 5.2. There is however, still a slight composition gradient, best illustrated by the In signal in the EDX linescan shown in figure 5.3 (b). This reveals a rather different nanowire growth behaviour compared with the lower growth temperature shown in figure 5.2. In order to obtain a truly three-dimensional (3-D) map of the composition evolution, the cross-sections of the nanowires taken from the first micrometer from the base of the nanowires were analysed using the EDX mapping. Representative maps are shown in Figure 5.3 (c-f). The Ga signal is uniform across the whole cross-section indicating that Ga is incorporated not only through the VLS mechanism.
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(precipitated under the droplet at the droplet/crystal interface) but also via the VS mechanism on the sidewalls. This shows a clear suppression of the spontaneous core-shell structure formation with higher growth temperature.

![Figure 5.3](image)

**Figure 5.3:** (a) HRTEM images of the first micrometer from the tip of the nanowire grown at 500°C with a V/III ratio of 40.0. The inset shows the corresponding SAED pattern (b) EDX line scan representing the composition distribution of each element along the nanowire. The image above the line scan is the dark field image of the corresponding nanowire lying on the TEM grid. (c-f) Cross-sectional HAADF image of a nanowire taken from the first micrometer from the base of the nanowire and the corresponding EDX maps of Ga, In.

Two possible growth scenarios can be taken into account for the higher incorporation of Ga in the radial growth at this growth temperature. One is that there is a higher desorption rate of In at higher growth temperature as compared to Ga thereby allowing Ga to be more readily adsorbed at the nanowires sidewall. However this effect should be negligible in the (low) temperature range investigated in this study. The second mechanism is the increase of TMGa decomposition with temperature. It is known that TMIn decomposes completely at temperatures just below 400 °C while TMGa decomposes completely at temperature around 475 °C in H$_2$ ambient [28]. Hence, when the temperature increases above 450 °C, there is an increase in TMGa decomposition which contribute to a higher available Ga/In adatom ratio. This allows more Ga to be readily incorporated into the nanowire.
To further investigate the effect of growth parameters on morphology, crystal structure and composition in this relatively high growth temperature regime, nanowires were grown at 500 °C with varying V/III ratios between 1.4 and 20.0. The SEM images of these nanowires with various V/III ratios are shown in figure 5.4 (a-e). At a V/III ratio of 1.4, nanowire growth is significantly impaired due to insufficient As to support nanowire growth. We observe nanowire growth at V/III of 2.4 onwards where tapering is found to increase as the V/III ratio increases. Figure 5.4 (f-h) shows the HR-TEM images of these nanowires for three V/III ratios and their corresponding EDX line scan along the nanowires. A gradual change of the crystal structure is observed from the low V/III ratio towards a higher ratio. At a V/III ratio of 2.4, the nanowires have a pure WZ crystal structure but as the V/III ratio increases, more ZB segments or stacking faults appear. The HR-TEM images shown here were taken within the first micrometer segment below the nanoparticle, that represents the typical structure of the whole nanowire. EDX compositional profile of the nanowires grown with different V/III ratios is shown on the right of figure 5.4 (b-d). It is clear that the composition is uniform along each nanowire except for small fluctuations within the measurement error. Interestingly, the composition is tunable by varying the V/III ratio. The Ga compositions, $X_{Ga}$ are approximately 0.30, 0.36 and 0.56 for nanowires grown with V/III ratio of 2.4, 5.0 and 20.0, respectively. From the analysis of the EDX spectrum, the actual molar fraction of Ga in the nanowire is much lower than the molar ratio of Ga in vapour, $X_{v(Ga)} = 0.70$. The higher In content could be due to the greater affinity of In towards the Au seed and higher In surface adatoms mobility as compared to Ga [29]. The presence of In has also been found to reduce the solubility of Ga in the Au alloy particle [30]. The estimated Ga content using Vegard’s Law and the lattice constant measured from the diffraction pattern of the In$_x$Ga$_{1-x}$As nanowires grown with a V/III ratio of 2.4 is 0.26, which is close to the EDX result.
Figure 5.4: (a-e) 45°-tilted FESEM views of nanowires grown at 500 °C with increasing V/III ratio from 1.4 to 40.0. Scale bars represent 500 nm. (f-h) HRTEM images from the first micrometer from the tip of the nanowire grown at 500 °C with V/III ratios of 2.4, 5.0 and 20.0, respectively. The inset shows the corresponding SAED pattern. On the right side of each TEM image is the EDX line scan representing the composition distribution along the nanowire with the dark field image of the corresponding nanowire lying on the TEM grid. From the EDX measurements, the Ga atomic percentage of the nanowires are found to be 15, 18 and 28 corresponding to a Ga molar fraction, $X_{\text{Ga}}$, of 0.30, 0.36 and 0.56 for nanowires grown with V/III ratio of 2.4, 5.0 and 20.0, respectively.
Earlier studies for InAs and GaAs nanowires have indicated that the perfection of the WZ phase (absence of stacking faults) is favoured at lower V/III ratio and high growth temperature compared to ZB phase which prefers higher V/III ratio and low growth temperature [19], [31]–[33]. Hence, it is not surprising that In$_{x}$Ga$_{1-x}$As nanowires would follow the same trend. Accordingly, in this work, it is found that while keeping the growth temperature constant at 500 ºC, the crystal structure can be tuned from WZ to more ZB phase by increasing the V/III ratio. The change of crystal structure of nanowires is commonly accepted to be a result of the change in supersaturation which relates to the change in chemical potential at the liquid-solid interface [30]. Recently, Lehmann et al. [31] found that a 50-100 times higher flow rate of group V can change the crystal structure from WZ phase directly to ZB phase for various type of binary III-V nanowires. In their report, they suggest that the abundance of As may reduce the surface energetics of the nanowire growth front which would affect the nucleation barrier for WZ and ZB phase. The change in the surface energetics at the VLS system at the nanowire growth front changes the critical chemical potential at the liquid-solid ($\Delta\mu_{LS}^{critical}$) interface which makes it more favourable to form either ZB or WZ phase [31]. Hence, it is believed in this case that increasing the As ratio, reduces the critical chemical potential at the liquid-solid interface for ZB phase nucleation ($\Delta\mu_{LS}^{ZBcritical}$) which favours the growth in ZB phase. This continues until it reaches again the critical chemical potential at the liquid-solid interface for WZ phase nucleation ($\Delta\mu_{LS}^{WZcritical}$) [34]. This cycle may fluctuate resulting in the random formation of ZB and defects along the nanowire. As the V/III ratio further increases, $\Delta\mu_{LS}^{ZBcritical}$ is reduced even more, making it more stable to form ZB phase than the WZ phase. Hence, at a V/III ratio of 40.0, the nanowire has even more ZB segments and twins rather than WZ segments as shown in figure 5.3. A further study by Lehmann et al. in ref. [34] shows that deviations from the V/III ratio which form WZ phase can easily trigger defects and introduce ZB phase.

In particular, the trend of WZ-ZB transition happens in the group-III limited regime where the V/III ratio is high [34]. A similar observation is realised with In$_{x}$Ga$_{1-x}$As nanowires in this study. A further increase in V/III ratio to 86.0 is found to form pure ZB phase as shown in figure 5.5. In this particular sample, the nanowires were grown on In$_{x}$Ga$_{1-x}$As stems which were grown at lower V/III ratio. Indeed, at high V/III ratio, nanowire nucleation is suppressed due to high planar growth rate. Therefore, the stems allow the nanowire to nucleate properly during the initial stage before the V/III ratio was ramped up to 86.0. Although this sample was grown with a stem which is slightly different to the other sample from the series, the trend of an increase in ZB phase with increasing V/III ratio is still valid and is therefore taken into account to further elaborate on the results. Also, note
that radial growth occurs over the stem due to the increase of V/III ratio that highly favours radial growth as previously discussed.

**Figure 5.5**: a) TEM image of the nanowire that was grown at 500 °C and V/III ratio of 2.4 for 30 minutes then V/III ratio of 86 for 10 minutes. b) HRTEM of the segment where the nanowire are grown with V/III of 86.0, showing a pure ZB phase.

Besides the change of crystal structure, it is also interesting to observe changes in the composition of the In$_x$Ga$_{1-x}$As nanowires with increasing V/III ratio. The similar method introduced in refs. [32], [33] is used to determine the percentage of twinned bilayers in the nanowires as a function of V/III ratio. This is plotted in figure 5.6 in order to further clarify the trend of crystal phase with V/III ratio. A 100% twinned bilayers fraction refers to a pure WZ phase while a ZB phase has no twinned bilayers and mixed phase is represented in between these two extremes. The average Ga molar fraction obtained by EDX measurements is also plotted against the V/III ratio in figure 5.6. Higher Ga concentration is observed in samples grown with higher V/III ratio where there is also more ZB phase observed.
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**Figure 5.6:** The average percentage of twinned bilayers and Ga molar fraction as determined by the EDX, $X_{Ga}$ against the V/III ratio. Nanowires were grown at a constant growth temperature of 500 °C. Error bars for the twinned bilayers are within data points.

There could be an increase of Ga concentration in the Au-alloy particle during growth as the V/III ratio increases. However, this cannot be confirmed as the composition of the Au-alloy particle after growth has very little Ga concentration and no clear variation is observed for various V/III ratios. A typical EDX spectrum representing the Au-alloy particle composition is shown in figure 5.7. Ga is known to deplete from the Au-alloy particle while cooling in AsH$_3$ ambient [35]. In all cases, there is always more In in the particle after growth which is supported by the fact that In is much harder to deplete out of Au compared to Ga when both species are present [29], [30].
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**Figure 5.7:** EDX spectrum was taken at the middle of the nanowire Au-alloy particle for the sample grown at 500 °C and V/III ratio of 20.0. Copper signal is from the copper grid used for holding nanowires for TEM characterisation. Only Ga, As, Au and In signal is taken into account in determining the composition of the Au-alloy particle. Ga and As peaks are typically very small peaks in all set of samples.

In addition to compositional variation, the V/III ratio series also reveals a direct correlation between radial growth and crystal structure. Although radial growth may increase due to the lower adatom diffusion at high V/III ratio, the crystal defects are believed to further enhance the radial growth. Crystal defects have been reported to act as nucleation sites for radial growth [36], [37]. Hence, a higher density of defects would lead to a higher degree of tapering. From this reasoning, one can propose that once the crystal phase purity is obtained, radial growth and compositional inhomogeneity would be minimised regardless of the length of the nanowires. Indeed, we demonstrated this in the optimised sample with pure WZ structure which was grown for 80 minutes (4 times longer growth time than for standard samples, as those grown in figure 5.1). Figure 5.8 (a) shows a 45°-tilted SEM view of the nanowires and figure 5.8 (f) is the bright field TEM image of a nanowire showing that the nanowire is 7 µm long with negligible tapering. A uniform composition is confirmed by the EDX mapping shown in figure 5.8 (c-e) and the EDX line scan measurements are from the areas at the top, middle and the base of the nanowire. Note that the composition is slightly different ($X_{Ga} = 0.20$ instead of 0.30) possibly due to the slight variation of density from the previous pure WZ nanowire shown in figure 5.4.
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**Figure 5.8:** (a) 45°-tilted FESEM view of the 7 µm long almost defect-free $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowire b) cross-sectional HAADF image of the nanowire obtained from the middle region of the nanowire. (c-e) EDX map of Ga and In of the corresponding cross-section in b). f) TEM image of the nanowire with EDX (~1 µm) line scan measurements at the top, middle and bottom of the nanowire.

The crystal structure of the long nanowire maintains almost defect-free wurtzite phase with a defect concentration of less than one stacking fault per micron, randomly located along the length of the nanowires. The ability to grow longer nanowires with high quality crystal structure further supports that the radial growth is further suppressed due to the absence of stacking faults and zinc-blende segments.
5.5 Effect of Au-seed particle size on morphology, crystal structure and composition

The size of the seed particle is known to have a pronounced effect on nanowire growth, especially on their crystal phase. [19], [32], [38]–[42]. Hence, to further gain insight on the effect of Au-seed particle size towards morphology, crystal structure and composition of In$_x$Ga$_{1-x}$As nanowires, different sized Au-seed were used in the growth at 500 °C and V/III ratio of 2.4. This was the growth condition for almost defect-free WZ In$_x$Ga$_{1-x}$As nanowire with uniform morphology and composition using 30 nm Au particles. It is of interest to see whether WZ phase can be maintained with larger diameters since this is not the case for InAs nanowires [19], [32].

Figure 5.9 shows the SEM images of the nanowires grown with 10, 20, 30, 50 and 80 nm Au-seed particles. It can be clearly observed that the lengths of the nanowires seeded by the smaller diameters, 10 and 20 nm are much shorter, possibly due to the Gibbs-Thompson effect which slows down the growth rate of the smaller diameter nanowires. A similar effect has been reported for InAs nanowires with a diameter of 25 nm and smaller [38]. The growth rate was observed to increase with the diameter up to 50 nm, then decreases slightly when grown with 80 nm seed particles. TEM images in figure 5.9 (f-j) show the crystal structure of the nanowires grown with various Au-seed particle sizes. Nanowires seeded by 10, 20 and 30 nm Au-seed particles show a pure WZ phase similar to the one previously discussed in this chapter while those seeded by 50 and 80 nm Au-seed particles have dominantly a ZB crystal structure with twins and small segments of WZ. This shows that the WZ phase cannot be maintained at larger diameters and goes through WZ-ZB transition with increasing diameter. This transition is similar to those of InAs nanowires [19], [32] and can be explained by the change in supersaturation of the Au-alloy particle as affected by the Gibbs-Thompson effect [39].
Figure 5.9: (a-e) Side views of nanowires grown at 500 °C with V/III ratio of 1.4 for 10, 20, 30, 50 and 80 nm, respectively. Scale bars represent 500 nm. (f-j) TEM images from the tip area of nanowire grown with 10, 20, 30, 50 and 80 nm, respectively corresponding to nanowires from sample in the SEM images of (a-e).
Figure 5.10: The average percentage of twinned bilayers and Ga molar fraction, $X_{Ga}$, against the Au-seed particle. Nanowires were grown at a constant growth temperature of 500 °C. Error bars are within data point for the twinned bilayers.

With regards to the composition, Ga incorporation is observed to increase with the diameter as shown by the graph in figure 5.10. This also follows with the increase of the ZB phase which again indicates a correlation between the crystal phase and the composition similar to the one previously discussed and shown in figure 5.6. As discussed earlier and shown by figure 5.7, the post-growth Au-alloy composition was found to have no traces of Ga and instead only contained In. Similar result are obtained for the Au-alloy in this set of samples. Further EDX composition mapping of the 80 nm Au-seeded nanowire shown in figure 5.11 reveals an interesting finding whereby the segment beneath the Au-alloy particle has a higher In content as compared to other parts of the nanowire. It is believed that this segment grew after the In and Ga supplies were shut off. Hence, the observation indicates that during growth there could be more In in the Au-alloy particle.
5. Controlling the phase and composition tunability of In$_x$Ga$_{1-x}$As nanowires

Figure 5.11: a) HAADF image of the tip area of 80 nm Au-seeded nanowire. (b-e) EDX maps of Au, Ga, In and the overlay of all there images showing the composition distribution around the tip area of the 80 nm Au-seeded nanowire.

5.6 Optical properties of WZ In$_x$Ga$_{1-x}$As /InP nanowire core-shell structures

To investigate the optical quality of the uniform pure WZ phase In$_x$Ga$_{1-x}$As nanowires achieved in this chapter, an additional sample of 30 nm Au-seeded In$_x$Ga$_{1-x}$As nanowires with InP shell was grown to passivate the In$_x$Ga$_{1-x}$As surface states. The core nanowires were grown for 45 minutes at 500 °C with V/III ratio of 2.4 and the InP shell was grown at 550 °C with V/III ratio of 780 for 8 minutes corresponding to about 10 nm in thickness. The structural properties of these nanowires are similar to the one shown in figure 5.4 (f) which has a WZ phase. The nanowires also maintain a taper-free morphology with a small InP tip that overgrew axially during the growth of the InP shell. The composition of the core, is In$_{0.65}$Ga$_{0.35}$As as obtained by EDX measurement of the nanowire cross-section shown in figure 5.12 (b-c). The shell was observed to be rather uniform around the core as shown by the EDX mapping in figure 5.12 (d-h).
5. Controlling the phase and composition tunability of In$_x$Ga$_{1-x}$As nanowires

**Figure 5.12:** a) SEM image of In$_x$Ga$_{1-x}$As/InP core-shell nanowire grown at 500 °C and V/III ratio of 2.4 with InP shell grown at 550 °C. b) HAADF image of the cross-section of the nanowire obtained from the middle region of the nanowire showing 10 nm InP shell surrounding In$_x$Ga$_{1-x}$As nanowire core. The crosses represent the spot where EDX measurement was carried out to determine the core composition. c) the composition of the core as measured by spot analysis at the centre of the nanowire cross-section in b). (d-g) EDX mapping of the cross-section for each composition species (h) the overlay of the EDX maps for all composition species.

The photoluminescence measurements were carried out on ensembles of nanowires spread on quartz substrate. The photoluminescence spectra measured at 6 K are shown in figure 5.13.
5. Controlling the phase and composition tunability of In$_x$Ga$_{1-x}$As nanowires

Figure 5.13: Photoluminescence spectra of ensemble of In$_{0.65}$Ga$_{0.35}$As nanowires and In$_{0.65}$Ga$_{0.35}$As/InP core-shell heterostructure nanowires measured at 6 K

Without the passivation, no significant PL peak was observed as shown in figure 5.13 which clearly indicates that a passivation layer is required to suppress surface recombination. This is further supported when a single peak at 0.815 eV (1.54 µm) is clearly observed for the In$_{0.65}$Ga$_{0.35}$As/InP heterostructure. However, this peak is blue shifted from the expected value calculated for In$_{0.65}$Ga$_{0.35}$As (at 6 K the expected value is for unstrained ZB In$_{0.65}$Ga$_{0.35}$As is 0.696 eV (1.78 µm)), which is understood to be a combination of the larger bandgap of the WZ phase [43] and the compressive strain imposed by the InP shell to the In$_x$Ga$_{1-x}$As core. A blue shift purely due to WZ phase without strain effect for In$_x$Ga$_{1-x}$As and InAs can be on the order of 30 -100 meV [43], [44]. An even higher blue shift can be caused by the compressive strain which has been reported to be larger in WZ phase [45]. However, it is difficult at present to differentiate between the shifts posed by the strain and the WZ phase as this also is very much dependent on the composition [46]. The broad PL linewidth, consistent with previous reports [7], [47] can also be due to the inhomogeneity of the strain along the nanowire and/or due to the small fluctuation of the composition, which is below the detection level of our EDX measurements. This interesting potential to tune the emission wavelength by strain engineering will be the subject of Chapter 7 where it is further explored with In$_x$Ga$_{1-x}$P shell.
5.7 Summary

This chapter presented a systematic study of In$_x$Ga$_{1-x}$As nanowire growth over a range of growth parameter combinations. A wide range of growth windows resulted in tapered morphology nanowires. However, an optimum set of growth conditions for pure crystal phase, taper-free and uniform composition In$_x$Ga$_{1-x}$As was found within the study. The optimum growth conditions suppress the self-forming core-shell structure, which is often reported for tapered ternary nanowires. The composition was found to depend on growth temperature, V/III ratio and seed particle size despite keeping the ratio of the In and Ga in vapour constant. Hence, this shows tunability of composition with growth temperature, V/III ratio and diameter. Further investigation of the nanowire crystal phase shows that Ga incorporation increases with the amount of ZB phase suggesting a crystal phase dependent In$_x$Ga$_{1-x}$As composition. Detailed TEM studies also reveal that radial growth is directly correlated with the amount of planar defects along the nanowires. Defects or ZB segments in the predominantly WZ crystal structure act as nucleation sites for radial growth and causes significant tapering of the nanowire. This allows us to tune their morphology thereby achieving taper-free In$_x$Ga$_{1-x}$As nanowires up to several microns in length whilst maintaining composition homogeneity along their entire length. PL measurements on InP capped WZ phase In$_{0.65}$Ga$_{0.35}$As nanowires reveal that the nanowires emit in the IR region of 1.54 µm at low temperatures and the PL peak is blue shifted compared to the expected emission from unstrained ZB In$_{0.65}$Ga$_{0.35}$As due to the WZ phase and compressive strain imposed by the InP shell.

In the following chapter, the ternary nanowire growth model is extrapolated with the experimental findings in order to gain a deeper understanding of the main factors that govern the composition and growth rate of In$_x$Ga$_{1-x}$As nanowires. Further investigations of other heterostructures with In$_x$Ga$_{1-x}$As core shall be presented in chapter 7, which could expand the possibility of strain in the bandgap tunability of the core-shell heterostructures.
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References


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Chapter 6

Towards understanding of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth

Overview

In this chapter, a growth model is proposed to explain the growth evolutions of Au-seeded In$_x$Ga$_{1-x}$As nanowires. The model is based on the irreversible nucleation rate of nanowire growth to minimize the uncertainties which could arise from the classical nucleation model. The model was found to match the experimental results well, thus providing a deeper understanding of the factors that govern the growth rate and the composition of In$_x$Ga$_{1-x}$As nanowires. The understanding may serve as the basic knowledge on how to control growth of In$_x$Ga$_{1-x}$As nanowires. Nonetheless, the model can still be extended to understand the growth of other ternary nanowires and cover a wider range of growth conditions including other issues that can be governing the growth of ternary nanowires. A large part of the results from this chapter have been published in ref. [1].
6. Towards understanding of Au-seeded In\textsubscript{x}Ga\textsubscript{1-x}As nanowire growth

### 6.1 Introduction

As previously presented in chapter 2, ternary nanowires are interesting as they allow for the desired bandgap tunability simply by changing the alloy fraction of the ternary compound. However, they bring additional complexity in terms of understanding and control because of compositional and structural inhomogeneity due to segregation [2], intermixing, different diffusion coefficients for each species, composition-dependent crystal structure [3], [4] and differing incorporation pathways for each element at the Au alloy particle-nanowire interface or on the exposed sidewalls [2], [5], [6]. This has been discussed earlier and more references can be found in chapter 2. Improving our fundamental understanding of ternary nanowire growth and composition evolution as a function of directly accessible experimental parameters would therefore be crucial to achieve better control over the device structures.

There has been a great amount of theoretical and modelling work in trying to enhance the understanding of single and binary nanowire growth in the past decades [7]–[13]. These works have served as a fundamental conceptual toolkit towards controlling the growth of nanowires. Despite recent interest [14]–[16], true understanding and modelling of ternary III-V nanowires obtained by the VLS mechanism with Au catalysts is still lacking. This is due to several issues such as: (i) complex equilibrium phase diagrams and non-equilibrium chemical potentials of quaternary alloys such as Au-Ga-In-As in our case [17], (ii) uncertainties in determining the composition of the initial critical nucleus even if both Au alloy particle and solid compositions were exactly known, (iii) absence of any data on relevant surface energies of different interfaces and (iv) lack of reliable data on the kinetic parameters (diffusion lengths, desorption rates of As etc.) as a function of the composition. Therefore, the existing approach based on chemical potentials, surface energies, and the Zeldovich nucleation rate for macroscopic islands [8], [18], [19] as presented earlier in chapter 2, may require some crude assumptions which cannot be easily checked against experimental data. Consequently, a simple model for complex growth phenomena in In\textsubscript{x}Ga\textsubscript{1-x}As nanowires is developed and discussed in this chapter.

In the previous chapter, the growth of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires under several combinations of growth parameters are already discussed providing practical knowledge on how to achieve nearly untapered, compositionally homogeneous, and pure crystal phase In\textsubscript{x}Ga\textsubscript{1-x}As nanowires. This chapter is aimed at providing deeper insights into the fundamental understanding using theoretical modelling to support the experimental
findings. The final nanowire axial growth rates and compositions as a function of different experimentally controlled conditions together with fittings from the model are presented and discussed. The main parameters that are expected to influence the nanowire growth and composition are: Au alloy particle diameter, V/III flow ratio in vapour and growth temperature. The model is capable of describing the main experimental trends and most importantly, may serve as the first step toward establishing a more advanced understanding of the growth of ternary nanowires.

6.2 Scientific hypotheses and assumptions for the model

6.2.1 General context of the growth model

The schematic for Au-seeded growth of In\textsubscript{x}Ga\textsubscript{1-x}As nanowires in metal-organic vapour phase epitaxy (MOVPE) reactor is illustrated in figure 6.1. The trimethylindium (TMIn), trimethylgallium (TMGa) and arsine (AsH\textsubscript{3}) precursors arrive at different surfaces from vapour in a given proportion, dissociate with different temperature-dependent rates, and incorporate on the sidewalls by the vapour-solid (VS) mechanism, or through the Au alloy particle \{111\}B surface by the vapour-liquid-solid (VLS) mechanisms. VS and VLS are the two generic mechanisms that govern the growth and final morphology of the nanowire. The Au alloy particle size, however, should be preserved during steady-state growth.

![Figure 6.1: Schematics of Au-assisted In\textsubscript{x}Ga\textsubscript{1-x}As nanowire growth by MOVPE reactor. The VLS growth in (a) results in a time-independent radius while the combination of VLS and VS growths in (b) yields nanowires with tapered morphology. The TMGa, TMIn and AsH\textsubscript{3} precursors decompose into Ga, In and As, respectively, releasing by-products. The As atoms incorporate through direct impingement only, while Ga and In adatoms are able to diffuse to the Au alloy particle from the nanowire sidewalls, with the diffusion lengths \(\lambda_{Ga}\) and \(\lambda_{In}\), respectively.](image)
6. Towards understanding of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth

6.2.2 Composition of Au alloy particle and nanowire solid

The composition of the Au alloy particle during the growth of nanowires is specifically important for growth of alloy nanowires with three or more species as it should correlates to the final nanowire composition. However, it is difficult to determine the composition of the Au alloy particle during the growth due to the limitation of currently available in-situ experimental techniques. Based on some of the ex-situ post growth measurements of the Au alloy particle composition as presented earlier in chapters 4 and 5 including some of others reports [6], [14], the composition of the Au alloy particle should reflect closely the composition of the final nanowire. To clarify, it is noted that in some cases this assumption may not be valid, since it has been suggested that In species, although found post-growth in the Au alloy particle, may not be precipitated into the solid nanowire phase [11].

Therefore, in this model, the relative atomic concentrations of In and Ga are assumed to be the same in the liquid and solid states, hence the nanowire composition is given by

$$x_{In} = \frac{c_{In}}{c_{In}+c_{Ga}}; \quad x_{Ga} = \frac{c_{Ga}}{c_{In}+c_{Ga}}$$

(1)

where $x_{In}$ and $x_{Ga}$ are the atomic concentrations of In and Ga atoms in the nanowire while $c_{In}$ and $c_{Ga}$ are the atomic concentrations in the Au alloy particle.

This invariant composition assumption implies a transport-limited regime of nanowire growth rather than a nucleation-limited growth mode in which the liquid and solid composition can be very different for many reasons (preferential nucleation and/or two-dimensional growth of one compound versus the other, non-stoichiometric nuclei etc.).

6.2.3 Nucleation model

While the nucleation-limited regime should be described by the Zeldovich nucleation rate [19] as presented earlier in chapter 2, some recent studies revealed that we really approach the limit of macroscopic theory in such modelling even for binaries. For instance, the nucleus critical size of Au-catalyzed GaAs nanowires grown by hydride vapour phase epitaxy approaches one III-V pair [19] and equals only two III-V pairs in Ga-catalyzed GaAs
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nanowires [20]. Clearly, the classical model for macroscopic island with well-defined boundaries is hardly suited to describe such situations. Furthermore, lack of knowledge on the parameters such as the surface energies and chemical potential for complex quaternary/ternary system required for assumptions in the classical Zeldovich nucleation model would lead to more uncertainties.

Hence, in this chapter, the irreversible growth model is adopted as a better solution in obtaining more understanding on the growth of Au-seeded InGaAs nanowires. Nucleation is irreversible if a dimer (i.e., a nucleus formed by the meeting of two adatoms) is thermally stable and evaporation is neglected. In such case, the nucleation rate depends on attachment rate constant that is related to the diffusion coefficient and the capture rate unlike in Zeldovich nucleation rate where the Zeldovich factor will depend on whether the nucleus will grow or shrink. Recently, the irreversible growth model is reported to provide insight into a larger range of growth conditions beyond the nucleation which includes transitions from mononuclear to polynuclear regime and also the atomistic growth of VLS nanowires [21].

As in the irreversible growth models [21], [22] and in line with the first assumption on the uniform composition, we write the nucleation rate, $J$, in the form of

$$J = \sigma D_{As} n_{As}^i (n_{In}^i + n_{Ga}^i)$$

Here, $D_{As}$ is the As diffusion coefficient in liquid, $n_k^i$ are the surface concentration of atoms of species $k$ ($k = As, In, Ga$) at the liquid-solid interface and $\sigma$ is the capture rate which is assumed identical for $k = In, Ga$. Otherwise, the nanowire composition would differ from the liquid one due to different aggregation probabilities of InAs and GaAs.

Assuming a spatially homogeneous composition in the Au alloy particle due to its small dimension and high diffusivities in liquid at typical growth temperatures, we can write

$$n_k^i = \left( \frac{h}{\Omega} \right) c_k$$

with $h$ as the height of a monolayer and $\Omega$ as the volume per III-V pair in the solid state. Using the atomistic growth picture, we can thus write the second central assumption of the model in the form of

$$J = \sigma D_{As} \left( \frac{h}{\Omega} \right)^2 c_{As} (c_{In} + c_{Ga}).$$

This nucleation rate gives the probability of nucleation per unit surface area. Hence the nanowire elongation rate can be approximated as
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\[ \frac{dL}{dt} = \hbar \pi R_d^2 J, \quad (5) \]

where $R_d$ is the radius of the nanowire top. Here, the nucleation is assumed to be effectively mononuclear [18] although the critical size is close to one. This holds only for narrow facets but in fact Eq. (5) will affect the resulting growth rate only for small enough $R$.

### 6.2.4 Diffusion transport

Another important factor that we have to take into account, which highly affects the growth of nanowires, is the diffusion transport of the species towards the nanowire growth interface and the nanowire sidewalls. This factor is critical in determining the final composition and morphology of ternary nanowires. For example the difference in Ga and In diffusion length is believed to have a pronounced effect on the nanowire composition homogeneity.

#### 6.2.4.1 Diffusion transport of group III species

For the diffusion transport of both group III species, the following simple expression is adopted from [18]:

\[ j_k = 2V_k \left[ 1 + \frac{\lambda_k}{R_d} \left( 1 - \frac{c_k}{c_k^A} \right) \right] \quad (6) \]

for $k = In, Ga$, written for hemispherical Au alloy particle with the radius equivalent to the radius of the nanowire top, $R_d$. Here $V_k$ is the atomic vapour influx of the group III species, accounting for the temperature-dependent cracking efficiencies of TMIn and TMGa [25]. The atomic influx, $V_k$ in this case refers to the deposition rate of In or Ga onto the substrate equivalent to $I.\Omega$ where $I$ is In and Ga flux and $\Omega$ is their elementary volume per III-V pair [18].

$\lambda_k = \sqrt{D_k \tau_k}$ is the effective diffusion length of the group III adatoms on the sidewalls (influenced by the As flux), $D_k$ is the diffusion coefficients of In and Ga adatoms, $\tau_k$ is their effective lifetimes (limited by radial growth) and $c_k^A = V_k \tau_k / \hbar$ is the effective adatom activities on the sidewalls. The first term in Eq. (4) describes direct vapour flux and the second represents surface diffusion of In and Ga adatoms [10], [18]. Desorption of both
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group III species from the Au alloy particle is insignificant and hence neglected at the typical growth temperatures between 400 and 525 °C [18], [23].

In the first approximation, the radial growth rate on the nanowire sidewalls is independent of height, and hence the nanowire shape is conical for the combined VLS-VS and cylindrical for the purely VLS incorporation pathways, as shown in Fig. 6.1. This radial growth can be well described within our model but is not elaborated here, since it does not affect the composition of VLS-grown nanowire cores, constituting the major fraction of the nanowire material. This radial contribution is however suggested as the future improvement for the model as described later in the chapter in section 6.4.2.

The Au alloy particle can maintain a time-independent radius \( R_d \), only when the material influx of group III atoms into the Au alloy particle equal their sink due to nanowire growth, i.e.

\[
x_k \frac{dL}{dt} = j_k
\]  
(7)

for \( k = In, Ga \). Summing up Eq. (7) for In and Ga, we obtain: \( dL/dt = j_{In} + j_{Ga} \), which gives the transport-limited elongation rate.

6.2.4.2 Diffusion transport of As species

Neglecting surface diffusion of As species [22], [24] and accounting for its desorption from the Au alloy particle, the As-limited elongation rate in the steady state is given by [25]:

\[
\frac{dL}{dt} = 2\left[V_{As}(1 + \varepsilon) - v_{As}^{des}\exp(R_{GT}/R_d)c_{As}\right]
\]

(8)

where \( V_{As} \) is the direct atomic flux of As and \( \varepsilon \) describes possible re-emission of As species. Desorption of As atoms from the Au alloy particle is assumed as being proportional to the As concentration with a certain temperature-dependent coefficient \( v_{As}^{des} \). Additionally, we take into account the Gibbs-Thomson (GT) effect [10], [26] which exponentially increases As desorption from small Au alloy particles due to the curvature effect, with a certain characteristic GT radius \( R_{GT} \).

6.2.4.3 Model derivation for In\(_x\)Ga\(_{1-x}\)As nanowire composition and growth rate

So far, the main modelling assumption has been proposed and the expression adopted from previous established works have been clarified. In order to solve the expressions to provide
a simple solution for growth of ternary In\textsubscript{x}Ga\textsubscript{1-x}As nanowires, another assumption of \( D_{Ga}/\lambda_{Ga} \cong D_{In}/\lambda_{In} \) is made to simplify the overall solution.

This assumption means that the reverse diffusion fluxes from the Au alloy particle onto the nanowire sidewalls is the same for both group III species. In this case, the composition is not influenced by the reverse diffusion fluxes from the Au alloy particle [the \(-c_k/c_k^A\) terms in Eq. (6)] which brings the composition ratio into the following equation:

\[
\frac{c_{Ga}}{c_{In}} = \frac{V_{Ga} \left( R_d + \lambda_{Ga} \right)}{V_{In} \left( R_d + \lambda_{In} \right)}
\] (9)

It is noted that this solid composition could diverge from Eq. (9) due to (i) different dimerization rates of InAs and GaAs pairs [neglected earlier in Eq. (4)] and (ii) different sinks of In and Ga atoms in the Au alloy particle, which are lumped together here in the parameters \( D_k/\lambda_k \) for \( k = Ga \) and \( In \) as per the additional assumption mentioned earlier.

Solution for the In\textsubscript{x}Ga\textsubscript{1-x}As nanowire axial growth rate based on equations (5-8) is obtained in the form of

\[
\frac{dL}{dt} = - \frac{V}{(2A+y)^2} \nu_{As} \nu = \sqrt{(1 + A - B)^2 + 4AB} - (1 + A - B)
\] (10)

The coefficients are given by

\[
A = \left( \frac{R_a}{R_d} \right)^3 \exp \left( \frac{R_G}{R_d} \right); B = \frac{2V_{Ga} \left( R_d + \lambda_{Ga} \right)}{V_{As} \pi \lambda_{In} \lambda_{As} d \left( \frac{\nu_{Ga}}{\nu_{As}} \right)} \nu_{In} \left( 1 + \lambda_{In} / R_d \right) ;
\] (11)

where \( \nu_{As} = V_{As} (1 + \varepsilon) ; \nu_{In} = V_{In} (1 + \lambda_{In}/R_d) \) and \( \nu_{Ga} = V_{Ga} (1 + \lambda_{Ga}/R_d) \) are the total influx of As, In and Ga atoms into the Au alloy particle, respectively.

6.3 Relationship between the model and the experimental results

To further enhance the understanding of Au-seeded In\textsubscript{x}Ga\textsubscript{1-x}As nanowires obtained in the experimental results, the model derived in this chapter is fitted to the growth trends. Firstly, the data for the composition and the growth rate were extracted from the experimental work done in chapter 5. This trend provides a better picture of the growth rate and In\textsubscript{x}Ga\textsubscript{1-x}As nanowire composition evolution with the growth parameters such as the Au alloy particle size, V/III ratio and growth temperature. Note that only the results from the single growth temperature are included here as the two-temperature growths may require further
refinement of the model as it may involve a change in the Au alloy phase and composition as mentioned earlier in chapter 4. However, it is believed that the model can be expanded to accommodate the condition. This possibility is later on explained in section 6.4 of this chapter.

Energy-dispersive x-ray (EDX) measurements were performed in scanning transmission electron microscopy (STEM) mode for at least 3 nanowires per sample along the [110] or [1120] zone axis of ~100 nm areas beneath the Au alloy particle. Figure 6.2 shows the typical method of extracting the nanowire composition with the electron beam focused on the top area of the nanowire. Careful consideration is given to ensure that the electron beam is not in the area right below the Au alloy particle where axial growth could have occurred during cooling down and to avoid radial growth contribution (VS growth on sidewall) which may affect the main composition as contributed due to VLS growth. It has been previously shown in chapters 4 and 5, that the composition at the tip area mainly represents the composition of the nanowire through VLS growth mode. The average composition is then plotted against the growth parameters as shall be presented in the following sections.

![Figure 6.2: a) High-angle annular dark-field (HAADF) STEM image of a nanowire grown with 50 nm Au alloy particle. The dotted line represents the region where EDX measurements are taken. b) The corresponding composition as measured by EDX in (a).](image)

As for the growth rate, the heights of the nanowires are measured as discussed in chapter 3 on more than 20 nanowires from scanning electron microscopy (SEM) images. Representative SEM images have been previously shown in chapter 4 for these nanowires. The nanowire growth rates are then plotted against the growth parameters and are discussed together with the model fitting in the following section.
6. Towards understanding of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth

6.3.1 In$_x$Ga$_{1-x}$As nanowire composition

Firstly, we note that the composition of the ternary solid generally differs from the vapour composition as previously discussed in chapter 4. For example, while the given vapour composition, $X_{V(In)}$ is 0.30, the nanowire composition, $X_{In}$ can reach up to 0.65. This effect has also been previously reported in other ternary nanowire growths [27]–[29]. To explain this, we look into Eq. (9) and discuss the possible reasons that may allow for such occurrence. From the equation, the nanowire composition in our model can be different from the vapour composition for two reasons: (i) different diffusion lengths of In and Ga adatoms and (ii) different cracking efficiencies of TMIn and TMGa at the growth temperature. We recall that $V_{Ga}/V_{In}$ gives the ratio of the group III flux entering the Au alloy particle but not the precursor fluxes impinging the Au alloy particle. Higher In composition in the nanowires than in vapour requires either $\lambda_{Ga} < \lambda_{In}$ or $V_{Ga} < V_{In}$. The former inequality is well known since indium is a faster diffuser than gallium. The latter inequality is supported, e.g., by the data by Stringfellow [30] showing that TMIn is a low-temperature precursor while the decomposition of TMGa at the solid surface starts only at above 400 °C and might be very sensitive to the group V flux. Hence the composition of the In$_x$Ga$_{1-x}$As alloy in solid will be affected by the growth conditions.

6.3.1.1 In$_x$Ga$_{1-x}$As nanowire composition and growth rate versus Au seed diameter

Figure 6.3 shows the graph of the composition and the axial growth rate of the In$_x$Ga$_{1-x}$As nanowire versus the Au alloy particle diameter at 500 °C, $V/III$ ratio = 2.4 and Ga/In ratio = 7/3 in vapour. From Eq. (7), the In composition is expected to gradually decrease with the Au alloy particle size due to lower diffusion flux, and reach the vapour composition at $R \to \infty$. From Eqs. (10) and (11), the axial growth rate must first increase with $R$ as $R^2$, then reaches a maximum and further decreases to a constant, as in most growth models for binary nanowires [10], [18], [24]. The solid lines in figure 6.3 show the fittings that are obtained with appropriate parameters. In particular, the best fits are obtained with zero Ga diffusion length on the sidewall ($\lambda_{Ga} = 0$) even at the lowest $V/III$ ratio of 2.4. Note that this diffusion length can be affected by the growth parameters and type of growth method due to the reactor pressure and the way precursors crack [7]. For example, in MOCVD the diffusion length may not be as prominent as those reported in other methods such as chemical beam epitaxy and molecular beam epitaxy [7], [31].
Since the best fit was achieved at \( \lambda_{Ga} = 0 \), this indicates that Ga incorporates mainly by direct impingement while In have additional incorporation via migrations of In to the Au alloy particle from the nanowire sidewalls. The model fitting shown in Fig. 6.3 are obtained at \( \lambda_{Ga} = 0 \), \( \lambda_{In} = 57 \text{ nm} \), \( R_0 = 7 \text{ nm} \) and \( R_{CT} = 9 \text{ nm} \). The cracking efficiencies for TMIn and TMGa are assumed to be equal to one at 500 °C according to Stringfellow [30] so that the ratio of Ga to In vapour atomic influxes, \( V_{Ga}/V_{In} = 7/3 \) is given by the vapour composition. No re-emission of As is required to obtain the fits (\( \epsilon = 0 \)) and thus \( V_{As} = V_{As} \), \( V_{Ga} = 0.292 \times V_{As} \) and \( V_{In} = 0.125 \times V_{As} \). \( V_{As} = 71 \text{ nm/min} \) are used for the overall normalization of the growth rates.

![Graph](image.png)

**Figure 6.3:** Experimentally determined nanowire composition and axial growth rate versus Au alloy particle diameter at fixed \( T=500 \text{ °C} \), \( V/III \) ratio = 2.4 and nominal Ga/In = 7/3 in vapour (symbols), fitted by the expressions used in the model (solid lines). The dotted lines represent \( x_{In} \) in vapour.

### 6.3.1.2 In\(_x\)Ga\(_{1-x}\)As nanowire composition and growth rate versus nominal V/III ratio

Figure 6.4 depicts the behaviour of \( dL/dt \) and \( x_{In} \) with V/III ratio at a fixed growth temperature of 500 °C and Ga/In ratio = 7/3, for 30 nm diameter seed particles. From Eq. (9), the In content decreases for higher V/III ratios due to a lower diffusivity of In adatoms [18], while the growth rate should feature a non-monotonic behaviour with V/III ratio. Eventually, raising the V/III ratio has the same effect on \( dL/dt \) as increasing the Au seed
size. For low V/III ratios and small $R_d$, growth rate and composition are limited by As transport in the excess of group III atoms (where In should reach very high concentrations as a faster diffuser). As the Au seed size or V/III ratio increases, VLS growth is transformed to a group-III limited transport regime such that the growth rate decreases with $R_d$ and V/III ratio and saturates to a constant. The Ga diffusivity is set to zero for all V/III ratios ($\lambda_{Ga} = 0$) as we find that it is the best fit even for lowest V/III ratio of 2.4 as discussed in the previous section. Hence, only the suppression of the In diffusivity for higher V/III ratios is taken into account. For that purpose, we assume that the diffusion length of In scales with the As flux as $\lambda_{In} \propto 1/V_{As}$, i.e., the upward path of In adatoms varies inversely proportional to the V/III flux ratio.

Figure 6.4: Experimentally determined nanowire composition and axial growth rate versus V/III ratio in vapour at fixed $T=500$ °C, nominal Ga/In = 7/3 in vapour and $2R_d=$30 nm (symbols), fitted by the expressions used in the model (solid lines). The dotted lines represent $x_{In}$ in vapour.

6.3.1.3 In$_x$Ga$_{1-x}$As nanowire composition and growth rate versus nominal growth temperature

Finally, the temperature dependence of the $dL/dt$ and $x_{In}$ should be non-monotonic. At low temperatures, the cracking efficiency of TMGa and the diffusion length of In adatoms tend to
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zero, which suppresses the axial growth rate, while at high temperatures VLS growth is suppressed by the As desorption. The In content in solid should tend to unity at low temperatures due to the low cracking efficiency of TMGa. It should also reach a high value at elevated temperatures due to enhanced thermally activated diffusion of In adatoms. These trends correspond to our experimental data, as shown in figure 6.5.

![Figure 6.5: Nanowire composition and axial growth rate versus growth temperature at fixed V/III ratio = 2.4, nominal Ga/In = 7/3 in vapour and 2Rd = 30 nm, (symbols), fitted by the expressions used in the model (solid lines). The dotted lines represent xIn in vapour.](image)

Fitting the temperature dependence of xIn and dL/dt require some additional parameters. We use the Arrhenius temperature dependence of In diffusion length and the coefficient A in Eq. (11) in the form \( \lambda_{In} \propto \exp(-T_A/T) \) and \( A \propto \exp(-T_{des}/T) \) respectively, assuming that the temperature dependence of A is dominated by the enhanced desorption of As through \( v_{As}^{des} \), with rather high values of the corresponding characteristic temperatures \( T_A = 6000 \text{ K} \) and \( T_{des} = 15000 \text{ K} \). The observed decrease of the growth rate toward lower temperatures can be attributed only to the low cracking efficiency of TMGa at low temperatures. For the latter, we use the temperature dependence of Ref. [32]: \( V_{Ga} \propto (1/2)[1 + \tanh((T - T_{Ga})/\Delta T_{Ga})] \) with the characteristic temperature of TMGa decomposition, \( T_{Ga} \) around 480ºC and very narrow transition width, \( \Delta T_{Ga} \) of the order of 10 ºC.
From these fittings with a plausible set of parameters of the experimental results, the model is capable of describing all the observed experimental trends, namely the growth rate and composition versus the Au alloy particle diameter, V/III flow ratio and temperature. Nonetheless, there is still a vast room to improve the model further to understand other aspects such as crystal phase and radial composition, which can also be used for other ternary nanowires.

6.4 Limitation and future improvement

6.4.1 Composition

Although in this chapter it was found that the simple model is able to fit the data and subsequent explanations to the evolution of In$_x$Ga$_{1-x}$As nanowire composition, there are other issues that can affect the final nanowire composition. For example, the solid composition could diverge from Eq. (9) due to (i) different dimerization rates of InAs and GaAs pairs [this was neglected earlier in Eq. (2)] and (ii) different sinks of In and Ga atoms in the Au alloy particle which in this model was lumped together in the parameters $D_k/\lambda_k$ for $k = \text{Ga and In}$. In order to further explore the possibility of how these could affect growth, the model be expanded out and explored to see how they affect the nanowire composition. The composition together with radial growth could also be modeled to provide a better picture on how to control the composition homogeneity across the nanowire cross-section.

6.4.2 Radial growth

As has been presented earlier in chapter 1, the main challenge in growing ternary nanowires is achieving composition homogeneity. Throughout chapters 4 and 5, it was shown that the inhomogeneity along the nanowire of Au-seeded In$_x$Ga$_{1-x}$As is due to the simultaneous radial growth via VS mode while the nanowire grows axially via the VLS mode. Although this model takes into account the radial growth, it has not been fully discussed in this chapter as it only focuses on axial growth rate and the composition of VLS grown nanowires. Thus, in the future this can be a part of the model which can take into account the effect of radial growth on different facets which could also be in relation with the crystal phase [33].
6.4.3 Crystal phase

It is clear that the crystal phase control is one of the main key aspects to improve the quality of the nanowires [34]–[37]. This has been previously discussed over in chapter 2 and pure phase $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ nanowires have been presented in chapters 4 and 5. However, an interesting finding was also observed in chapter 4 where the crystal phase was found to correlate with the composition. This is definitely something that still requires further understanding in which a theoretical model could be beneficial. However due to the complexity of the quaternary phase, lack of knowledge about certain parameters such as the chemical potentials and surface energies and certain assumptions such as the change in composition of Au alloy particle with growth parameters cannot be simplified [14], [38]. Hence, it requires more knowledge of these parameters or otherwise they have to be derived from the existing knowledge of binary systems.

6.5 Conclusions

In summary, a simple model is established to explain the observed trends and in particular to identifying the difference between the nanowire and precursor vapour compositions found in the experimental results. It is found that the small diameter and low V/III ratio result in VLS growths proceeding in the As-limited regime while for larger diameter nanowires at higher V/III ratios growth is governed by group III transport. In content in the nanowires is noticeably larger than that in the vapour. This effect is explained by high In diffusivity at higher temperatures and low cracking efficiency of TMGa at lower temperatures. $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ nanowire growth is most uniform when axial growth is maximized and radial growth is limited as presented in chapter 5. This condition is predicted to be in the As-limited regime by the model. However, the composition is far from the vapour composition. Nonetheless, we believe composition tunability can be achieved with high uniformity by simply tuning the In/Ga in vapour in this regime.

Further studies should include inhomogeneity of the composition along the nanowires length and cross-section. In particular, the In-rich shell can be observed due to VS radial growth on the sidewalls where there are more In adatoms due to better cracking efficiency and/or surface diffusion length of In with respect to Ga as presented in the
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previous chapters. The model can be extended to further understand how to gain control over the composition homogeneity and crystal phase. Nonetheless, the results and theoretical understanding presented in this chapter has shed more light on the complex growth phenomena in Au-seeded ternary III-V nanowires and allows for a better control over the nanowire composition by tuning their size and the growth parameters.
6. Towards understanding of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth

References


Towards understanding of Au-seeded In$_{1-x}$Ga$_x$As nanowire growth


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6. Towards understanding of Au-seeded In$_x$Ga$_{1-x}$As nanowire growth
Chapter 7

Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

Overview

This chapter discusses the growth and characteristics of InGaAs/InGaP core-shell heterostructures. While nanowire core growth and wurtzite (WZ) InGaAs/InP core-shell structure has been presented in chapter 5, this chapter aims at further tuning the wavelength emission of the InGaAs core by incorporating an InGaP shell which causes a larger compressive strain on the core as compared to InP shell. The chapter first discusses the growth aspect of the core-shell structure, which include a concomitant study of InGaP shell growth on WZ phase InGaAs and zinc-blende (ZB) InGaAs nanowires. Then, the optical properties of the heterostructures are presented which shows promising emission wavelength tunability with shell thickness.
7.1 Introduction

Core-shell nanowire structures have been the subject of intense research over the past few decades [1], [2]. Nanowire shape and the feasibility of material integration makes them one of the most promising heterojunctions as the building blocks of semiconductor nanoscale devices. In particular, core-shell structures have been well known for their passivating effect, which reduces the high non-radiative surface recombination rate at surface states. It has been shown that the nanowire PL efficiency is significantly enhanced with passivating shell [3]–[7]. Furthermore, core-shell structure also reduces charge carrier scattering at the nanowire surface [8]. Due to these advantages, core-shell structures have been used to demonstrate nanowire light emitting diodes and lasers [9]–[13].

As earlier discussed in chapter 2.2, the band gap of a semiconductor may change when strain is applied. Applied mechanical strain and strained core-shell structure has been reported to provide wavelength emission tunability [4], [14], [15]. For example, it was shown that the bandgap of GaAs/InGaP core shell structure could be tuned within 240 meV [15] and GaAs/GaP core-shell nanowires show about 260 meV blueshifted emission from the unstrained GaAs/AlGaAs nanowires [16].

Although InGaAs emission wavelength can be tuned by simply tuning the composition, this chapter focuses on exploring the possibility of tuning by applying strain to the core with a lattice-mismatched shell. The aim is to explore the growth and the structural properties of InGaAs/InGaP nanowire core-shell heterostructures and to demonstrate the emission wavelength tunability of the core with the growth of lattice-mismatched shell. In particular, InGaP, another ternary alloy that can be compositionally tuned to provide different strain onto the core InGaAs nanowire is chosen for the study. The growth aspect of this heterostructure is indeed challenging and present several key issues such as formation of stacking faults during shell growth, concomitant axial growth and thickness uniformity. Nonetheless, InGaAs/InGaP with different shell thicknesses show emission wavelength tunability, which could be of interest for future optoelectronic device development.

7.2 Experimental method

Nanowire growth was carried out on GaAs (111)B substrates and the core nanowire growth was carried out at a growth temperature of 500 °C and V/III ratio of 2.4. The molar flows of
TMIn and TMGa were at \(3.9 \times 10^{-6}\) and \(9.2 \times 10^{-6}\) mol.min\(^{-1}\), respectively. The growth time for the nanowire core was 45 minutes. The InGaAs core nanowires were seeded by 30 and 50 nm Au seed particles which results in a WZ and ZB InGaAs nanowires, respectively as previously presented in chapter 5. The WZ nanowires obtained from the 30 nm Au particle are almost defect-free. On the other hand, the 50 nm Au seeded ZB nanowires are defective with small segments of WZ phase. Note that two of these samples are chosen despite the defective phase of the ZB phase sample to explore the shell growth in general and to realize the possibility of tuning the wavelength. As previously presented in chapter 5, nanowires grown with the growth parameters used here should allow the nanowire core composition to be uniform with In content, \(X_{\text{In}}\) in the solid nanowire between 0.50 – 0.65.

After the core growth, the temperature was ramped up to a shell growth temperature of 550 °C. The temperature was stabilized for 2 minutes in AsH\(_3\) prior to introducing TMIn, TMGa and PH\(_3\) for InGaP shell growth. The TMIn and TMGa total flow was \(1.30 \times 10^{-5}\) mol.min\(^{-1}\) with \(X_{\text{V(In)}}\) TMIn/TMIn+TMGa = 0.50 and PH\(_3\) flow was \(2.23 \times 10^{-5}\) mol.min\(^{-1}\) corresponding to a V/III ratio of 165. Three different InGaP shell thicknesses corresponding to the growth time of 3:20, 8:00 and 40:00 were investigated.

The nanowire morphology and structural properties were characterized using field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Further composition analysis of the nanowire was carried out with energy-dispersive X-ray (EDX) spectroscopy in scanning transmission electron microscopy (STEM) mode. Quantitative EDX measurements and the cross-section samples fabrication were carried out as described earlier in chapter 3. Photoluminescence on single nanowires was carried out at room temperature using the \(\mu\)-PL setup presented in chapter 3.6.2 using 633 nm continuous wave HeNe laser with a spot size of \(\sim 1 \, \mu\text{m}^2\) and an excitation power of 30 \(\mu\text{W}\). PL was detected using nitrogen-cooled InGaAs array detector.

### 7.3 Morphology and structural properties of WZ and ZB phase InGaAs/InGaP core-shell heterostructures

Shell growth on both type of crystal phase InGaAs nanowire cores was studied as a function of shell growth time. The following section details the morphology and the structural properties of these nanowires.
7. Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

7.3.1 Morphology and structural properties of WZ InGaAs/InGaP core-shell heterostructures

Figure 7.1 (a-d) shows the SEM images for WZ phase InGaAs nanowire with no shell, 3:20, 8:00 and 40:00 of InGaP shell growth time. It is found that the length of the nanowire is slightly reduced which could be due to the decomposition of the InGaAs core during the temperature ramp up and at high temperature. Decomposition of WZ InAs was previously reported during InP shell growth at 500 °C [17]. Similar reverse growth mechanism has also been observed during annealing of GaAs nanowires which has been attributed to the negative growth mechanism [18].

Figure 7.1: 45°-tilted FESEM images of 30 nm-seeded InGaAs nanowires a) core-only InGaAs nanowires b-d) with InGaP shell grown for 3:20, 8:00 and 40:00, respectively. The inset in b) and c) shows the change in facet visible along the nanowire. Scale bars represent 1 µm.

The overall nanowire diameter is observed to be quite uniform for samples with shell growth time of 3:20 and 8:00. However, as the shell continues to grow for longer time, the thickness variation among nanowires is more visible. The shell thickness is measured from the SEM images for about 25 nanowires per sample. By taking the total diameter at mid-length and subtracting it to the average core diameter (34 nm), the shell thickness can
be quantified. Table 7.1 lists the average shell thickness and their standard deviation (SD) among the 25 nanowires measured.

**Table 7.1**: Dependence of InGaP shell thicknesses with growth time for 30 nm Au-seeded WZ nanowires.

<table>
<thead>
<tr>
<th>Shell growth time</th>
<th>Average shell thickness (nm)</th>
<th>Standard Deviation (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:20</td>
<td>11.2</td>
<td>2.6</td>
</tr>
<tr>
<td>8:00</td>
<td>18.2</td>
<td>4.9</td>
</tr>
<tr>
<td>40:00</td>
<td>63.4</td>
<td>9.3</td>
</tr>
</tbody>
</table>

It can be seen from the average thickness, the radial growth is nonlinear with time and the standard deviation is highest for the longest shell growth time confirming the inhomogeneity of shell growth as growth time increases. For further evaluation of the structural properties of this nanowire, TEM and EDX analysis were carried out on selected nanowires from each shell thickness.

The TEM image and the high-resolution TEM (HRTEM) for the sample with the thinnest shell (3:20 growth time) are shown in figure 7.2. From the TEM image, the nanowire is observed to be slightly protruding in the middle. Higher magnification HRTEM image and selective-area electron diffraction (SAED) pattern of this nanowire shown in figure 7.2 b) and c) indicating that the shell is WZ phase as expected due to the nature of crystal phase transfer [19]. However, several stacking faults are observed as indicated by the arrows. The stacking fault formation could have already been formed in the core growth or initiated during the annealing process or due to the strain caused by deposition of the InGaP shell at higher growth temperature. Stacking fault formation has been reported to be induced by thermal cracking of the shell even in lattice-matched core-shell structure [20].
Figure 7.2: a) TEM image of 30 nm-seeded InGaAs with 3:20 growth time of InGaP shell. b-c) high resolution images of the nanowire taken from the middle area of the nanowire as represented by the red box in a). The image is false-tinted in red and green to enhance the visibility of the core and shell sections. c) A higher magnification HRTEM image of the same nanowire showing the left hand side of the nanowire with uneven shell growth and few stacking faults. The inset is the SAED pattern taken from the same area. d) EDX spot analysis along the nanowire length showing a slight inhomogeneity along the nanowire length with higher P signal around the middle area.

The shell was observed to be slightly thinner on the left hand side of the image in figure 7.2 b) with a thickness of around 5 nm. The right hand side shows a shell thickness of about 8 nm which is closer to the average value as quantified from the SEM image in Table 7.1. The difference in the shell thickness on both sides can be attributed to the difference in the shell growth rate on the different polar {112} facets [21], [22]. The change of facet can be observed from the inset SEM images in figure 7.1.

To further investigate shell growth evolution, TEM and EDX results on nanowire grown with shell growth time of 8:00 are shown in figure 7.3 a-d. From the low magnification of the whole nanowire in figure 7.3 a), the nanowire morphology along the axial direction shows inverse tapering with uneven sidewall. The tip area of the nanowire is observed to be enlarged in comparison to the rest of the nanowire. HRTEM image in figure 7.3 b) shows that a higher amount of stacking faults is present in this region. However, pure ZB phase is found directly underneath the Au alloy particle in contrast with the phase of the
rest of the nanowire body. Further analysis with EDX composition mapping shows that this segment including the region of high density stacking faults directly underneath consists of InGaP. The initial high density stacking faults could be the region where instability of the chemical potential occurs while the Au alloy particle is transitioning with the change in vapour surrounding it. Once the Au alloy particle reaches a stable condition, ZB phase InGaP starts to grow. Similar occurrence in formation of heterointerfaces has been observed for Au-seeded axial heterostructures [23]–[25]. An overlay image of the P and As map is shown in figure 7.3 c).

Figure 7.3: a) Low magnification TEM image of the whole nanowire for the 30 nm-seeded sample with a shell growth time of 8:00. b) HRTEM image of the tip area below the Au particle. c) Overlay of P and As composition maps of the tip area of the nanowire. D) HRTEM image of the mid-length area with the SAED pattern.

HRTEM and SAED at the middle region of the nanowire show that it is WZ phase and contains several stacking faults which is similar to the one grown with thinner shell. The thickness of the shell is about 16 nm, close to the value quantified from the SEM image as earlier listed in Table 7.1. The shell is not as imbalanced on the left and right hand sides as previously shown for the sample with thinner shell which can be attributed to the change of facets [21].

To evaluate the details of the shell growth on the side facets, a cross-sectional view is essential. Figure 7.4 shows two typical cross-sections taken from the first 1 µm of a
nanowire grown with shell growth time of 8:00. The first type of cross-section is shown in figure 7.4 a-e). The HAADF image in figure 7.4 b) shows a higher contrast of the core-shell structure. This cross-section shows that the facet of the shell is growing in parallel to the core side facet. Since this is the WZ phase, we refer to the facets as the \{1-100\} facets. Such structure should show a balanced growth rate on both the left and right hand sides if the nanowire is viewed from the \(<11-20>\) zone axis such as the one shown in figure 7.3 d). Another type of cross-section is shown in figures 7.4 e-g). The core can be observed to have a symmetrical hexagonal shape but the shell is multifaceted with an overall truncated triangular shape. This cross-section indicates that the growth rate is different on the \{112\} polar facets with higher growth rate on one polar facet than the other. The \(<11-20>\) or equivalent to \(<110>\) view of the nanowire with imbalanced shell as previously discussed for the thinner shell shown by figure 7.2 c) can be represented by this cross-section although in that case the shell was thinner. This kind of transition has been observed in growth of GaP/GaAs core-shell structure with mixed phase ZB and WZ domains [21]. The triangular shape is believed to be the initial stage of the shell growth where it later forms a more stable facets with hexagonal \{112\} equivalent to \{1-100\} side facets. Such transformation from a triangular shape to hexagonal shape has been observed in Au-seeded GaAs nanowires [26].

From the cross-sectional view, the composition of the core and the shell was measured by EDX spot analysis. The composition for the core and the shell is measured by EDX map by combining intensities within the area of the core and the shell respectively. The results indicate that the core is In\(_{0.60}\)Ga\(_{0.40}\)As and the shell is In\(_{0.60}\)Ga\(_{0.40}\)As with 0.04 random errors as previously discussed in chapter 3. The difference in the In content from the core and the shell is very little showing little to no variation across the whole cross-section as can be observed in the In and Ga overlay map in figure 7.4 c). From these compositions, the lattice mismatch for this sample of In\(_{0.60}\)Ga\(_{0.40}\)As/In\(_{0.60}\)Ga\(_{0.40}\)As is about 3.3%.
7. Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

Figure 7.4: a) HRTEM cross-sectional image from the first 1 µm from the base of a 30 nm Au-seeded nanowire grown with InGaP shell growth time of 8:00. Both the core and shell show a hexagonal structure. b-d) HAADF image and compositional maps of In, Ga, As and P. e) HRTEM cross-sectional image from a different region of the same sample. A truncated triangle-like cross-section is observed with hexagonal core. b-d) HAADF image and compositional maps of As and P.

Finally, the evolution of shell growth is further portrayed by the sample with shell growth time of 40:00. Figure 7.5 a) shows the low magnification TEM of this nanowire where inverse tapering as previously observed for the shell growth time of 8:00 could be observed. The tip area of the nanowire shows about 200 nm of pure ZB InGaP axial growth as represented by the HRTEM image in figure 7.5 b). The shell is about 68 nm in thickness as shown by the HRTEM image in figure 7.5 c) and the EDX spot analysis across the nanowire in figure 7.5 d). The SAED pattern in the inset of figure 7.5 c) shows that the crystal phase is predominantly WZ with light streaking in between the spots indicating a high density of planar defects. This can be clearly observed in the HRTEM image where the stacking faults are indicated by the arrows. With higher strain due to the thicker shell, these stacking faults could be induced by the strain. An EDX spot analysis along the nanowire in figure 7.5 e) shows that P signal increases in the axial growth direction with the highest P signal observed at the tip where InGaP axial growth is observed. This clearly indicates that there is significant concomitant axial growth and there is a clear gradient of InGaP shell thickness.
where the thickness is larger at the tip. This can be attributed to preferable nucleation sites which is mostly at the tip due to the formation of stacking faults during the formation of the first InGaP segment as previously discussed for the 8:00 minute shell growth time sample. Enhanced nucleation sites with stacking faults has been observed in many reports [17], [27], [28]. In particular, step formation from the stacking faults has been observed in InAs/InP core-shell nanowires [17]. Therefore, in our case, the initial stacking faults formed during the first InGaP segment could be the initial step where radial growth starts to form and continues to grow thus causing the nanowire to have inverse tapering morphology.

**Figure 7.5:** a) Low magnification TEM image of the 30 nm Au-seeded InGaAs nanowire grown with 40:00 growth time of InGaP shell. b) HRTEM image of the tip area below the Au particle c) HRTEM image from the section of the nanowire as indicated by the red box in a). The inset is the diffraction pattern taken from the same area. d-e) EDX spot analysis of the nanowire across the radial and axial direction, respectively. The HAADF image for the nanowire is shown on top of e) with arrows indicating the top interface of the core.
7. Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

7.3.2 Morphology and structural properties of ZB InGaAs/InGaP core-shell heterostructures

The evaluation of the 50 nm Au-seeded InGaAs/InGaP nanowires with defective ZB phase is carried out using similar methods previously described for the 30 nm Au-seeded InGaAs nanowires. The growth evolution of the shell with the growth time is depicted in the SEM image in figure 7.6. The original core InGaAs nanowires are slightly tapered with a diameter of about 140 nm at the base and 80 nm at the tip. The shell thickness is measured at mid-length of the nanowires by subtracting the core diameter at mid-length (92.4 nm) from the total diameter. The average shell thickness and their standard deviation among the 25 nanowires measured are listed in Table 7.2.

![SEM images of nanowires](image)

**Figure 7.6:** 45°-tilted FESEM images of 50 nm Au-seeded a) core-only InGaAs nanowire b-d) InGaAs/InGaP nanowires grown with 3:20, 8:00 and 40:00 InGaP shell growth time, respectively. Scale bars represent 1 µm.

**Table 7.2:** Dependence of InGaP shell thicknesses with growth time for 50 nm Au-seeded ZB nanowires.

<table>
<thead>
<tr>
<th>Shell growth time</th>
<th>Average shell thickness (nm)</th>
<th>Standard Deviation (SD)</th>
</tr>
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<tbody>
<tr>
<td>3:20</td>
<td>9.9</td>
<td>7.56</td>
</tr>
<tr>
<td>8:00</td>
<td>22.3</td>
<td>7.1</td>
</tr>
<tr>
<td>40:00</td>
<td>71.2</td>
<td>13.1</td>
</tr>
</tbody>
</table>
7. Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

As can be observed from the average thickness and the standard deviation, the thickness is much higher for this set of samples compared to the 30 nm Au-seeded samples discussed earlier. This could be due to the higher nucleation rate on the sidewall of these defective ZB structures. To get more accurate thickness of the shell and to gain more insight on the shell growth on the structure, TEM analyses are performed. Figure 7.7 a) shows the low magnification TEM image of a sample with 8:00 minute shell growth time where the defective nature of the nanowire could be clearly seen. SAED pattern of the nanowire shown in the inset of figure 7.7 a) indicates that the nanowire is predominantly ZB with twins and some WZ phase. Figure 7.7 b) shows an EDX map of As and P signals which indicate a relatively uniform shell thickness along the nanowire length. Further EDX spot analysis across the structure shown in figure 7.7 d) of the corresponding HAADF image in 7.7 c) shows that the nanowire has a shell thickness of about 20-22 nm which agrees well with the average thickness listed in Table 7.2.

![Figure 7.7](image)

**Figure 7.7:** a) Low magnification TEM image of 50 nm Au-seeded InGaAs nanowire with 8:00 growth time of InGaP shell. The inset is the SAED pattern taken from the first 1 μm from the tip. b) Overlay composition map of As and P signals. c) HAADF image of the tip area of the nanowire. d) EDX spot analysis across the nanowire as shown in c). e) Cross-section view of the nanowire taken from the first 1 μm from the base. The inset is the SAED corresponding to the whole cross-section. f-h) HAADF and compositional maps of the cross-section.
A cross-section view of the sample from the first 1 µm from the nanowire base is shown in figure 7.7 e). The cross-section shows that the core facets are rough contributing to larger variation in the shell thickness. The shell thickness as measured from this cross-section is about 21 ± 4.4 nm which is within the range of the average thickness listed in Table 7.2. The HAADF and the composition maps shown in figure 7.7 f-h) clearly identify the core and shell region of the sample. The In and Ga overlay map in figure 7.7 g) shows that the In composition is higher in the shell than the core. The composition as measured by EDX shows that the core is In$_{0.55}$Ga$_{0.45}$As and the shell is In$_{0.60}$Ga$_{0.40}$As. From these compositions, the lattice mismatch for this sample of In$_{0.55}$Ga$_{0.45}$As/In$_{0.60}$Ga$_{0.40}$As is about 3%.

### 7.4 Optical properties of InGaAs/InGaP core-shell heterostructures

To investigate the optical properties of these nanowires, PL measurements were carried out on single nanowires. About 15-20 single nanowires from each sample were measured. More than half (10-12) of these nanowires emit at the wavelength as presented in the following sections. The rest of the nanowires show no emission or very low intensity emission.

#### 7.4.1 Photoluminescence of WZ In$_{0.60}$Ga$_{0.40}$As/In$_{0.60}$Ga$_{0.40}$P core-shell heterostructures

Figure 7.8 shows the typical PL spectra taken from the middle of a single nanowire for the InGaAs/InGaP core-shell nanowire with shell growth time of 8:00 and 40:00. The sample with shell growth time of 3:20 shows no reliable peak within the detection range of the InGaAs detector. Hence only these two spectra are discussed.
Figure 7.8: Normalized PL spectra of 30 nm Au-seeded WZ phase In\(_{0.60}\)Ga\(_{0.40}\)As/In\(_{0.60}\)Ga\(_{0.40}\)P nanowires with shell growth time of 8:00 and 40:00 (18 nm and 63 nm shell thickness, respectively). No peak is obtained for sample with shell growth time of 3:20.

The main peak position for the sample with shell growth time of 8:00 is around 1420 nm (0.87 eV). The main peak is attributed to the strained In\(_{0.60}\)Ga\(_{0.40}\)As core which shows about 400 nm (190 meV) shift from the ZB phase of unstrained In\(_{0.60}\)Ga\(_{0.40}\)As (1820 nm or 0.68 eV). A shoulder peak on the lower wavelength side of the main peak can be attributed to the inhomogeneity in the shell thickness along the sample as observed by the TEM. Variation of shell composition can also contribute to the shoulder peak.

Further shift is observed with thicker shell grown for 40:00 revealing a PL peak around 1260 nm (0.98 eV). The shift is about 560 nm (300 meV) from the ZB phase unstrained In\(_{0.60}\)Ga\(_{0.40}\)As. The exact shift could be less, as the WZ phase is known to have higher bandgap. In fact, the shift for a WZ phase has been shown to be in the order of 30-55 meV from their ZB counterpart for InGaAs [29], [30]. Nonetheless, shift due to strain has been reported to exceed 100 meV in InAs/InAsP core-shell nanowires even for very thin shell (~3 nm) and low content P (~0.3 contributing to about 0.9% lattice mismatch) [3]. Therefore in the case of a lattice-mismatch of about 3.3% in our case it is expected that the shift would be larger. There is a shoulder peak on the higher wavelength of the spectrum which at this stage can only be attributed to the inhomogeneity of the shell thickness.
The peaks are broad in both the shell growth time of 8:00 and 40:00 samples with a full width half maximum (FWHM) of 180 and 160 nm, respectively. The broadness of the peak can be attributed to the inhomogeneous shell growth on the facet as discussed earlier. However, the difference in the FWHM of the two samples is not substantial, indicating similar inhomogeneity in the composition.

Apart from the main peak, the spectrum for the thicker shell samples also shows a lower intensity peak around 800 nm which can be attributed to the InGaP axial growth as shown earlier by the TEM analysis.

### 7.4.2 Optical properties of ZB In_{0.55}Ga_{0.45}As/In_{0.60}Ga_{0.40}P core-shell heterostructures

Figure 7.9 shows the PL spectra for the 50 nm Au-seeded InGaAs nanowires with InGaP shell growth time of 3:20, 8:00 and 40:00. Only a single peak is observed for all three samples. This is expected as no significant InGaP axial growth is observed for these nanowires. The peak position and the FWHM is listed in Table 7.3 together with the estimated shift from the unstrained ZB In_{0.55}Ga_{0.45}As (1696 nm or 0.73 eV).

![Normalized PL spectra of 50 nm Au-seeded ZB phase In_{0.55}Ga_{0.45}As/In_{0.60}Ga_{0.40}P with shell growth time of 3:20, 8:00 and 40:00.](image-url)

**Figure 7.9:** Normalized PL spectra of 50 nm Au-seeded ZB phase In_{0.55}Ga_{0.45}As/In_{0.60}Ga_{0.40}P with shell growth time of 3:20, 8:00 and 40:00.
Table 7.3: The PL peak position for the InGaAs/InGaP core-shell nanowires with different shell growth time.

<table>
<thead>
<tr>
<th>Shell growth time</th>
<th>Peak position in nm and (eV)</th>
<th>FWHM (nm)</th>
<th>Peak shift based on unstrained ZB In$<em>{0.55}$Ga$</em>{0.45}$As in nm and (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:20</td>
<td>1330 (0.93)</td>
<td>199</td>
<td>366 (200)</td>
</tr>
<tr>
<td>8:00</td>
<td>1220 (1.01)</td>
<td>147</td>
<td>476 (280)</td>
</tr>
<tr>
<td>40:00</td>
<td>1120 (1.11)</td>
<td>89</td>
<td>576 (380)</td>
</tr>
</tbody>
</table>

With the 50 nm Au-seeded ZB phase In$_{0.55}$Ga$_{0.45}$As, the peak shows tunability shift towards lower wavelength in the range of 1100 to 1300 nm. This indicates that the shell thickness is effective in providing tunability to the emission wavelength of InGaAs nanowire core. Similar shoulder peak as observed with the 30 nm Au-seeded nanowire samples indicating inhomogeneity in the shell thickness along the sample or between core-shell facets in the sample as observed by the cross-sectional TEM. However, an improved FWHM is observed with the thickest shell, which could indicate a better uniformity with longer shell growth time. Given the complexity of the system studied here, further studies and modelling will be necessary to ascribe the physical origin of this evolution unambiguously.

7.5 Summary

In summary, the chapter has presented the growth of InGaAs/InGaP nanowire core-shell heterostructures and their photoluminescence spectra showing luminescence peak tunability of the core with the level of strain induced by the shell. The overall shell thickness along the nanowire is observed to be inhomogeneous for WZ nanowires. For the WZ phase InGaAs, the cross-section shows a more uniform shell along the facets although in some nanowires, a change of facets may occur, resulting in a thicker shell on one set of facets. For the ZB phase InGaAs, the shell is inhomogeneous on the side facets due to planar defects in the sample but shows a rather uniform shell thickness along the nanowire axial direction. The 30 nm Au-seeded WZ nanowires have significant InGaP axial growth concomitant with the radial growth. The growth conditions still require optimization in order to ensure
Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures

...thickness and composition homogeneity. Furthermore, the axial growth of InGaP promoted during the radial shell growth should also be minimized if only radial heterostructure is required. Nonetheless both WZ and ZB phase structure show great promise in tuning the wavelength emission of InGaAs nanowires with various shell thickness.

Room-temperature PL emission in the range of 1260 to 1420 nm is demonstrated for WZ In0.60Ga0.40As/In0.60Ga0.40P core shell nanowire with two different shell thicknesses showing about 190 and 300 meV shift from the expected value for unstrained In0.60Ga0.40As. For ZB In0.55Ga0.45As/In0.60Ga0.40P, PL emission ranging from 1100 to 1330 nm is achieved with different shell thicknesses. Peak shift up to 380 meV from the expected value for unstrained In0.55Ga0.45As is observed for the thickest shell of ZB samples. Therefore, with strained core-shell structure it is shown that tunability can also be achieved without changing the composition of the core which can be beneficial once the optimized core InGaAs has been achieved.
References


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7. Bandgap tunability of InGaAs/InGaP nanowire core-shell heterostructures


Chapter 8

Summary and future outlook

8.1 Summary

This thesis explored the growth of Au-seeded InGaAs nanowire growth in a wide range of growth conditions. While there is still significant work left in order to achieve the potential applications described in Chapter 1, this work has made important steps toward understanding some of the fundamental issues including composition homogeneity, controlled crystal phase and tunability of InGaAs nanowires emission wavelength.

Growth of defect-free zinc-blende (ZB) InGaAs nanowires is achieved by growing using the two-temperature growth mode. The tapered morphology is reduced as the growth temperature is lowered. In the low-temperature growth regime, high In incorporation rate in InGaAs nanowires is observed due to the higher diffusion length of In and reduction of TMGa decomposition at low temperature. Furthermore, a spontaneous shell is formed via the vapour-solid (VS) mechanism. Reducing the TMIn flow in vapour in this two-temperature growth mode shows some degree of tunability of the alloy composition in the core while maintaining a defect-free ZB phase. The spontaneous shell maintains a high-In content regardless of the reduced TMIn in vapour. The difference in the core and the shell compositions contributes to the inhomogeneity of composition along the nanowire axis. High composition uniformity can be achieved when the InGaAs core has an In
content of about 95%. This limited tunability shows that the growth of InGaAs is complex in the low-temperature growth regime where there is a fine balance between the roles of decomposition and diffusion length. Nonetheless, the highly uniform high-In InGaAs nanowires with defect-free ZB can be utilized for applications in the near infra-red regime as an alternative to InAs which is known to be plagued by current leakage issues.

Single growth temperature in combination with several V/III ratios are investigated to provide composition and phase tunability of Au-seeded InGaAs nanowires (chapter 5). It is found that at relatively high growth temperatures (500 °C) the nanowire composition significantly becomes more homogenous as observed by the EDX line scan along the nanowire and by the cross-sectional mapping of the nanowire. Varying the V/III ratio at this temperature leads to phase and composition (X_{In} = 0.25-0.70) tunability within good compositional homogeneity. An increase in V/III ratio allows more Ga to be incorporated into the nanowires and at the same time increases the probability for ZB phase to nucleate. At high V/III ratio pure ZB phase of InGaAs nanowires was achieved. The increase in the amount of ZB stacking within the nanowire is found to vary with Ga incorporation rate where higher Ga was found in higher ZB phase InGaAs nanowires. This finding is further confirmed when Au seed particles of different size are used. While nanowires seeded by small diameters (10-30nm) have pure wurtzite (WZ) phase, nanowires seeded by larger diameters Au seed particles (50 and 80 nm) are mainly ZB with stacking faults. An increase in the amount of ZB phase is also accompanied by an increase in Ga despite the Au particles having a high concentration of In. Nonetheless, with the combination of relatively high growth temperature and low V/III ratio, the nanowires can be grown with homogenous composition and morphology in pure WZ phase that are straight with negligible tapering and smooth sidewalls. Further characterization shows that the nanowire is of WZ phase. The nanowires continue to maintain the homogeneity even when grown for a substantially longer time. The uniform In_{0.65}Ga_{0.35}As nanowires passivated with InP shell shows photoluminescence at 1.5 µm indicating a strain related blueshift.

Understanding on the growth of Au-seeded InGaAs nanowires is further strengthened through a kinetic modeling approach. The kinetic approach fits the experimental results well, and provides an explanation of the factors governing the axial growth rate and the composition of InGaAs nanowires. The growth of InGaAs nanowires is found to be in As-limited regime when the diameter and V/III ratio are small. Thus in these two cases, the axial growth is limited. The In content in the nanowires is significantly higher
than the nominal In-to-Ga provided in vapour due to the diffusion length of In which is strongly dependent on the V/III ratio. The Ga diffusion length is found to be negligible for all the cases investigated indicating that the Ga mainly comes from direct impingement on the nanoparticle. Hence to increase the amount of Ga in the nanowire solid, the growth condition should provide more Ga adatoms such as by increasing the growth temperature to provide more decomposition of TMGa. Furthermore, Ga may also increase when the V/III ratio is high due to the lowering of In diffusion length. This finding shows that the growth is group III limited when the V/III is high and the diameter is large. This insight provides a better view of the growth in general and should serve as a ground for further studies to understand the complex mechanisms involved during the growth of ternary nanowires.

Successful growth of InGaAs nanowires can be challenging and complex as there is only a small growth windows for this to happen. The growth window for successful growths of uniform, high purity phase InGaAs nanowires is highly likely to change with the change in composition thereby making it challenging to tune the composition of InGaAs while maintaining the high-quality crystal structure. Hence, another method of accessing bandgap tunability is essential such as applying strain to the core-shell structure. The growth of strained InGaAs/InGaP core-shell nanowires is discussed. Growth on the WZ phase InGaAs shows inhomogeneity in shell thickness along the nanowire while growth on defective ZB shows inhomogeneity at the side facets. Nonetheless, the bandgap emission from the InGaAs core can be tuned within a broad range of interest from around 1100 to 1420 nm by changing the shell thickness as a result of strain-induced blueshift. This technique is promising for extending the range of InGaAs nanowires in the near infra-red applications.

8.2 Future Outlook

Based on the results obtained in this thesis, there are few suggestions that can be made for future work, which can provide a deeper understanding and a wider range of composition tunability of Au-seeded ternary nanowires. Firstly, TMIn/TMGa flow ratio in the two-temperature growth method is shown to affect the core composition. Therefore, if the radial growth can be controlled by other means such as in-situ HCl or HBr etching [1], [2], the nanowires can be more uniform in composition and morphology.
Mass transport is found to affect the growth substantially and thus needs to be controlled in such a way that the growth should be in the regime where diffusion length plays a limited role (e.g., high density nanowires). Relatively high growth temperature should provide a better proportion of the competing group III species and eliminate the possibility of decomposition issues. Tunability with high compositional homogeneity, pure crystal phase and uniform composition supposedly can potentially be achieved with by varying the TMIIn/TMGa supply ratio, which has not been explored in detail for the single temperature growth.

To extend the growth understanding of alloy systems, a quaternary system such as InGaAsP can be explored. Potentially, the effect of group V on the growth of quaternary system could be also of interest due to its profound effect on the crystal phase as recently reported [3], [4]. Hence, having two group V species could bring interesting and new understanding towards growth of alloy semiconductor nanowires. Figure 8.1 is the result of a preliminary growth of InGaAsP nanowires showing a complex irregular morphology due to a modulation of the faceting along the nanowire. High resolution TEM shows that the nanowire has a self-modulated crystal phase along the axial direction with pure ZB phase and As-rich defective regions.

![Figure 8.1](image)

**Figure 8.1:** a) 45°-tilted FESEM image of InGaAsP nanowire with nominal composition of In$_{0.30}$Ga$_{0.70}$As$_{0.40}$P$_{0.60}$. b-c) TEM image of the InGaAsP nanowire showing clear rotation of facets in $\langle 110 \rangle$ and $\langle 211 \rangle$ zone axis respectively. d) HRTEM of the transitional area from defective region to pure ZB phase as zoomed in from the red box in b). e) EDX spot analysis along the nanowire.

For the future work, the growth model can also be extended to further understand the evolution of the crystal structure and the composition of the radial growth. The
understanding gained from such model should be beneficial not only for growth control of InGaAs nanowires but also for other ternary and possibly quaternary alloy semiconductor nanowires as well.

Core-shell structures as presented in this thesis show that the luminescence properties can be enhanced, and strained core-shell structure can provide tunability of the wavelength. In particular, InGaAs/InGaP core-shell structure can be further investigated with a variation of InGaP composition, which can provide a way of tuning the strain imposed on the core InGaAs nanowires. Improving InGaP shell with different compositions will provide more room for bandgap tunability while maintaining high structural and crystal qualities (e.g. minimal defects).

A deeper understanding on the luminescence properties of the strained core-shell and the origin of peaks can be further studied using a spatially resolved PL or cathodoluminescence. Detailed studies can also be accompanied with a modelling calculation of the bandstructure to further understand the effect of strain on the band gap of the complex ternary/ternary alloy semiconductor core-shell structure.

Lastly, the optimized InGaAs nanowires presented here can further be utilized for device applications. Doping of the nanowire can be explored to realise p-i-n junctions for photodiodes and photovoltaics.
References


